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Design and Synthesis of New Organic Dyes for Highly Efficient Dye-Sensitized Solar Cells (DSSCs)

HUA Yong

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Principal Supervisor: Prof. WONG Wai-Kwok, Rick

Hong Kong Baptist University

January 2014
DECLARATION

I hereby declare that this thesis represents my own work which has been done after registration for the degree of PhD at Hong Kong Baptist University, and has not been previously included in a thesis or dissertation submitted to this or any other institution for a degree, diploma or other qualifications.

Signature: HUA YONG

Date: January 2014
Abstract

Dye-sensitized solar cell (DSSC) has attracted increasing interest as a promising hybrid organic-inorganic solar cell. At the heart of the device is a photosensitizer, which is anchored onto a wide-bandgap semiconductor metal oxide. It harvests solar light and transfers the energy via electron transfer to a suitable material (e.g. TiO₂) to produce electricity as opposed to chemical energy in plant. The topic of this thesis focuses on the design and synthesis of metal-free organic dyes for applications in DSSCs. Specific attention has been paid to the correlation between the molecular structures and physical properties, as well as their performances in DSSCs.

Chapter 1 presents the major components and working principle of DSSC, following by a brief overview of the development of organic dyes and their application in DSSCs.

In chapter 2, we have designed two types of new phenothiazine-based dyes to investigate the positioning effect a donor group on the cell performance. The structural features of a donor aryl group at the C(7) position of phenothiazine core extend the π-conjugation of the chromophore and efficiently suppress the dye aggregation on TiO₂ film. As a result, Type 1 dyes have better light harvesting properties in contact with TiO₂ films, and give much better photovoltaic performance than Type 2 dyes.

Chapter 3 presents the synthesis and characterization of a series of simple phenothiazine-based dyes, in which, a linear electron-rich (4-hexyloxy)phenyl group at C(7) of the phenothiazine periphery as the donor, and an alkyl chain with
different length at N(10). The dye molecules show a linear shape which is favorable for the formation of a compact dye layer on the TiO₂ surface, while their butterfly conformations can sufficiently inhibit molecular aggregation. Moreover, the alkyl substituents with different chain length at N(10) could further optimize the performance through complete shielding the surface of TiO₂ from the I⁻/I₃⁻ electrolyte. Under simulated AM 1.5G irradiation, the PT-C₆ based DSSC produces a short-circuit photocurrent of 15.32 mAcm⁻², an open-circuit photovoltage of 0.78 V, a fill factor of 0.69, corresponding to a power conversion efficiency (PCE) of 8.18%. Moreover, we designed a stepwise approach for co-adsorption of the organic dye PT-C₆ with a porphyrin dye (ZnP) for DSSCs. Upon optimization, the device made of the PT-C₆ + ZnP system yielded Jₘ = 19.36 mA cm⁻², Vₘ =0.735 V, FF = 0.71 and η = 10.10%.

In chapter 4, we further developed five organic dyes appended with T, TT, E, ET, or EE (T and E denote thiophene and 3,4-ethylenedioxythiophene (EDOT), respectively) on the C(7) atom of phenothiazine core as electron donors. We have also analyzed the structure-performance corelations of dye molecules in the aspect of dye aggregation, electron injection, dye regeneration and interfacial charge recombination of electrons with electrolytes and/or oxidized dye molecules, through DFT calculation, impedance analysis and transient photovoltage studies.

In chapter 5, we extended our studies by using phenothiazine as a building block to construct 3D bulky organic dyes. We systematically investigated the influence of 3D bulky substituents on dye aggregation and charge recombination, as well as photovoltaic performance of DSSCs. The molecular design strategy
demonstrates that high $V_{oc}$ can be realized by employing 3D-phenothiazine dyes featuring a bulky substituent, such as, hexylcarbazole and dihexylfluorene units. Impressively, the co-adsorbent-free DSSCs based on dye TP3 exhibits a photovoltaic performance with efficiency up to 8.00 %. In order to realize a panchromatic absorption and further enhance the energy conversion efficiency of DSSCs, we also designed a stepwise approach for co-adsorption of the organic dye TP3 with a NIR dye YR6 for co-sensitized DSSCs. Upon optimization, the device made of the TP3 + YR6 system yielded $J_{sc} = 19.18$ mA cm$^{-2}$, $V_{oc} = 0.721$ V, FF = 0.712 and $\eta = 9.84$ %. The power-conversion efficiency is the highest reported efficiency for a squaraine dye-based co-sensitized panchromatic DSSCs.

From chapters 6 and 7, a series of new simple panchromatic dyes based on thiaadiazolo[3,4-c]pyridine (PyT) have been designed for panchromatic DSSCs. These new organic dyes exhibit broad absorption spectrum in the range of 300–850 nm and high molar extinction coefficients. The electrochemical analyses demonstrate that the incorporation of the auxiliary electron-deficient thiaadiazole[3,4-c]pyridine unit can fine-tune the HOMO and LUMO energy levels and red-shift the absorption spectra to NIR region. The overall conversion efficiencies of liquid-electrolyte DSSCs based on these sensitizers range from 0.46 to 6.30 %.

We draw some conclusions in chapter 8 together with the outlooks in DSSCs.
Acknowledgements

First of all, I would like to express my profound gratitude and sincere thanks to my supervisor Prof. Rick Wai-Kwok Wong for his invaluable advice, inspiration and uninterrupted support throughout my studies. His guidance and encouragement are gratefully acknowledged. Moreover, I would like to give special thanks to Dr. Xunjin Zhu for his kind help, great discussing and invaluable advice throughout the research, and for his hardworking and patience when reviewing my manuscripts. A warm thank to Prof. Wai-Yeung Wong for his valuable contribution in revising manuscripts.

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Last but not least I wish to thank to my family for their endless love. My wife and my son who make me happy-thank you so much and I love you.
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<th>Full Form</th>
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<tr>
<td>AM</td>
<td>Air mass</td>
</tr>
<tr>
<td>CDCA</td>
<td>Chenodeoxycholic acid</td>
</tr>
<tr>
<td>DSSCs</td>
<td>Dye-sensitized solar cells</td>
</tr>
<tr>
<td>D-π-A</td>
<td>Donor-π-bridge-acceptor</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped-tin oxide</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HTM</td>
<td>Hole transporting material</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident photon-to-current conversion efficiency</td>
</tr>
<tr>
<td>NIR</td>
<td>Near Infrared</td>
</tr>
<tr>
<td>J-V</td>
<td>Current-Voltage</td>
</tr>
<tr>
<td>LHE</td>
<td>Light harvesting efficiency</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MLCT</td>
<td>Metal-to-ligand charge transfer</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaic</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>SSDSCs</td>
<td>Solid-state dye-sensitized solar cells</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conductive oxide</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>$ff$</td>
<td>Fill factor</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>Short-circuit current density</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>$\tau_e$</td>
<td>Electron lifetime</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>NBS</td>
<td>N-Bromosuccinimide</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>M+</td>
<td>Molecular ion</td>
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Chapter 1 Introduction

1.1 Solar Light

As the world is becoming more advanced in economy and technology, more energy is being consumed to keep up with the development and demand on energy boomed over past decades. Presently, the energy demands are still highly dependent on fossil fuels, natural gases and coal with percentages of 36.4%, 23.5% and 27.8%, respectively.\(^1\) However, the world will shortly come to an end of fossil fuels due to its non-renewable. Meanwhile, the wasteful use of fossil fuels actually causes irreversible environmental damage, geopolitical tensions, and tragically climate changes.\(^2\) We definitely must move toward a more sustainable energy economy. Of all the available technologies to produce renewable energy, solar energy has become a hot topic in current research of replacing fossil fuels. One simple reason is that the earth receives \(1.2 \times 10^{17}\) W insolation or \(3 \times 10^{24}\) Joule energy per year from the sun and this means covering only 0.13% of the Earth’s surface with solar cells with an efficiency of 10% would satisfy humanities’ energy needs.\(^3\) Apart from the abundance of potentially exploitable solar energy, photovoltaic cells also have other competitive advantages such as little need for maintenance, off-grid operation and silence, which are ideal for usage in remote sites or mobile applications. Currently, mankind has made use of three main ways of converting sunlight to a useable source of energy. Biomass is a form of stored solar energy. Solar furnaces are devices that collect solar energy and convert it into heat, either for water heating
for residential or commercial use or for electric power generation through steam production. A third possibility is to use light for moving electrons and therefore generating electricity.\cite{4}

Silicium photovoltaic cells currently dominate the market with commercial devices having conversion yields, varying upon the technology, from 5 to 25 \%. However, this technology is limited by the high production costs, high energetic costs and problematic integration in the built environment. Several alternative photovoltaics are competing with the silicium based devices.\cite{5} Thin-film photovoltaics (CdTe, CIGS, amorphous silicium) is a competitive PVs technology, doubling production from 2006 to 2007. They are very durable and low-cost materials even though indium is rare. Finally, dye-sensitized solar cells are photovoltaic devices in which a dye is used as the light absorber and a semiconductor electrode (essentially titania) allows for the charge separation and the transport of the electron to the external circuit. This technology offers the following advantages: low production and investment cost, flexible design opportunities and feedstock availability to large scale application. The next section will give more details on this type of photovoltaics.

1.2 Dye-Sensitized Solar Cells

The modern version of dye-sensitized solar cell (DSSC), also known as the Grätzel cell, was originally invented by O’Regan and Grätzel in 1991.\cite{6} Since the initial work, DSSCs have received considerable attention as a new generation of sustainable photovoltaic devices because of their high solar-light to electricity
conversion efficiency, colorful and decorative natures, low materials cost and potential large scale application under outdoor condition. A conventional DSSC configuration\textsuperscript{[7]} is basically a thin-layer solar cell formed by sandwich arrangements of two transparent conducting oxides (TCO) electrodes on a glass substrate. The most commonly used substrate is glass coated with fluorine-doped tin oxide (FTO). The heart of the device is constructed with a monolayer of the charge-transfer dye-adsorbed on a wide band gap nanocrystalline oxide semiconductor film, such as TiO\textsubscript{2}, ZnO, NiO and SnO\textsubscript{2}, an organic electrolyte containing a redox mediator, usually a mixture of triiodide/iodide in acetonitrile and a finely divided platinum-coated counter electrode onto TCO. A schematic diagram of the interior of a DSSC device is shown in Figure 1.1. To date, several thousands of dyes have been investigated, in combination with hundreds of electrolyte systems and numerous types of mesoporous films with different morphologies and compositions.

\textbf{Figure 1.1.} A schematic diagram of dye-sensitized solar cell.
The general operating principle of a DSSC is illustrated in Figure 1.2.\cite{8-10}

Firstly, the photosensitizer (S) is excited by absorption of a photon to form its electronically excited state (S\(^+\)) (eqn 1). Then, this photosensitizer in excited state (S\(^+\)) can inject an electron into the conduction band of the semiconductor TiO\(_2\) (eqn 2). The injected electron moves through the mesoporous network of particles to reach the back-collector electrode through the external load. The oxidized sensitizer is regenerated rapidly back to the ground state by the redox mediator iodide (eqn 3). As a result, no net chemistry occurs, this completes in a regenerative and stable photovoltaic energy conversion system. The overall efficiency of the device is determined by the compatibility and optimization of each of the constituents.

\[
\begin{align*}
S + h\nu & \rightarrow S^+ \quad \text{(photoexcitation)} \\
S^+ & \rightarrow S^+ + e_{\text{injected}}^- \quad \text{(electron injection)} \\
2S^+ + 3I^- & \rightarrow 2S + I_3^- \quad \text{(dye regeneration)}
\end{align*}
\]

The recombination of the injected electron of the titania layer takes place either with the oxidized sensitizer (eqn 4) or with the oxidized redox couple at the TiO\(_2\) surface (eqn 5).

\[
\begin{align*}
S^+ + e^-_{\text{TiO}_2} & \rightarrow S \quad \text{(TiO}_2/\text{Dye recombination)} \\
I_3^- + e^-_{\text{TiO}_2} & \rightarrow 3I^-_{\text{anode}} \quad \text{(TiO}_2/\text{electrolyte recombination)}
\end{align*}
\]

If cited reactions alone take place, the overall effect of irradiation with sunlight is to drive the electrons the external circuit, i.e., direct conversion of sunlight to electricity. Actually, the recombination of injected electron is
inevitable in the process of electron transfer in DSSCs. To date, a great deal of work has been carried out to solve the recombination issue. How to suppress recombination of the photocarrier is still one of the most challenging issues for improving the conversion efficiency of DSSCs in future investigation.

**Figure 1.2.** Schematic depicting of a device operation in DSSC and the required relative energy level of each component. The main steps are: (1) Light absorption; (2) Electron injection; (3) Dye regeneration; (4) TiO₂/dye recombination; (5) TiO₂/electrolyte recombination.

### 1.2.1 Electron Injection

Many early studies have been dedicated to understand photoinduced electron injection from the molecular excited state of the photosensitizer into the conduction band of the nanocrystalline metal oxide in DSSCs. These results show ultrafast electron injection process is very important to an efficient DSSCs device. Generally, the ultrafast electron injection is often explained in terms of the strong electronic overlap of the LUMO orbitals of the dye and the acceptor.
states on the metal oxide electrode, the distance between the dye and the acceptor, TiO$_2$, and dye aggregation.$^{[15-21]}$ For Ru(II) compounds, the HOMO is delocalized mainly over the –NCS ligands and ruthenium metal, whereas the LUMO is located on the $\pi^*$ orbitals of the bipyridyl ligands. As these bipyridyl ligands are directly adsorbed to the electrode surface through the –COOH anchoring groups, photo-excitation of this photosensitizer will result in migration of electron density towards the electrode surface. An efficient organic sensitizer will therefore be designed to locate the LUMO of the dye as close as possible to the TiO$_2$ surface, which can be extended to the anchoring group for a better overlap. Moreover, the distance between the dye and the acceptor, TiO$_2$ affects the injection dynamics. Lian and co-workers$^{[16,17]}$ found a slower electron injection for Re complexes when saturated CH$_2$ spacer groups were introduced between the bipyridine ligand and the carboxylic acid binding groups. The effect of distance has also been studied by introducing an insulating layer such as Al$_2$O$_3$ between dye and the metal oxide. Guo et al.$^{[22]}$ found a systematic decrease in injection rate with increasing the number of application cycles for Al$_2$O$_3$ deposition. Large $\pi$-conjugated organic sensitizers such as coumarines and perylenes have a remarkable tendency towards aggregation on the surface of TiO$_2$, which results in their lower electron injection efficiency, corresponding to lower PCE, due to the seriously quench of dye excited states. One way to avoid aggregation is to adsorb dyes in solutions containing coadsorbates such as chenodeoxycholic acid, which can help break up dye aggregates on the TiO$_2$ surface leading to improved cell efficiencies.$^{[23,24]}$ In addition, the introduction of sterically hindered substituents
(bulky groups), such as long alkyl chains and aromatic units, into dye structures should efficiently suppress dye aggregation owing to a disturbance in the intermolecular $\pi-\pi$ stacking.$^{[25,26]}

1.2.2 Charge Recombination

The timescale for the recombination reaction in dye-sensitized TiO$_2$ nanoparticles, also known as the back electron transfer, takes place in the hundreds of micro- to milliseconds time domain. The charge recombination has a significant negative effect on the photovoltaic performance. In order to suppress the disadvantage, much effort has been devoted to optimizing the molecular structure of those organic dyes, through controlling the molecular orientation and assembling modes of the dyes on the TiO$_2$ surface. The results indicate that the introduction of bulkyl groups, long hydrophobic alkyl and alkoxy chains on the donor (D) moiety or/$\pi$-bridges, effectively blocks the approach of hydrophilic I$_3^-$ ions to the TiO$_2$ surface, and thus, suppress charge recombination, resulting in an increase in the electron lifetime and $V_{oc}$ value. Tian et al.$^{[27]}$ and Sun et al.$^{[28]}$ found that these organic sensitizers with a bulkyl starburst triarylamine structure could form a compact dye-sensitizer layer on TiO$_2$ surface and increase the distance between the dye cation centre and the TiO$_2$ surface, resulting in a slow rate of charge recombination. Diau and co-workers$^{[29,30]}$ designed some enveloped porphyrin sensitizers with two phenyl groups attached at the 5,15-$meso$-positions bearing two long alkoxy chains at the $ortho$-position of each phenyl group. The long alkoxy chains can block the approach of the charged oxidized electrolyte
towards the TiO$_2$ surface to protect the porphyrin core for retarded charge recombination and also to decrease effectively the dye aggregation for an efficient electron injection.

1.2.3 Dye Regeneration

Fast dye regeneration is a prerequisite for an efficient DSSC. In DSSC, the electrolyte comprises a redox mediator. The reduced form of this mediator has to regenerate the dye ground state prior to the back electron transfer. Ideally, this redox mediator should not absorb light for avoiding the photon-to-current efficiency losses. The first data reporting efficient interception of a Ru(III) complex cation by iodide was assigned to a mechanism involving the prior formation of ion pairs.$^{[31]}$ Generally, effective regeneration of oxidized sensitizer can be occurred when the oxidation potential of a sensitizer is more positive than the triiodide/iodide (I$_3^-$/I$^-$) redox potential (0.4 V). A large number of organic oxidized sensitizers can be rapidly regenerated by iodide, as demonstrated by their good photovoltaic performances. However, the major drawbacks of using the iodide-based liquid electrolyte are the potential leakages in devices and the corrosive nature of iodine. Therefore attention has been focused on replacing this liquid electrolyte with alternative redox systems. Two pseudohalide selenocyanate mediators$^{[32]}$ comprising (SeCN)$_2$/SeCN$^-$ or (SCN)$_2$/SCN$^-$ have been investigated in dye-sensitized TiO$_2$ photoelectrochemical cells. However, these redox systems exhibited much slower regeneration rate than that in the presence of iodide under the same conditions. A solid-state hole-transporter such as spiro-OMeTAD had
also been broadly used for making solid-state DSSCs.[33,34] Unfortunately, the interception reaction in itself and its governing parameters have been only poorly investigated for this mediator. Fast dye regeneration kinetics were also found for the new one-electron redox mediators based on some cobalt(II)/cobalt(III) complexes in DSSCs. Cobalt(II)-bis[2,6-bis(1′-butylbenzimidazol-2′-yl)-pyridine] (Co(dbbip)²⁺) gave dye regeneration times of some microseconds and regeneration efficiencies of more than 0.9.[35,36] Dynamics of the recombination reaction between the injected electron and the oxidized mediator was determined with a behavior close to that of the I₃⁻/I⁻ redox couple, which made it a promising candidate to replace this widely used system in DSSCs.

1.3 Key Efficiency Parameters of DSSCs

The performance of DSSC mainly depends on a number of experimentally accessible parameters, which are incident-photo-current conversion efficiency (IPCE), photocurrent (Jₘ), photovoltage (Vₘ), fill factor (ff), overall solar energy to electricity conversion efficiency (η). These photovoltaic parameters are discussed below.

1.3.1 Incident-Photo-Current Conversion Efficiency (IPCE)

The IPCE is a quantum-yied term for the overall charge-injection collection process measured using a single wavelength source. It is defined as the number of photo-electrons move through the external load divided by the number of incident photos as a function of excitation wavelength. It can be expressed as the product
of light harvesting efficiency (\( \text{LHE}(\lambda) = 1 - 10^{-A} \)) at wavelength \( \lambda \), quantum yield of electron injection (\( \Phi_{\text{inj}} \)) from the the excited sensitizer into the conduction band of the TiO\(_2\) electrode, and the efficiency of collection of the injected electron (\( \eta_{\text{coll}} \)) at the FTO glass (\( \text{eqn 6} \)).

\[
\text{IPCE}(\lambda) = \text{LHE}(\lambda) \Phi_{\text{inj}} \eta_{\text{coll}} \quad (6)
\]

The IPCE is therefore directly related to the amount of adsorbed dyes on the TiO\(_2\) surface (or LHE), electron injection efficiency into the CB of the TiO\(_2\), and electron collection efficiency in the external circuit under monochromatic illumination of the cell.

1.3.2 Open-Circuit Photocurrent (\( J_{\text{sc}} \))

The \( J_{\text{sc}} \) value is the photocurrent per unit area (mA cm\(^{-2}\)) when a DSSC under irradiation is short-circuited. The \( J_{\text{sc}} \) value can be derived by integrating the IPCE spectra to give Equation (\( \text{eqn 7} \)).

\[
J_{\text{sc}} = e \int \text{IPCE} (\lambda) I_{\lambda} (\lambda) d\lambda \quad (7)
\]

In which, \( I_{\lambda}(\lambda) \) is the photo flux at wavelength \( \lambda \) under standard AM 1.5 simulated sunlight. Thus, to gain a high \( J_{\text{sc}} \) value, ideal molecular designs of organic dye sensitizers should feature the following characteristics: 1) intense and broad sunlight-harvesting capability, 2) strong interactions between dye sensitizers and TiO\(_2\) surfaces.
1.3.3 Open-Circuit Photovoltage ($V_{oc}$)

The $V_{oc}$ value is the difference in electrical potential between two terminals of a cell under illumination when the circuit is open. The $V_{oc}$ can be expressed by the equation 8.

$$V_{oc} = \frac{E_{cb}}{e} + \frac{k_B T}{e} \ln \left( \frac{n}{N_{cb}} \right) - E_{\text{redox}} \quad (8)$$

where $e$ is the elementary charge, $n$ is the number of the electrons in TiO$_2$, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $N_{cb}$ is the effective density of states, and $E_{\text{redox}}$ is the redox potential of the redox couple. Thus, the maximum $V_{oc}$ value of a DSSC corresponds to the difference between the energy level ($E_{cb}$) of the CB of TiO$_2$ and the redox potential of the electrolyte (I$_3^-$/I$^-$/T). However, the actual $V_{oc}$ value is lower than the theoretical value due to the recombination of injected electrons with I$_3^-$ ions in the electrolyte and with dye cations.

1.3.4 Fill Factor ($ff$)

The $ff$ is an important parameter for a solar cell and is related with the maximum power output ($J_{mp}V_{mp}$) divided by the product of $J_{sc}$ and $V_{oc}$ (eqn 9).

$$ff = \frac{J_{mp}V_{mp}}{J_{sc}V_{oc}} \quad (9)$$

The $ff$ is determined from the $JV$ curve and is an indication of how much of the area of the rectangle for $J_{sc}V_{oc}$ is filled by that described by $J_{mp}V_{mp}$. Thus, the maximum $ff$ value is 1. However, such value cannot be achieved owing to the
sheet resistances of the substrate and counter electrode, electron transport resistance through the photoanode, ion transport resistance, and the charge-transfer resistance at the counter electrode. Therefore, careful fabrication of the cell is important for attaining high photovoltaic performance.

1.3.5 Solar Energy-to-Electricity Conversion Yield ($\eta$)

The light-to-electrical power conversion efficiency of a solar cell ($\eta$) is determined by $V_{oc}$, $J_{sc}$, $ff$, and $I_0$ (generally AM 1.5, 100 mW cm$^{-2}$) (eqn 10).

\[
\eta(\%) = \frac{J_{sc} \text{ (mA cm}^{-2}\text{)} V_{oc} \text{ (V)} ff}{I_0 \text{ (mW cm}^{-2}\text{)}} \tag{10}
\]

To attain a higher $\eta$ value, optimization of the $V_{oc}$, $J_{sc}$, $ff$ values of the cell is essential. To date, the $\eta$ values have been improved gradually through designing many efficient organic sensitizers.

1.4 Key Components of DSSCs

The general configuration of DSSCs consists of four main components: a transparent photoanode, sensitizers adsorbed on mesoporous nanocrystalline metal oxide, an inorganic liquid electrolyte or solid organic hole-transporter, and a counter electrode.

1.4.1 Photo-anode

The photo-anode is related to light harvesting, electron injection and collection as well as undesirable electron recombination. The ideal photo-anode,
most typically made from a nanoporous semiconducting oxide layer (TiO$_2$), requires having a high specific surface area for dye adsorption and good interconnection between nanoparticles. Moreover, the nanostructured metal oxide also plays a very important role in DSSC. It acts as a substrate for dye adsorption and a sink for the transport of the photogenerated electrons. The ideal nanostructured semiconductor should have a mesoporous morphology, giving a high specific surface area along with a network free of recombination sites. To date, TiO$_2$ has been widely used for DSSCs applications due to its properties such as a high refraction index, a good chemical stability, an amphoteric surface and a low production cost.

In a typical DSSC device, the size of TiO$_2$ particles is around 20nm and normally colloidal TiO$_2$ dispersions are applied to deposit nanocrystalline TiO$_2$ films on FTO substrate. For the deposition of the TiO$_2$ layer, screen-printing and doctor-blading techniques are widely used.$^{[37]}$ After coating TiO$_2$ on the substrate, annealing at 450 °C ~ 550 °C is required to remove organic additives and afford good interconnection between the TiO$_2$ particles. The breakthrough in DSSCs technology was due to the TiO$_2$ film, which had a mesoporous semiconductor structure instead of a flat electrode. The mesoporous TiO$_2$ films provide a surface area more than 1000-times greater compared to a flat electrode. Moreover, the open porosity of these films allows electrolyte to fill all pores of the film and make good contact with the dye molecules and electrolyte.
1.4.2 Counter Electrode

Counter electrode (CE) is the interface where the oxidized species in the electrolyte (or holes) is reduced and is an equally important component of DSSCs. Normally, fluorine-doped tin oxide (FTO) glass is coated with platinum (by pyrolysis, sputtering, and vapor deposition) to afford more reversible electron transfer with charge transfer resistance of less than 1 Ω cm². However, Pt counter electron is scarce and expensive. So far, non-Pt materials, such as graphite,\textsuperscript{[38-40]} carbon black,\textsuperscript{[41]} carbon nanotubes,\textsuperscript{[41]} activated carbon on FTO-glass and organic ion-doped conducting polymers of poly(3,4-ethylenedioxythiophene) (PEDOT) on both indium tin oxide (ITO) and FTO-glass, have been proposed as CEs in DSSCs. Kay and Grätzel developed a CE from a mixture of graphite and carbon black for use in DSSCs with good electronic conduction as well as catalytic activity.\textsuperscript{[42]} Very recently, electrodeposited CoS has been identified as a suitable catalyst for the I⁻/I₃⁻ redox couple.\textsuperscript{[43]} Deposited on a flexible substrate (ITO/PEN) it outperforms Pt on the same substrate, with a charge transfer resistance down to 1.8 Ω cm², while thermal Pt on FTO gave 1.3 Ω cm² using the same ionic liquid electrolyte. Over 9% efficiency under AM 1.5 simulated sunlight was achieved with carbon catalyst-based DSSCs recently,\textsuperscript{[41]} rendering a new option with low cost and high corrosion resistance.

1.4.3 Electrolyte and Hole Conductors

Since the first work reported by Grätzel, I⁻/I₃⁻ system as an redox electrolyte has been widely applied in DSSCs. Efficiencies of more than 11% with
acetonitrile-based electrolyte and 8% long-term stability at 80 °C with a low volatile electrolyte have been achieved.\cite{44-47} However, the I \(^{-}/I_3^-\) redox electrolyte is liable to evaporation or leakage. Recently, room temperature ionic liquids (ILs) have attracted considerable interests as a potential candidate for replacing the volatile organic solvents due to their negligible vapor pressure and high ionic conductivity.\cite{48-50} Stable DSSCs devices were obtained by using binary mixtures of the viscous, pure imidazolium I \(^{-}/I_3^-\) IL with a low viscosity, highly stable IL. Following similar logics, quasi-solid electrolytes have been designed by gelating the electrolytes with aliphatic gels, \cite{51,52} polymers\cite{53,54} or even nanoparticles.\cite{55} Other strategies for solidifying the electrolyte include the introduction of polymer cations \cite{56,57} or plastic crystal.\cite{58} Alternatives to the I \(^{-}/I_3^-\) system are always a topic of interest. Although Br\(_2/Br^-\)\cite{59} and pseudohalogen systems of (SCN)\(_3/SCN^-\) and (SeCN)\(_3/SeCN^-\)\cite{60,61} have been reported, the high corrosion and toxicity of these electrolyte hamper further research and application. Fast outer-sphere one-electron-transfer redox couples like ferrocene/ferrocinium (Fc\(^+/Fc\)) and phenoxazine usually show facile back reaction problems from the TiO\(_2\) and substrate.\cite{62-64} Nusbaumer et al reported DSSCs based on Co\(^{II/III}\) polypyridyl complexes as a redox couple in combination with ruthenium dyes, showing an impressive efficiency of over 8% at a low light intensity under full sunlight illumination.\cite{65-67} Recently, Yella et al. boosted the efficiency of DSSC to 12.3% by using a Co\(^{II/III}\) (bipyridine)\(_3\)-based redox electrolyte in conjunction with a donor–π-bridge–acceptor zinc porphyrin dye as a sensitizer (YD2-o-C8).\cite{68} Solid organic hole conductors (HTMs) are also a focus of current research since the
majority of them are solids or nonvolatile liquids. Crystalline inorganic salts of CuSCN,[69-71] CuI,[72-74] organic molecular solids of triarylamines[75] and polymer HTMs of poly(3-alkyl thiophene),[76] polyaniline[77] have already been tested in solid-state dye-sensitized solar cells (ssDSSCs). Among all the candidates, spiro-OMeTAD remains the best photovoltaic performance to date.[78,79] Recent advances in the photovoltaic performance of ssDSSCs have augmented the PCE to a level of 4.0 to 9.3%. However, the conversion efficiencies of DSSCs employing solid HTMs still remain lower than that of their liquid electrolyte based counterparts, which could be attributed to the low electron conductivities of organic solid HTMs, incomplete penetration of solid-state HTMs into the pores of the mesoporous TiO$_2$ electrodes and fast interfacial charge recombination from the TiO$_2$ to HTM.

1.4.4 Sensitizers

The sensitizer is an essential component to absorb light in the DSSCs, converting the incident light into photocurrent. Its properties have much effect on the light harvesting efficiency and the overall power conversion efficiency. The role of the sensitizer is not only light harvesting but also charge injection. The following properties are required for the ideal sensitizer. First it should cover a wide range of the solar spectrum for high photocurrent, especially, the highest photon-flux region in order to harvest as much light as possible. Secondly, it must have anchoring groups such as carboxylate or phosphonate to graft itself on the TiO$_2$ surface and to inject electrons from the excited dye to the TiO$_2$ conduction
band. Thirdly, the LUMO level of dyes must be higher than the $E_{CB}$ of the applied semiconducting electrode for efficient electron injection from the excited dye into the conduction band (CB) of electrode, and the highest occupied molecular orbital (HOMO) level must be lower than the redox potential of the applied electrolyte for efficient dye regeneration from its oxidized state. In addition, a dye with high molar extinction coefficient is advantageous to absorb more light with a thinner TiO$_2$ film. Finally, it should sustain its photoactive property at least 20 years of throughout current generation cycle under illumination.

**Ruthenium polypyridyls compounds**

Since Grätzel and O’Regan$^6$ reported an efficient DSSCs system with polypyridyl ruthenium(II) complex dyes adsorbed on a nanocrystalline n-type semiconductor TiO$_2$ electrode in 1991, ruthenium(II) complexes have been investigated intensively for DSSCs application due to their favorable photovoltaic properties, such as broad absorption spectra through metal-to-ligand charge transfer, the longer excition lifetime and chemical stability. To date, Ru(II) polypyridyl complexes based sensitizers, which comprise with a central metal ion Ru, ancillary ligands, and anchoring groups are the most successful family in DSSCs. Ancillary ligands typically of bipyridines or terpyridines, can be tuned by different substituents like alkyl, aryl, and heterocycle units to change the photophysical and electrochemical properties and thus improve the photovoltaic performance. Anchoring groups like carboxylated bipyridine are employed to link the dye with the semiconductor and facilitate the injection of the excited electron
into the CB of the semiconductor. Ru complexes with carboxylated bipyridine ligands were first used for sensitization of TiO$_2$ single crystals in 1979.$^{[80]}$ In 1985, Desilvestro and co-workers$^{[81]}$ used a similar dye, which contains three carboxylated bipyridine ligands, to obtain the first reported efficient DSSC with an IPCE of 44%. By improving the light absorption, using a trinuclear Ru complex, a novel mesoporous TiO$_2$ electrode, and an organic solvent based electrolyte, O'Regan and Grätzel achieved 7.1-7.9% solar cell efficiency in their breakthrough report in 1991. In 1993, Grätzel and co-workers$^{[82]}$ published a series of mononuclear Ru complexes, cis-(X)$_2$bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) (Figure 1.3), where X are Cl, Br, I, CN, and SCN. The thiocyanato derivative, cis-(SCN)$_2$bis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II), coded as N3, was found to exhibit outstanding properties, such as broad visible light absorption spectrum and a photon-to-current conversion efficiency (IPCE) spectrum extending to 800 nm, sufficiently long excited state lifetime, and strong adsorption on the semiconductor surface due to binding with up to four carboxyl groups. As a result, a solar-to-electric energy conversion efficiency of 10% was first attained with the N3 dye. Many efforts have been made to change the ligands of Ru complexes and optimize the photosensitizers. To further improve the efficiency of DSSCs, extending the spectral response region of the sensitizer to the near-IR region is desirable. Therefore, Grätzel and co-workers$^{[83]}$ designed the “black dye”, coded as N749, in which the ruthenium center contains one terpyridine ligand substituted with three carboxyl groups and three thiocyanato ligands. The sensitizer showed the red shift in the MLCT
absorption band owning to the decrease in the $\pi^*$ level of the 4,4',4''-tricarboxy-2,2' : 6A',2'' terpyridine ligand and an increase in the energy of the t$_{2g}$ metal orbital. The DSSCs based on N749 exhibited a broad IPCE spectrum extending into the near-IR region up to 920 nm and yielded an overall conversion efficiency of 10.4% ($J_{sc} = 20$ mA cm$^{-2}$, $V_{oc} = 720$ mV, FF = 0.7) under AM 1.5 G, 100 mW cm$^{-2}$ irradiation. Wang and co-workers\cite{84} reported a family of high molar extinction coefficient heteroleptic polypyridyl ruthenium sensitizers featuring conjugated electron-rich units like alkyl thiophene, alkyl furan, alkyl selenophene, and alkyl thieno[3,2-b]thiophene as their $\pi$ conjugatied ancillary ligands. The new dye (coded as C101) achieved recorded conversion efficiency under AM 1.5 G illumination. It gave 11.0% efficiency with an acetonitrile based I$^-$/I$_3^-$ electrolyte and a long-term stable ($\eta \approx 7.4\%$) device employing an ionic liquid electrolyte. They found that because of the high extinction coefficients of the sensitizer, the TiO$_2$ film thickness may be reduced, which favors the charge collection efficiency as well as reduces the charge recombination. Recently, Chou et al\cite{85} reported a series of bis-tridentate, thiocyanate-free ruthenium sensitizer (TFn) for DSSCs, containing the 2-azolyl-6-phenylpyridine cyclometalate. These Ru(II) sensitizers presented notable near-infrared absorptions up to 880 nm, which exhibited an IPCE value of 85% and prominent conversion efficiency, 9.04 % at AM 1.5 G. Finally, highly stable DSSCs have been achieved, showing an efficiency degradation of only 3–6% under 1000 hours of light soaking at 60 °C. This opens up possibilities to design the next generation of ruthenium sensitizers.
Figure 1.3. Molecular structures of Ruthenium-based sensitizers

Porphyrin

Recently, porphyrin-based DSSCs have been received many attentions owing to intense spectral response of porphyrins between 400-450 (Soret band) and 500-700 (Q-band) nm, as well as their good chemical, photo-, and thermal stability. These properties suggests that porphyrins can be good potential candidates for panchromatic DSSCs. The first meso-substituted copper porphyrin (P1) (Figure. 1.4) based DSSC with an overall energy conversion efficiency of 2.6% and IPCE value of over 80% was reported by Kay and Grätzel in 1993.[86] In the succeeding decade there were almost no progress in developing porphyrins as sensitizers for DSSCs until 2004. Grätzel and co-workers[87] reported a zinc porphyrin (P2)-based DSSC fabricated in a THF dye bath to achieve an overall
efficiency of 5.6% in the presence of co-adsorbent chenodeoxycholic acid (CDCA) under AM 1.5 G irradiation. In 2007, the same group\cite{88} reported $\beta$-substituted zinc-porphyrin sensitizer (P3) to obtain an impressive efficiency of 7.1% in liquid electrolyte-based DSSCs and 2.4% in solid state DSSCs. Their results open a great opportunity for the development of various porphyrin sensitizers to enhance the efficiency in DSSCs. The low conversion efficiencies in porphyrins-based DSSCs are ascribed to the serious dye aggregation on TiO$_2$ films compared with Ru(II) based DSSCs. To solve the aggregation problem of porphyrins, 3,5-di-tert-butylphenyl groups and long alkyl chains were introduced at the meso-positions of the porphyrin ring. Yeh and Diau\cite{89} designed another promising push–pull porphyrin, YD2 in that two tert-butyl groups in the diarylamino substituent were replaced with two long alkyl chains to improve the thermal and photochemical stability of the device. The device performance of YD2 was further improved to 6.8% when co-adsorbed with CDCA, slightly less than that of the referenced N719 (7.3%). In 2010, the device performance of YD2 was further improved when cosensitized with a metal-free organic dye by Grätzel and co-workers,\cite{90} thus exhibiting an unprecedented efficiency of 11% with $J_{sc} = 18.6$ mA cm$^{-2}$, $V_{oc} = 0.77$ V, FF = 0.764 under standard illumination test conditions.
To extend the absorption of porphyrin dyes to the near infrared region to harvest more solar photons, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels must decrease. The two strategies are to introduce a highly conjugated \( \pi \)-extended chromophore coupled with the porphyrin ring or to make fused or dimeric porphyrins. Lin and Diau designed a series of fluorene/pyrene-modified porphyrins bearing cyclic aromatic substituents at the meso-position of the macrocycle opposite to the anchoring group. They found that the fluorene-functionalized porphyrin (LD22)\(^{[91]} \) featured an impressive efficiency of 8.1% with a broad IPCE response from 300 to 750 nm, and the pyrene-functionalized porphyrin (LD4)\(^{[92]} \) displayed the amazing efficiency up to
10.1% with a remarkable open-circuit photocurrent ($J_{sc}$) of 19.63 mA cm$^{-2}$, which was superior to that of a referenced N719 dye (9.3%) under the same working conditions. The superior photovoltaic performance of the LD4-based DSSCs was attributed to its strong light harvesting ability with the broad IPCE action spectrum covering the entire visible spectral region and extending beyond 800 nm.

In 2011, Wang and Wu$^{[93]}$ designed two perylene anhydride fused nickel porphyrin sensitizer (Figure 1.5, WW1) to show broad incident monochromatic photon-to-current conversion efficiency spectra covering the entire visible spectral region and even extending into the near-infrared (NIR) region up to 1000 nm. The WW1-based DSSC attained relatively a low photovoltaic performance (1.36%) owning to the fused porphyrin suffered from serious dye aggregation. Another strategy to extend light spectral region of the sensitizer is to combine two porphyrin moieties through a chemical bond. Segawa$^{[94]}$ designed a series of bis(4-methoxyphenyl)amino, bis(4-tert-butylphenyl)amino, and 3,6-di-tert-butyl, carbazol-9-yl units at the meso-position of the porphyrin edge to form a push–pull porphyrin dimers, BMPA, BTBPA, and DTBC. These porphyrin dimers obtained highly efficient light-to-current conversion throughout the visible and NIR region. In the absence of a TBP additive, the DTBC device exhibited IPCE with a plateau values up to 80% from 800 to 900 nm, yielding a remarkable $J_{sc} = 14.26$ mA cm$^{-2}$, but also showing a low $V_{oc} = 0.57$ V, corresponding to an optimized device photovoltaic performance of 5.2%. The reported NIR fused porphyrins and dimeric porphyrins introduced herein are facile to aggregate formations that significantly decrease the efficiency of electron injection due to their planar
structural feature. To solve this problem for porphyrins, a new strategy was introduced by designing a zincporphyrin sensitizer with long alkoxy chains to decrease effectively the degree of dye aggregation for an efficient electron injection and also to protect the porphyrin core for suppressing charge recombination. The first research work based on such a molecular design was reported in 2009 by Imahori and co-workers. They had announced their results based on ortho-substituted porphyrins, but the alkyl chains (only methyl and ethyl groups were considered) substituted at the ortho-positions were too short to protect effectively the porphyrins from dye aggregation. The highest cell performance was obtained based on 5-(4-carboxyphenyl)-10,15,20-tris(2,4,6-trimethylphenyl)porphinatozinc(II) as a sensitizer with a maximal incident photon-to-current efficiency of 76%, a short circuit photocurrent density of 9.4 mA cm⁻², an open-circuit voltage of 0.76 V, a fill factor of 0.64, and a power conversion efficiency of 4.6% under standard AM 1.5 sunlight. After that, Hupp and co-workers designed two π-extended porphyrin sensitizers attaching two phenyl groups at the 5,15-meso-positions bearing two dodecoxyl (–OC₁₂H₂₅) chains at the ortho-position of each phenyl group. Under AM 1.5 illumination, LH₃ and ZnPdCA-sensitized cells displayed the best performance of each series with a short circuit photocurrent density \( J_{sc} \) of 11.3 mA cm⁻², an open circuit voltage \( V_{oc} \) of 680 mV, and fill factor (FF) of 0.70, yielding an overall conversion efficiency of 5.5%. Work developed along this track led to an advance for a device made of an ortho-substituted push–pull zinc porphyrin, YD₂-OC₈, for which the four ortho-substituted octyloxy side chains in the each of the
meso-phenyls of porphyrin. The specific molecular design has greatly decreased the degree of dye aggregation and retard effectively the rate of interfacial back electron transfer, which enable large photocurrent and high photovoltage. An optimized performance of the YD2-OC8 device using Co(II/III)tris(bipyridyl)-based redox electrolyte under AM1.5 one-sun irradiation: $J_{sc} = 17.3$ mA cm$^{-2}$, $V_{oc}$ = 0.965 V, FF = 0.71, and $\eta$ = 11.9%. The cosensitization of YD2-OC8 with the previously prepared organic dye Y123, produced an efficiency of 12.3% under AM1.5 one-sun irradiation. The power conversion efficiency even exceeds 13% under AM 1.5 solar light of 500 Wm$^{-2}$ intensity. The transient photocurrent and photovoltage decay measurements of the devices supported that the high $V_{oc}$ observed with YD2-OC8 is due to the presence of the four octyloxy groups caused an upward shift of the TiO$_2$ conduction band and reduced the recombination rate as well as the back-electron transfer rate. These reported results might provide a fertile base for the molecular design of porphyrin sensitizers to produce even greater efficiencies of power conversion in the future DSSCs investigation.
Figure 1.5. Molecular structures of porphyrins-based NIR sensitizers.

Metal-Free Organic Dyes

In recent years, considerable efficient organic dyes as an alternative to the noble Ru complexes sensitizers have been developed to optimize DSSCs performance and have obtained impressive efficiencies. Compared with Ru complexes based sensitizers, these metal-free organic sensitizers exhibit many advantages: (1) The molecular structures of organic dyes are in diverse form and can be easily designed and synthesized. (2) Concerning the cost and environment issues, organic dyes are superior to noble metal complexes, allowing the fabrication of foldable and flexible large area devices. (3) The molar extinction coefficients of organic dyes are usually higher than those of Ru complexes, making them attractive for thin film and solid-state DSSCs. Generally, the
skeleton of metal-free organic sensitizers are constituted by electron donor (D), π-conjugated spacer (π) and electron acceptor (A) moieties, so called D–π–A character. This push–pull structure can induce the intramolecular charge transfer (ICT) from the donor to acceptor through π-conjugated spacer when a dye absorbs light. Moreover, with D–π–A construction it is easy to design new sensitizers, tune the absorption spectra and the HOMO and LUMO levels of the dyes by variation of the D, π and A units. Considerable works have been concentrated on changing the different parts of organic dyes to optimize DSSCs performance. To date, hundreds of n-type metal-free organic dyes have been synthesized and successfully adopted to act as sensitizers for DSSCs. Among the metal-free organic dyes, the arylamine organic dyes C219, [98] holding the record for validated efficiency of over 10.3% measured at the AM 1.5G conditions for DSSC.

**Triphenylamine Dyes**

Triarylamine and its derivatives (Figure 1.6) have been widely investigated in optoelectronics and electro-active materials due their good electron donating ability and hole transporting capability. In recent years, a very large number of new organic dyes with triarylamine as electron donor have been developed and most of them have shown good power conversion efficiencies in DSSCs. Yanagida and co-workers[99] first introduced the triphenylamine unit as electron donating group in organic sensitizers and obtained overall DSSCs conversion efficiencies of 3.3% and 5.3% for dye 1b and 2b, respectively (N719, 7.7%). To
further optimize triphenylamine sensitizers, Tian and co-workers\textsuperscript{[100]} designed and synthesized a novel type of starburst triarylamine based sensitizers (S1-S4) with D–D–π–A configuration by adding electron donor groups on the outside of triarylamine. Starburst triarylamine based sensitizer $S_4$ exhibited higher conversion efficiency than the one with single triphenylamine unit, yielding maximum 85% IPCE and 6.02% power conversion efficiency. The introduction of a starburst triarylamine group as the electron-donor unit showed bathochromic shift in the absorption spectrum and higher molar extinction coefficient as well as effectively inhibited aggregation between molecules, and thus enhanced the stability of the solar cells. Great efforts in developing tailored dimethylfluorenylarnino-based triarylamine derivative as the donor in designing organic sensitizers have been made by Ko and co-workers\textsuperscript{[101]} The advantage of the structure of JK2 can ensure greater resistance to degradation when exposed to light in comparison with simple triphenylamine (TPA). Moreover, the nonplanar character of the dialkylfluoreneaniline disfavored molecular stacking to suppress dye aggregation on TiO$_2$ film. Under standard global AM 1.5 solar conditions, the JK2-sensitized cell gave an overall conversion efficiency of 7.63% ($J_{sc} =14.54$ mA cm$^{-2}$, $V_{oc} = 0.70$V, FF = 0.74). Wang and co-workers\textsuperscript{[98]} have made a great progress in developing efficient triarylamine-based organic sensitizers. They designed a very promising sensitizer coded $C_{219}$ featuring a lipophilic alkoxy-substituted TPA electron-donor, a hydrophilic cyanoacrylic acid electron-acceptor, and the ethylenedioxythiophene and dithienosilole as binary π-conjugated spacer. The $C_{219}$-based sensitizer exhibited a broad absorption band
from 300 nm to 780 nm and a molar extinction coefficient $57.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 493 nm in chloroform. When this dye was fabricated in liquid electrolyte based DSSCs, even with a preliminary optimization this novel photosensitizer C219 has already achieved a remarkably high conversion efficiency of 10.3% ($J_{sc} = 17.94$ mA cm$^{-2}$, $V_{oc} = 770$ mV, FF = 0.730) measured under irradiation of AM1.5G full sunlight. More importantly, a solvent-free ionic liquid cell based on this new dye has yielded a high conversion efficiency of 8.9% under a low light intensity of 14.39 mW cm$^{-2}$, making it very favorable for the indoor large-scale application of flexible DSSC.

![Molecular structures of triphenylamine-based sensitizers](image)

**Figure 1.6.** Molecular structures of triphenylamine-based sensitizers

**Indoline Dyes**

In recent years, it was found that the excellent photoelectric function of indoline was desirable for organic sensitizers, and a substantial number of
photosensitizers with indoline as electron donor were developed for low cost organic solar cells. Horiuchi and co-workers\textsuperscript{[102]} first reported this type of organic dye and achieved a good power conversion efficiency of 6.1%, compared to 6.3% for N3 under the same working conditions. Furthermore, to improve the DSSCs photovoltage performance, the same group\textsuperscript{[103]} reported a series of novel indoline dyes by introducing an additional rhodanine framework into the molecular structure. The new indoline dyes (Figure 1.7) exhibited broad light absorption spectra with high molar extinction coefficient of 68700 M\textsuperscript{-1} cm\textsuperscript{-1} at 526 nm for D149. As a result, the dye D149 showed the most prominent efficiency, 8.0% ($J_{sc}$ =18.50 mA cm\textsuperscript{-2}, $V_{oc}$ = 693 mV, $ff$ = 0.624), under AM 1.5 G irradiation. Since then, many aspects of indoline dyes have been designed and synthesized for DSSCs application. Later, Grätzel and co-workers\textsuperscript{[104]} scrutinized the effect of the film thickness of nanocrystalline TiO\textsubscript{2} films on the photovoltaic performance of the D149-sensitized cell employing acetonitrile- and ionic-liquid-based electrolytes. The optimized thickness of the D149-sensitized nanocrystalline TiO\textsubscript{2} layers for the acetonitrile- and ionic-liquid-based electrolytes were 6.3 and 12.6 um with conversion efficiencies of 6.67 and 9.03%, respectively. In order to avoid the \pi-stacked aggregation between indoline dye molecules on TiO\textsubscript{2} film to generate high photocurrent, dye D205\textsuperscript{[105]} was designed by introducing the long $n$-octyl chains on the rhodanine ring of D149 for use in DSSCs. The ionic liquid electrolyte based device sensitized by D205 gave a progressive PCE of 9.52% ($J_{sc}$ = 18.56 mA cm\textsuperscript{2}, $V_{oc}$ = 0.717 V, and FF = 0.716) with the use of chenodeoxycholic acid (CDCA) as a co-sensitizer under AM 1.5 radiation, which
is the highest power conversion efficiency reported so far among DSSCs based on an indoline dye under AM 1.5 radiation.

**Figure 1.7.** Molecular structures of indoline-based sensitizers

**Phenothiazine Dyes**

Phenothiazine is a well-known heterocyclic compound containing electron-rich nitrogen and sulfur heteroatoms with high electron-donating ability, and its non-planar butterfly conformation (Figure 1.8) can sufficiently inhibit molecular aggregation and the formation of intermolecular excimers. Meanwhile, the substituents on the N(10) atom can further enhance the charge separation at the oxide solution interface. Furthermore, the two phenyl groups are arranged in a small torsion angle related to the N(10) and S(9) atoms, so that π-delocalization can be extended over the entire chromophore. The structural features of phenothiazine-based dye make it a promising type of sensitizers for DSSCs. Recently, a diversity of strategies have been utilized to extend the range of π-electron delocalization and increase the molar absorptivity of the materials. In 2007, Sun and co-workers\(^{106}\) first reported novel organic sensitizers based on the low-cost phenothiazine chromophore with simple synthetic procedures for DSSCs.
Even with a simple molecular structure, it has achieved a prominent solar energy-to-electricity conversion efficiency of 5.5% ($J_{sc} = 10.9\ mA\ cm^{-2}$, $V_{oc} = 712\ mV$, and $ff = 0.71$) in a T2-1-based DSSC, in comparison with the reference Ru-complex (N3 dye) with an conversion efficiency of 6.2% under similar experimental conditions. After that, Park et al.\cite{107} designed and synthesized novel organic dyes of double electron acceptor type (cyanocrylic acid and rhodanine-acetic acid) based on phenothiazine framework, as photosensitzers for DSSC. They found that the organic dyes of double electron acceptor type gave about 20% higher performance than their counterparts of single electron acceptor type and the organic dyes with cyanocrylic acid as acceptor gave much higher efficiencies than that of dyes with rhodanine-acetic acid as acceptor. The DSSCs based on PR6C2 containing double cyanocrylic acid based-electron acceptor exhibited a maximum $\eta$ value of 6.8% ($J_{sc} =14.96\ mA\ cm^{-2}$, $V_{oc} = 676\ mV$, $FF = 0.68$), which was the most efficient photon-to-electricity conversion efficiency compared to other dyes, under simulated AM 1.5G light irradiation. To further improve the photovoltaic performance, extending the $\pi$-conjugated linker is a good strategy. Kim and co-workers\cite{108} designed some phenothiazine derivatives with various five-membered heteroaromatic conjugated linkers (furan, thiophene, and 3,4-ethylenedioxythiophene) to study the effect of conjugated linkers on device performance. The highest solar energy-to-electricity conversion efficiency of 6.58% ($J_{sc} = 12.18\ mA\ cm^{-2}$, $V_{oc} = 771.7\ mV$, $FF = 70.02\%$) was sensitized by a cell fabricated with SH-6 with furan as a conjugated linker, which has an enhancement of over 24% compared with the efficiency of 5.29% achieved by the
referenced dye T2-1 under similar conditions. Notably, they found that the PTZ-torsion angle values of the dyes were consistent with the sequence of $V_{oc}$ values in the devices. They proposed that an increased in torsion angle could reduce molecular aggregation through steric hindrance and improve the $V_{oc}$. To study the effect of the conjugated linkers length on the performance of the DSSCs, Lee and Kim$^{[109]}$ synthesized three phenothiazine-based organic dyes (H-PTZ, HPTZ-BT and H-PTZ-TPA-T) with a thiophene, bithiophene, and TPA as $\pi$-conjugated bridges. The results showed that $J_{sc}$ value increases with increasing $\pi$-conjugated bridge length. Grätzel’s group$^{[110]}$ reported two novel organic dyes (V5 and V7), using electron-rich 10-butyl-(2-methylthio)-10H-phenothiazine as a donor with/without vinyl thiophene group as a $\pi$-bridge and cyanoacrylic acid as an acceptor. As a result, extending the $\pi$-conjugated linker by the introduction of a vinyl thiophene group vastly enhanced the spectral response of the sensitizer V7. The absorption band of V7 exhibited a bathochromic shift of 27 nm as well as higher molar extinction coefficient with respect to that of V5. The cell sensitized with V7 had a greatly improved IPCE and broadened the onset to 750 nm, which in turn translated to an enhanced photocurrent ($J_{sc}$) from 11.2 to 15.2 mA cm$^{-2}$. The PCE of the device based on V7 reached 7.3% with a volatile electrolyte under standard AM 1.5 irradiation conditions.
Kim and co-workers\cite{111} developed a novel class of organic dyes containing the multi-chromophororic system in a molecule by connecting two individual phenothiazine-based chromophores with alkyl chain directly for use in DSSCs (Figure 1.9). Each of chromophore contains phenothiazine moiety as an electron donor and various electron acceptor/anchor to identify the effects of the number of electron acceptor and the kind of electron acceptor on the performance of DSSCs. They found that the molecular structure having multi-chromophoric system (DYE 4) containing cyanoacrylic acid moieties provided about 10% higher $J_{sc}$ value than their counter parts of singlechromophore type (DYE 1). The PCE of the device based on DYE4 reached 3.4 % with a volatile electrolyte under standard AM 1.5 irradiation conditions. Cao et al.\cite{112} designed three simple double donor-acceptor (D-A) branched dyes (DBD) with a phenothiazine unit as electron donor and a 2-cyanoacrylic acid unit as electron acceptor for dye-sensitized solar cells. They found that the molar extinction coefficients of these double D-A branched dyes (DBD) are nearly twice as high as that of SB because the two donor–acceptor

\begin{figure}
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\caption{Molecular structures of phenothiazine-based sensitizers}
\end{figure}
units of DBD displayed stronger light-harvesting ability. Thus, the $J_{sc}$, $V_{oc}$ and PCE of the DSSCs fabricated by DBD ($J_{sc} = 6.98–8.27$ mA cm$^{-2}$, $V_{oc} = 0.74-0.75$ V, PCE = 3.56–4.22%) were effectively enhanced in comparison with the corresponding single SB dye ($J_{sc} = 6.13$ mA cm$^{-2}$, $V_{oc} = 0.71$ V, PCE = 2.91%).

Based on this finding, they synthesized three phenothiazine-based dyes (DC1-3) bearing two asymmetric double D-$\pi$-A chains.$^{[113]}$ An improved PCE of 5.19% was obtained for the DC3-sensitized solar cells under standard global AM 1.5 solar condition as a result of its longer electron lifetime and its broader and more intensive absorption in the UV-visible region.

![Molecular structures of phenothiazine-based sensitizers](image)

**Figure 1.9.** Molecular structures of phenothiazine-based sensitizers

For efficient design of donor-spacer-acceptor dyes, one of the key issues relates to the positioning of the electron donor group on the macrocycle periphery of phenothiazine. Zhu et al.$^{[114]}$ designed two types of new phenothiazine-based
dyes (Figure 1.10), in which Type 1 molecules are appended with a donor aryl group at the C(7) position and n-hexyl group at the N(10) of phenothiazine (PT1 and PT2), and Type 2 molecules are with the donor aryl group at the N(10) of phenothiazine (PT3 and PT4), together with a cyanoacrylate moiety at the C(3) position in both types of species. The structural features of a donor aryl group at the C(7) position of phenothiazine extends the \( \pi \)-conjugation of the chromophore, while the donor aryl group at N(10) significantly increases the steric hindrance of the dye due to its mutually perpendicular structural characteristics with either phenyl ring of bent phenothiazine. As a result, Type 1 dyes have better light harvesting properties in contact with TiO\textsubscript{2} films, and give much better DSSC performance than Type 2 dyes. The PT1-sensitized DSSC shows a higher \( V_{oc} \) of 0.829 V and lead to a final PCE of 6.72% based on PT1. Tian and co-workers\textsuperscript{[115]} studied the effect of different electron-donors of phnothiazine organic dyes (PH1-PH3) on the photovoltaic performance. They found that the introduction of a triphenylamine group as the electron-donor could improved photocurrent and photovoltage in comparison with methoxytriphenylamine and 1,1,2-triphenyl-ethene for phenothiazine dyes. The PH2 sensitized DSSCs showed the best PCE of 4.41\% (\( J_{sc} = 10.84 \text{ mA cm}^{-2}, V_{oc} = 592 \text{ mV}, \text{FF} = 0.69 \)) under AM 1.5 light irradiation. Most importantly, long-term stability of the phenothiazine DSSCs was attained under 1000h light-soaking. In a study of PTZ dyes, Chi, Kuang and co-workers\textsuperscript{[116]} reported a series of polyphenyl-substituted ethylene end-capped phenothiazine dyes (VP2, VP3 and VP4) for dye-sensitized solar cells. Comparisons between the molecular structures of VP2, VP3 and VP4 indicated
that the more twisted triphenylethylene and tetraphenylethylene cap structures as well as larger sizes of the dyes are superior to diphenylethene in terms of effectively slowing down the recombination of injected electrons at the interface dye/TiO$_2$ interface or in the electrolyte, and lengthening the electron lifetime. For this reason, the $V_{oc}$ in the DSSCs increased in the following order: VP1 (712 mV) < VP2 (759 mV) < VP3 (789 mV) < VP4 (804 mV). The introduction of a twisted structure onto the end of the organic dye molecules is beneficial for the enhancement of the charge collection efficiency. As a results, the performance efficiencies of the DSSCs based on VP2 (PCE = 5.84%), VP3 (PCE = 6.29%), and VP4 (PCE = 5.76%) were better than those of their parent-compound-sensitized counterpart VP1 (PCE = 5.5%). Further modifications$^{[117]}$ of VP1 have been performed through the introduction of the triphenylethylene phenothiazine (C2, C3) and triphenylethylene carbazole (PH4, P5) moieties as additional electron donors in organic dyes. The PH5-based cell attaching a more twisted triphenylethylene phenothiazine group, achieved a better photovoltaic performance (PCE = 6.55%, $J_{sc} = 12.18$ mA cm$^{-2}$, $V_{oc} = 826$ mV, and FF = 0.64). These results demonstrated that the twisted non-planar configuration in organic dyes could suppress the charge recombination in the charge-separated state and hence contributes to the improvement of the performance of DSSCs.
Chow and co-workers\cite{118} designed a series of phenothiazine-based organic sensitizers, in which, a triarylamino moiety was attached at the C(7) position as an electron donor, a cyanoacrylate moiety was added at the C(3) position of the phenothiazine as an electron acceptor and a variety of substituents, i.e., methyl, hexyl and TPA groups, at the N(10) of phenothiazine in order to examine its influence on the device properties (Figure 1.11). Certain structural features were found to be related to the performance of devices: (i) adding a triarylamino donor moiety at the C(7) position of phenothiazine extends the π-conjugation of the chromophore, therefore enhancing the photocurrent response region; (ii) adding a hexyl substituent at the N(10) of phenothiazine seems to be more beneficial than a TPA substituent. The latter then perform better than that with a methyl substituent; (iii) inserting a thiophene moiety between the phenothiazine and the acceptor...
group reduced the loading amount of the dyes, as well as the device efficiency. The best performance was found with NSPt-C6, in which a hexyl group was attached at the N(10) and a thiophenylene at the C(7) position of of phenothiazine. It displayed a short-circuit current ($J_{sc}$) of 14.42 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 0.69 V, and a fill factor (ff) of 0.63, corresponding to an overall conversion efficiency of 6.22%. Chow et al.\cite{119} have designed a series of oligo-phenothiazine-based organic dyes. In these compounds the phenothiazine moiety functions both as an electron donor and also as a π- conjugated bridge, in which, the hexyl and hexyloxyphenyl substituents were added onto the N(10) of phenothiazine for a comparison. They found that the length of the organic dyes limited their performance. The photovoltaic performance of the dimer system performed better than the trimers. The highest $V_{oc}$ values reached a level of 0.83 V, and a conversion efficiency of 7.78% was obtained in PT2b ($J_{sc} = 14.3$ mA cm$^{-2}$, $V_{oc} = 830$ mV, FF = 0.65) in combination with CDCA. The development of low-cost and simple metal-free organic dyes for highly efficient DSSCs is always desirable. Recently, Zhu and co-workers\cite{120} designed a series of simple phenothiazine-based dyes, in which a cyanoacrylate acceptor directly attached to the C(3) position of phenothiazine, and an additional linear electron-rich (4-hexyloxy)phenyl group at C(7) on the opposite side of the acceptor, and an alkyl chain with different length at N(10) of the phenothiazine periphery. The dye molecules showed a linear shape which was favorable for the formation of a compact dye layer on the TiO₂ surface, while their butterfly conformations can sufficiently inhibit molecular aggregation. Moreover, the structural features of
(4-hexyloxy)phenyl donor moiety at the C(7) position of phenothiazine extended the π-conjugation of the chromophore, thus enhancing the performance of DSSCs. Furthermore, the alkyl substituents with different chain length at the N(10) atom of phenothiazine could further optimize the performance through completely shielding the surface of TiO₂ from the I⁻/I₃⁻ electrolyte and subsequently reducing the leakage of dark current. Under simulated AM 1.5G irradiation, the PT-C₆ based DSSC produced a short-circuit photocurrent of 15.32 mA cm⁻², an open-circuit photovoltage of 0.78 V, a fill factor of 0.69, corresponding to a power conversion efficiency (PCE) of 8.18%, which exceeded the reference N₇₁₉ (7.73%) under identical fabrication conditions. Notably, the designed molecular structure represented the highest photovoltaic conversion efficiency value when compared with other reported phenothiazine-derived dyes. These findings will facilitate our understanding of the crucial importance of molecular engineering and shed light on optimizing phenothiazine-based metal-free organic dyes for highly efficient DSSCs.
1.5. Objectives of the Thesis

The photovoltaic performances of DSSCs have been progressed by applying new metal-free organic dyes, optimizing the device components and carrying out some fundamental studies. The objective of the present work is basically to improve the power conversion efficiency of the DSSCs device by exploring new organic dyes. In addition, this research assists to gain more insight into the structure-property relationship of organic dyes, and the photovoltaic performance of DSSCs devices based on these organic sensitizers. The ultimate target is to reach a high conversion efficiency of 15% in DSSCs based on organic dyes, while retaining their stability under standard reporting conditions.
1.6 References


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Phys. 2005, 5, 149.


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2.1. Introduction

Dye-sensitized solar cells (DSSCs) have been considered as a promising alternative for energy harvesting in order to solve the energy crisis as well as other environmental problems.\(^1\) A typical DSSCs includes three main ingredients: nanocrystalline semiconductor, the redox electrolyte, and a dye sensitizer.\(^2\) Among the three key components, the sensitizer plays a vital role in the light conversion efficiency and the device stability. The "champion" DSSCs using ruthenium-based complexes, i.e., \(\text{N3,}^3 \text{N719,}^4\) and black dye\(^5\) reported by Grätzel et al., have achieved power conversion efficiencies (PCEs) over 11%. Recently, co-sensitization of donor-\(\pi\)-acceptor zinc(II) porphyrin dye with another organic dye further enhanced the performance of the device, leading to PCE of 12.3%.\(^6\) Though the PCE climaxes cast light on the promising practical applications, such high efficiencies are rarely seen in the literature. In this regard, comprehensive investigations are required to understand the working principle and further improve the PCE,\(^7\) especially in the development of new dye molecules with enhanced absorption coefficient, fast charge injection kinetics and favorable spatial configurations.\(^2,8\)

Compared with metal complexes, metal-free organic dyes have also attracted considerable attention due to the advantages of easier preparation and purification,
higher structural flexibility, environmental friendliness and avoiding the use of noble metals. In particular, the design and synthesis of donor-π-acceptor metal-free organic dyes with a wide range of donor groups such as, triphenylamine,[9] coumarin,[10] indoline,[11] carbazole,[12] squaraine,[13] and phenothiazine (PT) [14], has led to a number of efficient sensitizers for DSSCs. However, it is known that most organic sensitizers usually appear in a rod-shape configuration, and they are inclined to aggregate on the semiconductor surface, leading to lower photovoltaic performance of DSSCs than N719 because of intermolecular quenching of molecules residing in the system not functionally attached to the TiO₂ surface and thus acting as filters.[15] It is worth noting that a phenothiazine dye contains electron-rich nitrogen and sulfur heteroatoms in a heterocyclic structure with high electron-donating ability, and its non-planar butterfly conformation can sufficiently inhibit molecular aggregation and the formation of intermolecular excimers.[14a, 14b] Meanwhile, the 10-substituent on N can further enhance the charge separation at the oxide solution interface.

Furthermore, the two phenyl groups are arranged in a small torsion angle related to N(10) and S(9) atoms, so that π-delocalization can be extended over the entire chromophore. The structural features of phenothiazine dye make it a promising type of sensitizer for DSSC applications. Recently, a diversity of strategies have been utilized to extend the degree of π-electron delocalization and increase the molar absorptivity of the materials.[12a, 14c-e, 14g, 14h, 14k, 16] For example, the addition of thiophene and triarylamine moieties in some of the structures extend π-conjugation of the chromophore and increases the molar absorptivity of the
materials, meanwhile make the whole molecule to occupy a larger surface area than a molecule of linear shape, leading to the reduction of loading capacity.\[14b\] At the same time, the molecular engineering of sensitizers can enhance the charge separation at the oxide solution interface.\[14c\] As a result, certain structural modifications of this kind of dyes have resulted in moderate improvement of PCEs. And the development of phenothiazine based dyes stimulates further structural optimization of low-cost organic dyes, facilitating the practical application of DSSCs.

In this chapter, two types of new phenothiazine-based organic dyes have been synthesized to investigate the positioning effect of a donor group on the performance of dye-sensitized solar cells (DSSCs) (Figure 2.1), in which Type 1 molecules are appended with a donor group, i.e., carbazolyl and fluorenyl groups, at C(7) and 1-hexyl unit at the N(10) of phenothiazine (PT1, PT2, Type 1), and Type 2 molecules with the donor group at N(10) of the phenothiazine periphery (PT3, PT4, Type 2), together with a cyanoacrylate moiety at the C(3) position of phenothiazine in both types of species. In addition, the dye PT5 was prepared according to the literature method for comparison.\[14a\] Our results demonstrate that the molecular design strategy in Type 1 dyes can effectively improve the photovoltaic performance, resulting in the highest efficiency of 6.72% in DSSC based on PT1. To understand the structural effect of these dyes on the photovoltaic performance in DSSCs, density functional theory (DFT) calculations and electrochemical impedance spectroscopy (EIS) were also performed, which
enable us to get insight of these phenomena and allow their extension into general principles for the design and synthesis of effective dyes.

Figure 2.1. Chemical structures of the dyes PT1-PT5 based on phenothiazine.

2.2 Results and Discussion

2.2.1 Synthesis and Characterization

As illustrated in Scheme 2.1, the synthesis of PT1 and PT2 follows the previously reported strategy of a Suzuki cross coupling of aryl boronic acid and 7-bromo-10-hexyl-10H-phenothiazine-3-carbaldehyde(3), and the widely employed Knoevenagel condensation to construct classical donor-π-acceptor dyes. And dyes PT3 and PT4 were prepared in 3 steps, including N-arylation, Vilsmeier-Haack reaction with POCl3 and N,N-dimethylformamide (DMF), and finally Knoevenagel condensation. All of the new photosensitizers for PT1-PT5
are air-stable and can be stored without any special precautions. All the new compounds have been characterized by NMR spectroscopic and mass spectrometric methods from which they are shown to consist of well-defined structures.

Scheme 2.1. Synthesis of PT1-PT4. Reaction conditions: (a) 1-bromohexane, K$_2$CO$_3$, DMSO; (b) POCl$_3$, DMF, reflux; (c) NBS, THF; (d) Pd(Ph$_3$P)$_4$, 2 M K$_2$CO$_3$, THF; (e) cyanoacetic acid, CH$_3$COOH, CH$_3$COONH$_4$, 120 °C; (f) Cu, K$_2$CO$_3$, 18-crown-6.
2.2.2 UV-vis Absorption Spectra

The UV-Vis absorption spectra of dyes PT1-PT5 in CH₂Cl₂ solutions (Figure 2.2) and on TiO₂ surface have been recorded (Figure 2.3), and the detailed spectroscopic data are summarized in Table 2.1. All of these dyes exhibit two major distinct broad absorption bands in the range of 300–600 nm. The shorter wavelengths in the range of 300–370 nm are ascribed to aromatic π-π* electronic transitions of the chromophores, while the longer wavelengths in the range of 380–600 nm are attributed to the intramolecular charge transfer (ICT) from the donor to the acceptor, which provides efficient charge separation at the excited state. Compared with the dye PT5, new dyes PT1-PT4 exhibit a slight red-shift of the absorption spectra, leading to a better light harvesting property in the visible region. In addition, the absorption spectra of Type 1 dyes with a donor substitution at the C(7) position of phenothiazine are slightly blue shifted as compared to the Type 2 dyes with the donor group at N(10). Because of the simple donor-π-acceptor structures, these phenothiazine-based dyes show relatively low molar extinction coefficient with values of around 15,000 M⁻¹ cm⁻¹, which are still higher than those of the benchmark ruthenium dyes N3 and N719 (13,900 and 14,000 M⁻¹ cm⁻¹, respectively).[3, 4] When adsorbed onto a transparent nanocrystalline TiO₂, the absorption bands of PT1-PT5 in the ultra-violet region show a red shift, while the absorption bands in the visible region show a red shift and become broader and stronger for PT1 and PT2, and decrease dramatically for dyes PT3 and PT4, when compared with the spectra in CH₂Cl₂ solution. This may be a result of deprotonation of carboxylic acid groups anchored on the TiO₂
surface, decreasing the electron-withdrawing ability of the acceptor.\textsuperscript{[16]} The spectroscopic properties indicate that the introduction of a donor group at the C(7) atom of phenothiazine (Type 1) can effectively suppress the dye-dye intermolecular aggregation and broaden the absorption spectra when adsorbed on the TiO\textsubscript{2} surface, leading to enhanced photocurrent response and higher short circuit photocurrent density in DSSCs.

\textbf{Figure 2.2.} Absorption spectra of PT\textsubscript{1}-PT\textsubscript{5} in CH\textsubscript{2}Cl\textsubscript{2} solution (1 × 10\textsuperscript{-5} M).
2.2.3 Electrochemical Properties

To fabricate an efficient DSSCs, besides the light-harvesting yield of a dye-adsorbed TiO$_2$, it is also of much pertinence that there are favorable energy-offsets of the dye molecules with respect to the TiO$_2$ nanocrystals and redox electrolytes. Here, the electrochemical behaviors of these dyes were measured by cyclic voltammetry (Figure 2.4) and energetic data are listed in Table 2.1. The oxidation potentials ($E_{ox}$) correspond to the highest occupied molecular orbitals (HOMO). The HOMO levels of PT1-PT5 are more positive than iodide/tri-iodide redox potential value (0.4 V vs. NHE), which indicate the oxidized dyes could be efficiently regenerated by the electrolyte. It is worthy of noting that the introduction of a donor group at C(7) of phenothiazine in Type 1 dyes can lift the HOMO energy levels (0.59 and 0.64 V) relative to Type 2 dyes.
(0.53 and 0.57 V) with a donor group at N(10). The larger the difference between iodide/tri-iodide potential and the HOMO level is, the more efficient the dye regeneration, which can effectively avoid the geminate charge recombination between oxidized dye molecules and photo-injected electrons in the TiO₂ film, and may result in a higher short-circuit photocurrent and open-circuit photovoltage. Furthermore, based on the zero-zero band gaps ($E_{0-0}$) estimated from the onset of the UV-visible absorption spectra, the lowest unoccupied molecular orbitals (LUMO) were obtained. And the LUMO levels of all dyes are more negative than the conduction band edge (CB) of TiO₂ (-0.5 V vs. NHE), indicating that the electron could be energetically injected into the TiO₂ conduction band from the excited dyes.

![Cyclic voltammograms of PT1-PT5 in CH₂Cl₂ solution.](image)

**Figure 2.4.** Cyclic voltammograms of PT1-PT5 in CH₂Cl₂ solution.
Table 2.1. Photophysical and electrochemical properties of dyes PT1-PT5.

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<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{max}$&lt;sup&gt;a&lt;/sup&gt; (nm)</th>
<th>$\lambda_{max}$&lt;sup&gt;b&lt;/sup&gt; (nm)</th>
<th>$E_{ox}$&lt;sup&gt;c&lt;/sup&gt; (V)</th>
<th>$E_{0-0}$&lt;sup&gt;d&lt;/sup&gt; (eV)</th>
<th>$E_{red}$&lt;sup&gt;e&lt;/sup&gt; (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT1</td>
<td>474 (1.71), 304 (5.77)</td>
<td>447</td>
<td>0.59</td>
<td>2.12</td>
<td>-1.53</td>
</tr>
<tr>
<td>PT2</td>
<td>466 (1.92), 320 (5.77)</td>
<td>445</td>
<td>0.64</td>
<td>2.13</td>
<td>-1.49</td>
</tr>
<tr>
<td>PT3</td>
<td>484 (1.52), 337 (2.29)</td>
<td>348</td>
<td>0.53</td>
<td>2.11</td>
<td>-1.58</td>
</tr>
<tr>
<td>PT4</td>
<td>479 (1.28), 329 (1.99)</td>
<td>349</td>
<td>0.57</td>
<td>2.13</td>
<td>-1.56</td>
</tr>
<tr>
<td>PT5</td>
<td>461 (1.42), 321 (1.76)</td>
<td>348</td>
<td>0.58</td>
<td>2.22</td>
<td>-1.64</td>
</tr>
</tbody>
</table>

[a] Absorption maximum measured in CH$_2$Cl$_2$ solution (1 $\times$ 10$^{-5}$ M). [b] Absorption maximum of dye adsorbed on TiO$_2$. [c] Oxidation potential measured in CH$_2$Cl$_2$ solution containing 0.1 M (n-C$_4$H$_9$)$_4$NPF$_6$ with a scan rate of 100 mV s$^{-1}$ (vs. NHE). [d] Zero-zero band gap determined from the onset of absorption spectrum. [e] $E_{red} = E_{ox} - E_{0-0}$.

2.2.4 Molecular Calculations

The structures of dyes were analyzed by using the B3LYP/6-31G(d)* hybrid functional for full geometrical optimization (Figure 2.5). In the ground state, the geometry of phenothiazine is not totally planar, but rather slightly bent in the middle giving a shape of a butterfly. That is, the angle between two terminal phenyl rings is 146º from the nitrogen side, while the cyanoacrylic acid functionality is in-plane with the substituted phenyl ring of phenothiazine. The non-planar shape of the phenothiazine reveals the non-aromatic character of the central heterocycle, which can suppress dye-aggregation and reduce the rate of
internal charge recombination, thus increasing the efficiency of solar cells. The charge distribution in the frontier molecular orbitals can be depicted in Figure 2.5. Due to a relatively smaller dihedral angle of about $34^\circ$ between the phenothiazine core and the aryl donor groups in PT1 and PT2, the HOMO levels are delocalized throughout the entire system, while the LUMO lies mainly on the cyanoacrylic acid acceptor and partly on the neighboring phenothiazine core, which would have a favorable effect on the electronic transition from HOMO to LUMO. On the other side, the dihedral angles between the aryl donor group at N(10) and either of the phenyl rings of phenothiazine indicates little $\pi$-overlap of the two systems. Here, the HOMO level in dyes PT3 and PT4 mainly localizes on the phenothiazine heterocycle, while the LUMO lies mainly on cyanoacrylic acid acceptor and partly on the neighboring phenothiazine core.

![Figure 2.5. Computed frontier orbitals and optimized structures of PT1-PT4.](image-url)
2.2.5 Photovoltaic Properties of DSSCs

A set of DSSCs have been fabricated as described in the experimental section and tested under standard conditions (AM 1.5G, 100 mW cm\(^{-2}\)) in order to investigate the photovoltaic performance of the dyes. The parameters of DSSCs fabricated with these dyes, i.e., short-circuit current (\(J_{sc}\)), open-circuit photovoltage (\(V_{oc}\)), fill factor (FF), and total power conversion efficiency (\(\eta\)), are summarized in Table 2.2, and the photocurrent–voltage (\(J–V\)) plots are shown in Figure 2.6. The DSSCs based on Type 1 dyes (PT1 and PT2) show much better photovoltaic performance than Type 2 dyes (PT3 and PT4) and PT5. And PT1-PT4 dyes show higher \(V_{oc}\) in the range of 0.748–0.829 V than that of PT5 (0.714 V), which indicates that the presence of a donor group at the C(7) or N(10) site can suppress dye aggregation on the TiO\(_2\) surface, and shield the surface of TiO\(_2\) from the iodide/tri-iodide electrolyte, therefore reducing the dark current and increasing the \(V_{oc}\) of the devices. However, the total conversion efficiency would be balanced out by the lower dye loading and relaxed morphology of the films arising from the bulky aryl substituents.\(^{16}\) As a result, the \(J_{sc}\) values of \(N\)-hexyl derivatives with donor aryl substituents at C(7) of phenothiazine (PT1 and PT2) are better than those of \(N\)-aryl derivatives (PT3, PT4 and PT5). In particular, dye PT4 with a very congested 9,9-dihexyl-9\(H\)-fluorene substituent at N(10) shows the lowest \(J_{sc}\). In addition, the FF values of all dyes ranged 0.614–0.698, and yet did not show much difference among each other.
Figure 2.6. \(J–V\) curves of DSSCs based on PT1-PT5 and N719.

The incident photon-to-current-conversion efficiency (IPCE) of Type 1 dyes displays a broad band in the region of 400–700 nm with values mostly > 60 to 80%, while IPCE of Type 2 dyes shows narrower bands in the region of 400–650 nm with much lower values mostly < 60%. The much lower dye loading capacity due to steric hindrance is the main reason for the much poor IPCE.\(^{[16]}\) It is worth noting that Type 1 dyes show somehow higher maximum IPCE values in the range of 300–600 nm than that of N719, implying the introduction of a substituent at the C(7) position of phenothiazine would be effective to optimize the photosensitizers for DSSC application. The aforementioned results demonstrate that the addition of donor group on the opposite side to the acceptor group can effectively increase the \(\pi\)-conjugation system and broaden the visible absorption spectrum in both solution and TiO\(_2\) film, leading to significant enhancement of DSSC performance. On the other side, the bulky aryl substituents at N(10) of
phenothiazine do not contribute to the \( \pi \)-conjugation system or broaden the visible absorption spectrum due to its mutually perpendicular structural characteristics with either of the phenyl rings of bent phenothiazine. Moreover, the linear N(10)-hexyl substituents are not only beneficial to improving the film morphology, but also can help suppress dye aggregation and the dark current upon reducing the recombination of conduction-band electrons with electrolyte. Considering all the above factors, DSSCs based on PT1 exhibit the highest PCE of 6.72\%, corresponding to \( J_{sc} \) of 12.38 mA cm\(^{-2} \), \( V_{oc} \) of 0.829 V, and FF of 0.691.

**Figure 2.7.** IPCE spectra of DSSCs based on PT1-PT5 and N719.

Electrochemical impedance spectroscopies (EIS) have been performed to elucidate the interfacial charge recombination process in DSSCs based on these dyes under the dark conditions. As shown in Figure 2.8, a major semicircle for each dye was observed in the EIS Nyquist plot, which is related to the resistance of electron transport at the \( \text{TiO}_2 \)/dye/electrolyte interface, i.e. the resistance of the
recombination between electrons on TiO$_2$ conduction band and I$_3^-$ species in the electrolyte.$^{[10a,17]}$ The calculated resistance values ($R_{\text{rec}}$) are listed in Table 2.2. The larger the $R_{\text{rec}}$, the slower the recombination kinetics. It is clear that the recombination resistance, from PT1, PT2, PT3, PT4 to PT5, is gradually decreased, which are consistent with the values of open-circuit voltage. It should be noted that the value of $R_{\text{rec}}$ of DSSCs based on PT1 dye is about 31 times larger than that of PT5, which demonstrates unambiguously that a donor group at the C(7) site of phenothiazine together with the 10-hexyl substitution on N can be more efficient to provide a blocking layer on the TiO$_2$ surface and impede a direct contact between the charge and oxidized species (I$_3^-$) in the electrolyte, thereafter remarkably slowing down the charge recombination rate for high $V_{\text{oc}}$.

![EIS Nyquist plots for DSSCs based on PT1-PT5 and N719 under dark conditions](image)

**Figure 2.8.** EIS Nyquist plots for DSSCs based on PT1-PT5 and N719 under dark conditions
Table 2.2. Photovoltaic parameters in DSSCs based on PT1-PT5 and N719 at full sunlight (AM 1.5G, 100 mW cm\(^{-2}\)).\(^{[a]}\)

<table>
<thead>
<tr>
<th>Dye</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>(V_{oc}) (V)</th>
<th>FF</th>
<th>(\eta) (%)</th>
<th>(R_{rec}) ((\Omega) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT1</td>
<td>12.38</td>
<td>0.829</td>
<td>0.655</td>
<td>6.72</td>
<td>1238.7</td>
</tr>
<tr>
<td>PT2</td>
<td>12.43</td>
<td>0.767</td>
<td>0.643</td>
<td>6.13</td>
<td>239.6</td>
</tr>
<tr>
<td>PT3</td>
<td>9.68</td>
<td>0.742</td>
<td>0.713</td>
<td>5.12</td>
<td>57.6</td>
</tr>
<tr>
<td>PT4</td>
<td>7.62</td>
<td>0.748</td>
<td>0.698</td>
<td>3.98</td>
<td>56.2</td>
</tr>
<tr>
<td>PT5</td>
<td>9.50</td>
<td>0.714</td>
<td>0.644</td>
<td>4.73</td>
<td>39.8</td>
</tr>
<tr>
<td>N719</td>
<td>16.28</td>
<td>0.731</td>
<td>0.614</td>
<td>7.31</td>
<td>/</td>
</tr>
</tbody>
</table>

\(^{[a]}\) the effective areas of all the DSSCs are 0.24 cm\(^2\). Dyes were maintained at 0.5 mM in CH\(_2\)Cl\(_2\) solution for dyes PT1-PT5 and in acetonitrile/tert-butyl alcohol (1/1, v/v) for N719. Electrolyte: LiI (0.05 M), I\(_2\) (0.1 M), and DMPII (0.6 M) in acetonitrile/tert-butyl alcohol (1/1, v/v).

2.3 Conclusions

In summary, two types of new phenothiazine-based organic dyes were synthesized, in which Type 1 dyes are appended with a donor aryl group, i.e., carbazolyl or fluorenlyl unit, at the C(7) position and 1-hexyl group at N(10) of phenothiazine (PT1 and PT2), and Type 2 dyes with the donor aryl group at N(10) (PT3 and PT4), together with a cyanoacrylate moiety at the C(3) atom in both types. The structural feature of a donor aryl group at the C(7) atom of phenothiazine extends the \(\pi\)-conjugation of the chromophore, therefore enhancing the performance of DSSCs, while the donor aryl groups at N(10) significantly
increases the steric hindrance of the dye due to its mutually perpendicular structural characteristics with either of the phenyl rings of the bent phenothiazine. As a result, Type 1 dyes exhibit much better light harvesting properties for TiO$_2$ films, higher photocurrents and photovoltages, corresponding to higher level of power conversion efficiencies. The best DSSC has a PCE of 6.72%, which reaches 92% with respect to that of the reference Ru(II)-based N719 under the same conditions. The high efficiency achieved can be attributed mainly to the enhanced light harvesting capacity, electron lifetime and resistance to recombination of electrons, because of a bilateral conjugation of aryl substituent at C(7) and 1-hexyl group on N of phenothiazine. These findings will facilitate our understanding of the crucial importance of molecular engineering and shed light on optimizing phenothiazine-based metal-free organic dyes for highly efficient DSSCs.

2.4 Experimental Section

2.4.1 Materials and Characterization

All solvents and reagents were purchased from Sigma-Aldrich Company and used as received. TiO$_2$ paste (DSL 18NR-T) and iodide-based liquid electrolyte (HL-HPE) were purchased from Dyesol Company. The intermediates were prepared according to the literature method. $^1$H NMR and $^{13}$C NMR spectra were recorded with a Bruker Ultrashield 400 Plus NMR spectrometer with tetramethylsilane (TMS) as the internal standard. High Resolution matrix-assisted
laser desorption/ionization time of flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer.

The intermediates 1, 2, 3,[14a] (9-hexyl-9H-carbazol-3-yl)boronic acid,[18] (9,9-dihexyl-9H-fluoren-2-yl)boronic acid,[19] 9-hexyl-3-iodo-9H-carbazole,[20] and 9,9-dihexyl-2-iodo-9H-fluorene[21] were prepared according to the procedures reported, and confirmed by comparing their characterization data with the literature data.

The general procedure for the preparation of 4 and 5: A mixture of 3 (100 mg, 0.26 mmol), (9-hexyl-9H-carbazol-3-yl)boronic acid (or (9,9-dihexyl-9H-fluoren-2-yl)boronic acid) (0.40 mmol), Pd(PPh₃)₄ (25 mg, 0.04 mmol), 2 N aqueous solution of K₂CO₃ (2 mL) in THF (10 mL) under a N₂ atmosphere was heated to reflux for about 12 h. Then, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 1:1 mixture of hexane and dichloromethane as eluent to afford the yellow compound.

4: 104 mg, 72% yield. ¹H NMR (400 MHz, CDCl₃): δ = 9.82 (s, 1H), 8.17 (d, J = 8.8 Hz, 1H), 7.89 (s, 1H), 7.82 (d, J = 8.8 Hz, 2H), 7.71-7.68 (m, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.43 (t, J = 8.8 Hz, 2H), 7.36-7.39 (m, 2H), 7.25-7.26 (m, 1H), 6.89 (d, J = 8.8 Hz, 1H), 4.16 (t, J = 6.4 Hz, 2H), 3.85 (t, J = 6.4 Hz, 2H), 1.31-1.49 (m, 4H), 1.26-1.38 (m, 12H), 0.86-0.94 (m, 6H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ = 190.01, 150.65, 141.70, 140.40, 137.78, 130.92, 130.55, 130.16, 128.84, 128.44, 127.56, 126.52, 126.19, 125.97, 125.84, 124.61, 124.50, 123.56, 123.30, 122.82, 120.34, 118.92, 116.14, 114.62, 109.25, 48.13, 47.55,

5: 108 mg, 69% yield. ¹H NMR (400 MHz, CDCl₃): δ = 9.80 (s, 1H), 7.69-7.73 (m, 2H), 7.64-7.67 (m, 1H), 7.61 (d, J = 2.0 Hz, 1H), 7.51 (d, J = 2.0 Hz, 1H), 7.47 (d, J = 2.0 Hz, 1H), 7.45 (d, J = 2.0 Hz, 1H), 7.41 (d, J = 2.0 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.34-7.36 (m, 2H), 7.30-7.32 (m, 1H), 6.91-6.97 (m, 2H), 3.94 (t, J = 7.2 Hz, 2H), 1.97 (t, J = 8.4 Hz, 4H), 1.32–1.35 (m, 2H), 1.08–1.12 (m, 6H), 1.02–1.05 (m, 12H), 0.88-0.91 (m, 4H), 0.74-0.78 (m, 6H), 0.65-0.68 (m, 3H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ = 189.99, 151.49, 150.91, 150.51, 142.33, 140.65, 140.46, 138.33, 137.24, 131.04, 130.24, 128.39, 127.07, 126.80, 126.23, 125.91, 125.30, 124.56, 124.10, 122.88, 120.79, 119.98, 119.72, 116.09, 114.71, 65.17, 48.14, 42.12, 40.45, 31.51, 31.44, 29.74, 26.75, 26.58, 23.73, 22.61, 14.05, 14.04 ppm. HRMS (MALDI-TOF, m/z): [M⁺] calcd for (C₄₄H₅₃NOS) 643.3823; found, 643.3830.

The general procedure for the synthesis of compounds 6 and 7: A mixture of 10H-phenothiazine (2.0 g, 10 mmol), 9-hexyl-3-iodo-9H-carbazole (or 9,9-dihexyl-2-iodo-9H-fluorene) (11 mmol), K₂CO₃ (1.7 g, 12.5 mmol), copper powder (0.4 g, 6.2 mmol) and 18-crown-6 (0.08 g, 0.3 mmol) in o-dichlorobenzene (20 mL) was heated to reflux overnight under a N₂ atmosphere. Then, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 4:1 mixture of hexane and CH₂Cl₂ as eluent to afford the product.
6: 2.77g, 62% yield. \( \text{^1H NMR (400 MHz, CDCl3): } \delta = 8.25 \text{ (s, 1H), 8.21 (d, } J = 8.0 \text{ Hz, 2H), 7.88 (t, } J = 8.0 \text{ Hz, 2H), 7.65 (d, } J = 8.0 \text{ Hz, 2H), 7.45-7.50 (m, 2H), 7.17 (t, } J = 8.0 \text{ Hz, 2H), 6.77-6.85 (m, 4H), 4.44 (t, } J = 7.2 \text{ Hz, 2H), 1.74–1.86 (m, 2H), 1.24–1.25 (m, 6H), 0.82 (t, } J = 7.2 \text{ Hz, 3H) ppm. } \text{^13C NMR (400 MHz, CDCl3): } \delta = 146.43, 140.55, 139.01, 132.66, 131.44, 130.09, 129.08, 128.98, 127.10, 126.24, 126.00, 125.33, 124.55, 122.89, 121.84, 119.09, 114.66, 111.40, 43.34, 31.95, 28.50, 26.14, 22.09, 13.87 \text{ ppm. HRMS (MALDI-TOF, } m/z): \ [M^+] \text{ calcd for (C}_{30}\text{H}_{28}\text{N}_{2}\text{S) 448.2067; found, 448.2069.}

7: 3.77g, 71% yield. \( \text{^1H NMR (400 MHz, CDCl3): } \delta = 8.12 \text{ (s, 1H), 7.90-7.94 (m, 1H), 7.67 (d, } J = 8.0 \text{ Hz, 2H), 7.18-7.22 (m, 4H), 7.05 (d, } J = 8.0 \text{ Hz, 2H), 6.86-6.97 (m, 4H), 6.76 \text{ (s, 1H), 3.45 (t, } J = 8.8 \text{ Hz, 4H), 1.45–1.47 (m, 4H), 1.28–1.37 (m, 12H), 0.88 (t, } J = 8.8 \text{ Hz, 6H) ppm. } \text{^13C NMR (400 MHz, CDCl3): } \delta = 154.76, 150.35, 142.77, 136.77, 135.89, 133.45, 131.96, 130.51, 127.65, 127.59, 125.27, 124.73, 123.90, 123.23, 115.92, 115.86, 114.95, 93.5, 65.78, 48.16, 31.39, 26.71, 26.52, 22.60, 14.00 \text{ ppm. HRMS (MALDI-TOF, } m/z): \ [M^+] \text{ calcd for (C}_{37}\text{H}_{41}\text{NS) 531.3087; found, 531.3090.}

The intermediates 8 and 9 were prepared according to the methodology reported.\[^{14g}\]

8: 90 mg, 56% yield. \( \text{^1H NMR (400 MHz, CDCl3): } \delta = 9.85 \text{ (s, 1H), 8.17 (d, } J = 8.0 \text{ Hz, 1H), 8.09 (d, } J = 8.0 \text{ Hz, 1H), 7.84 (d, } J = 8.0 \text{ Hz, 2H), 7.65 (s, 1H), 7.45-7.48 (m, 2H), 7.29-7.31 (m, 2H), 7.16 (d, } J = 8.0 \text{ Hz, 1H), 6.77-6.85 (m, 4H), 4.47 (t, } J = 7.2 \text{ Hz, 2H), 1.79–1.85 (m, 2H), 1.26–1.28 (m, 6H), 0.82 (t, } J = 7.2 \text{ Hz, 3H) ppm. } \text{^13C NMR (400 MHz, CDCl3): } \delta = 189.89, 163.89, 162.66, 156.89,
152.33, 148.90, 144.41, 140.53, 139.21, 130.96, 127.98, 127.14, 126.38, 126.30, 122.54, 121.82, 120.88, 119.03, 118.40, 115.68, 111.40, 109.55, 42.38, 30.94, 28.55, 26.16, 22.03, 13.83 ppm. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{31}H_{28}N_{2}O_{5}) 476.1984; found, 476.1986.

9: 89 mg, (67%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 9.87\) (s, 1H), 7.87 (d, \(J = 6.4\) Hz, 1H), 7.55 (d, \(J = 6.4\) Hz, 2H), 7.47 (s, 1H), 7.39-7.43 (m, 2H), 7.32-7.38 (m, 2H), 7.28 (t, \(J = 6.4\) Hz, 2H), 6.83-6.90 (m, 2H), 6.27-6.29 (m, 2H), 4.35 (t, \(J = 7.6\) Hz, 4H), 1.94-1.99 (m, 4H), 1.37-1.41 (m, 4H), 1.32-1.35 (m, 8H) 0.87-0.89 (t, \(J = 5.2\) Hz, 6H) ppm. \textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 188.04, 154.39, 148.65, 143.47, 141.23, 139.97, 132.18, 131.31, 129.86, 128.89, 127.15, 126.78, 125.13, 124.56, 123.86, 122.29, 121.43, 120.11, 119.58, 118.89, 117.93, 115.96, 110.96, 109.23, 92.38, 65.01, 44.43, 31.90, 29.03, 27.63, 22.76, 14.09 ppm. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{38}H_{41}NOS) 559.2912; found, 559.2916.

The general procedure for the synthesis of PT1-PT4: A mixture of precursor 4, 5, 8 or 9 (0.32 mmol) and cyanoacetic acid (89 mg, 1.10 mmol) in acetic acid (20 mL) was refluxed overnight under a N\textsubscript{2} atmosphere in the presence of ammonium acetate (200 mg). Then, water was added and the reaction was extracted with CH\textsubscript{2}Cl\textsubscript{2}. Next, the solvent was removed under vacuum and the crude compound was purified by column chromatography on silica gel eluting with CH\textsubscript{2}Cl\textsubscript{2}/MeOH (20:1, v/v) to give a dark red solid.

PT1: 74 mg, 61.5% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 8.25\) (s, 1H), 8.15 (d, \(J = 7.6\) Hz, 1H), 7.96 (s, 1H), 7.81-7.83 (m, 1H), 7.64-7.66 (m, 1H), 7.58 (s, 1H), 7.49 (t, \(J = 7.6\) Hz, 2H), 7.38-7.42 (m, 3H), 7.27-7.29 (m, 1H), 6.91 (d, \(J =
7.6 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 4.17 (t, J = 3.2 Hz, 2H), 3.85 (t, J = 3.2 Hz, 2H), 1.84–1.86 (m, 2H), 1.45-1.49 (m, 2H), 1.27-1.38 (m, 12H), 0.90-0.96 (m, 6H) ppm. $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta =$ 168.62, 154.40, 149.69, 141.36, 140.66, 140.44, 137.86, 132.03, 130.30, 130.21, 126.12, 125.85, 125.64, 125.01, 124.40, 123.77, 123.33, 123.15, 122.84, 120.37, 118.97, 118.02, 116.05, 114.52, 109.31, 109.81, 96.89, 48.28, 47.52, 39.46, 31.45, 31.04, 28.85, 26.58, 24.43, 23.09, 22.67, 14.08, 14.05 ppm. HRMS (MALDI-TOF, m/z): [M$^+$] calcd for (C$_{40}$H$_{41}$N$_3$O$_2$S) 627.7828; found, 627.7806.

**PT2**: 53 mg, 60% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 8.10 (s, 1H), 7.92-7.94 (m, 1H), 7.69-7.73 (m, 3H), 7.48-7.51 (m, 1H), 7.44-7.47 (m, 2H), 7.38 (d, J = 2.0 Hz, 1H), 7.28-7.35 (m, 3H), 6.96 (d, J = 8.4 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 3.92 (t, J = 7.2 Hz, 2H), 1.96-2.00 (t, J = 7.2 Hz, 4H), 1.84–1.88 (m, 2H), 1.46–1.50 (m, 2H), 1.33-1.36 (m, 5H), 1.05-1.11 (m, 4H), 1.01-1.04 (m, 7H), 0.88-0.92 (m, 4H), 0.77 (t, J = 7.2 Hz, 6H), 0.63-0.66 (m, 3H) ppm. $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta =$ 168.04, 154.55, 151.55, 150.96, 149.98, 141.65, 140.65, 140.58, 138.19, 137.56, 132.01, 130.51, 127.10, 126.81, 126.28, 125.90, 125.36, 125.30, 124.25, 123.56, 122.91, 120.79, 120.00, 119.74, 116.07, 115.94, 114.87, 97.61, 55.18, 48.25, 40.42, 31.60, 31.49, 31.41, 29.71, 26.70, 26.54, 23.78, 22.58, 14.13, 14.00 ppm. HRMS (MALDI-TOF, m/z): [M$^+$] calcd for (C$_{47}$H$_{54}$N$_2$O$_2$S) 710.3900; found, 710.3873.

**PT3**: 52 mg, 75% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 8.06 (t, J = 6.4 Hz, 2H), 7.96 (s, 1H), 7.62 (d, J = 6.4 Hz, 2H), 7.43-7.53 (m, 3H), 7.36-7.38 (m, 1H), 7.28 (t, J = 6.4 Hz, 1H), 6.95-6.97 (m, 1H), 6.75-6.85 (m, 2H), 6.15-6.19 (m, 2H),
4.37 (t, $J = 7.2$ Hz, 2H), 1.90-1.96 (m, 2H), 1.39-1.49 (m, 2H), 1.28-1.38 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 3H) ppm. $^{13}$C NMR (400 MHz, CDCl$_3$): δ = 168.04, 154.39, 149.68, 142.74, 141.08, 139.95, 132.09, 130.31, 129.29, 127.18, 127.13, 126.68, 126.58, 125.17, 124.78, 123.82, 122.29, 122.15, 120.70, 120.05, 119.57, 118.80, 116.99, 115.96, 115.60, 110.92, 43.48, 31.58, 29.02, 27.05, 22.59, 14.04 ppm. HRMS (MALDI-TOF, m/z): [M$^+$] calcd for (C$_{34}$H$_{29}$N$_3$O$_2$S) 543.1974; found, 543.1946.

PT4: 53 mg, 77% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.97 (s, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.75-7.77 (m, 1H), 7.60 (s, 1H), 7.38-7.43 (m, 4H), 7.28 (t, $J = 8.0$ Hz, 2H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.77-6.84 (m, 2H), 6.11-6.19 (m, 2H), 1.96 (t, $J = 8.0$ Hz, 4H), 1.04-1.11 (m, 12H), 0.72-0.75 (m, 2H), 0.58-0.66 (m, $J = 1.8$ Hz, 6H) ppm. $^{13}$C NMR (400 MHz, CDCl$_3$): δ = 168.45, 154.11, 153.82, 151.08, 148.66, 142.35, 142.09, 139.82, 138.05, 131.95, 129.18, 128.95, 127.93, 127.15, 127.06, 126.70, 125.51, 124.98, 123.83, 123.02, 122.13, 120.20, 120.01, 118.88, 116.47, 116.28, 115.15, 55.54, 40.23, 31.49, 29.51, 23.85, 22.45, 14.02 ppm. HRMS (MALDI-TOF, m/z): [M$^+$] calcd for (C$_{41}$H$_{42}$N$_2$O$_2$S) 626.2961; found, 626.2938.

2.4.2 Photophysical and Electrochemical Characterization

The UV-Vis absorption spectra were recorded on a Varian Cary 100 UV-Vis spectrophotometer. Square-wave voltammetric measurements: The cyclic voltammograms were measured with Versastat II electrochemical workstation using a normal three-electrode cell with a glassy carbon disk working electrode,
Pt wire counter electrode and a Ag/AgCl reference electrode, 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte in CH₂Cl₂ solution. The scan rate was 100 mV s⁻¹. The ferrocene/ferrocnium (Fc/Fc⁺) redox couple was used as an internal potential reference.

2.4.3 Theoretical Calculations

Theoretical calculations: Gaussian 09 package was used for density functional theory (DFT) calculations.[22] The geometries and energies of dyes PT1-PT5 were determined by TDDFT on B3LYP/6-31G(d) basis set. Importantly, none of the frequency calculations generated negative frequencies, being consistent with an energy minimum for the optimized geometry.

2.4.4 Fabrication of Dye-Sensitized Solar Cells

Cell fabrication: A layer of ca. 6 μm TiO₂ paste (20 nm, T/SP) was doctor-bladed onto the FTO conducting glass and then dried for 6 min at 150 °C. This procedure was repeated two times (to prepare a thickness of ca.12 μm) and the resulting surface was finally coated by a scattering layer (ca. 3 μm) of TiO₂ paste (200 nm) to improve the device performance. The TiO₂ electrodes were gradually heated under an air flow at 275 °C for 5 min, 325 °C for 5 min, 375 °C for 5 min, 470 °C for 30 min to remove polymers. Then, these sintered films were soaked with 0.02 M TiF₄ aqueous solution for 60 min at 70 °C, washed with deionized water, further annealed at 450 °C for 30 min. After cooling down to room temperature, the electrodes were immersed into a 5 × 10⁻⁴ M dye bath in
CH₂Cl₂ solution for PT1-PT5 or in acetonitrile/tert-butyl alcohol (volume ratio, 1:1) for N719 dye and maintained in the dark for 16 h at room temperature. The electrodes were then rinsed with ethanol to remove the non-adsorbed dyes and dried in air. Pt counter electrodes were prepared by sputtering method at 15 mA for 90 s at a power of 150 W. Two holes (0.75 mm in diameter) were pre-drilled in the FTO glass for introducing electrolyte. The dye-adsorbed TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a 60 μm hot-melt parafilm at about 120 °C. The liquid electrolyte consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I₂ in a mixture of acetonitrile and tert-butyl alcohol (volume ratio, 1:1) was introduced into the cell through the drilled holes in the back of the counter electrode. At last, the holes were sealed by parafilm and covering glass (0.1 mm thickness) at elevated temperature. The effective areas of all the TiO₂ electrodes were 0.24 cm².

2.4.5 Characterization of Dye-Sensitized Solar Cells

Characterizations of dye-sensitized solar cells: The photocurrent action spectra were measured with a Model SR830 DSP Lock-In Amplifier, a Model SR540 Optical Chopper (Stanford Research Corporation, USA), a 7IL/PX150 xenon lamp with power supply, and a 7ISW301 Spectrometer. The irradiation source for the photocurrent density-voltage (J-V) measurement were measured by a semiconductor characterization system (Keithley 236) at room temperature in air under the spectral output from solar simulator (Newport) using an AM 1.5G filter with a light power of 100 mW cm⁻². The Electrochemical impedance
spectroscopy (EIS) were recorded under one sun illumination over a frequency range of 0.1-105 Hz with an AC amplitude of 10 mV by using electrochemical workstation (CHI660D). The parameters were calculated from Z-View software (v2.1b, Scribner Associate, Inc.). The IPCEs of DSSCs were recorded in Solar Cells QE/IPCE Measurement System (Zolix Solar Cell Scan 100) using DC mode.

2.5 References


Chapter 3 Co-sensitization of the Simple Phenothiazine-Based Dye and a Porphyrin Dye for Efficient DSSCs

3.1 Introduction

Conversion of solar energy into electricity will play a substantial role in meeting the rising demand for energy. Dye-sensitized solar cells (DSSCs), comprising chromophores, redox shuttles, and nanoporous semiconductors, have been intensively investigated since the pioneering work of O’Regan and Grätzel in 1991,[1] because they are regarded as promising alternatives to silicon photovoltaic devices.[2] The update of energy conversion limit is always dependent on the development of new dyes, as well as new electrolytes,[3-5] which leads to the PCE increasing from 11% to 12.3% in a recent report.[6] In particular, the design and synthesis of donor-π-acceptor metal-free organic dyes has led to a number of efficient sensitizers for DSSCs.[7-14] However, it is known that most organic sensitizers are usually in a rod-shape configuration, and they are inclined to aggregate on the semiconductor surface, leading to lower photovoltaic performance in DSSCs than N719 because of intermolecular quenching of molecules residing in the system not functionally attached to the TiO₂ surface and thus acting as filters.[15] It is worth noting that a phenothiazine-based dye contains electron-rich nitrogen and sulfur heteroatoms in a heterocyclic structure with high electron-donating ability, and its non-planar butterfly conformation can sufficiently inhibit molecular aggregation and the formation of intermolecular excimers.[16,17] Meanwhile, the 10-substituent on N can further enhance the charge
separation at the oxide solution interface. Furthermore, the two phenyl groups are arranged in a small torsion angle related to N(10) and S(9) atoms, so that \( \pi \)-delocalization can be extended over the entire chromophore. The structural features of phenothiazine-based dye make it a promising type of sensitizers for DSSCs. Recently, a diversity of strategies have been utilized to extend the range of \( \pi \)-electron delocalization and increase the molar absorptivity of the materials.\(^{[18-27]}\) For example, the addition of thiophene and triarylamine moieties in some of the structures extends \( \pi \)-conjugation of the chromophore and increases the molar absorptivity of the materials, meanwhile, this makes the whole molecule to occupy a larger surface area than a molecule of linear shape, leading to the reduction of dye loading capacity.\(^{17}\) At the same time, the molecular engineering of sensitizers can enhance the charge separation at the oxide solution interface.\(^{[22]}\) As a result, certain structural modifications of this kind of dyes give moderate improvement of the PCEs. And the development of phenothiazine-based dyes encourages further structural optimization of low-cost organic dyes, boosting the practical application of DSSCs.

In this chapter, a series of new organic dyes (PT-C\(n\)) based on the phenothiazine unit were synthesized, in which a cyanoacrylate moiety was added at the C(3) position of the phenothiazine ring as an electron acceptor, a 4-(1-hexyloxy)phenyl group at the C(7) atom as an electron donor on the opposite side, and an alkyl chain with different length at the N(10) atom of phenothiazine as a block against electrolyte (Figure 3.1). The molecular design strategy was demonstrated to effectively improve the photovoltaic performance with the best
efficiency up to 8.18%, which exceeds the reference Ru(II)-based N719 dye (7.76%) in parallel investigations. Co-sensitization is an effective approach to enhance the device performance through a combination of two or more dyes sensitized on semiconductor films together, extending the light-harvesting ability so as to increase the photocurrents of the devices. To further improve the PCE of PT-C$_6$, we designed a stepwise approach for co-sensitization of the organic dye PT-C$_6$ with a porphyrin dye (ZnP) for dye-sensitized solar cells. The co-sensitized PT-C$_6$ + ZnP device showed significantly enhanced $J_{sc}$ relative to its individual single-dye sensitized devices. Upon optimization, the device made of the PT-C$_6$ + ZnP system yielded $J_{sc} = 19.36$ mA cm$^{-2}$, $V_{oc} = 0.735$ V, FF = 0.71 and $\eta = 10.10$ %; this performance is superior to that of either individual device made from PT-C$_6$ (8.18%) and ZnP (7.44%) under the same conditions of fabrication.

![Diagram](Figure 3.1. Structures of dyes PT-Cn and ZnP.)
3.2 Results and Discussion

3.2.1 Synthesis and Characterization

The synthesis of PT-Cn is depicted in Scheme 1. The alkyl chain attached to the phenothiazine group can improve the solubility, forming a tightly packed insulating monolayer blocking the I$_3^-$ or cations from approaching the TiO$_2$ and enhancing the open circuit voltage. The synthesis of PT-Cn was started from a commercially available phenothiazine precursor. The N-alkylation of phenothiazine gave 1a-1e. Compound 2a-2e were obtained by the followed Vilsmeier reaction, in which the bromination of 2a-2e with N-bromosuccinimide (NBS) provided compound 3a-3e in good yield, followed the previously reported strategy of a Suzuki cross coupling of (4-(1-hexyloxy)phenyl)boronic acid with 7-bromo-N-hexyl-10H-phenothiazine-3-carbaldehyde and its analogues, respectively, followed by the widely employed Knoevenagel condensation to construct the classical donor-π-acceptor dyes PT-Cn. All the new compounds were characterized by their $^1$H NMR, $^{13}$C NMR and MALDI-TOF MASS spectra data.
3.2.2 UV-Vis Absorption Properties

The UV-Vis absorption spectra of all dyes in CH$_2$Cl$_2$ solutions (Figure 3.2) and adsorbed on TiO$_2$ films have been recorded (Figure 3.3), the detailed spectroscopic data are summarized in Table 3.1. All of these dyes exhibit two major distinct broad absorption bands in the range of 300~600 nm. The shorter wavelengths located at 300~370 nm are ascribed to the aromatic $\pi-\pi^*$ electronic transitions of the chromophores, while the longer wavelengths located at 380~600 nm are attributed to the intramolecular charge transfer (ICT) from the donor to the acceptor, providing efficient charge-separation at the excited state. Because of the very simple donor-$\pi$-acceptor structures based on phenothiazine, these dyes show relatively low molar extinction coefficient ($\varepsilon$) with values of around 20000 M$^{-1}$ cm$^{-1}$, which are still higher than those of standard ruthenium dyes N3 and N719 (13900 and 14000 M$^{-1}$ cm$^{-1}$, respectively).[28] Also, the molar extinction...
coefficients of these dyes for the maximum visible absorption peaks are in the order of PT-C_6 > PT-C_8 > PT-C_{12} > PT-C_2 > PT-C_{6.2}. The results indicate that the linear 1-hexyloxy group at N(10) gives a simple and balanced structure and better absorption of light, which favors the light harvesting and hence photocurrent generation in DSSCs. When these dyes are adsorbed onto nanocrystalline TiO_2 films, the absorption bands display a blue-shift with respect to those in solutions, which can be ascribed to the deprotonation of carboxylic acid, as well as to the formation of H-aggregation on the semiconductor surface for most organic dyes of this type.\cite{29-31}

![Absorption spectra of dyes in CH_2Cl_2 solution.](image)

\textbf{Figure 3.2.} Absorption spectra of dyes in CH_2Cl_2 solution.
3.2.3 Electrochemical Properties

To fabricate an efficient DSSCs, besides the light-harvesting yield of a dye-coated TiO₂, it is also of much pertinence that there are favorable energy-offsets of the dye molecules with respect to the TiO₂ nanocrystals and redox electrolytes. Here, the electrochemical behaviors of these dyes were measured by cyclic voltammetry (Figure 3.4). The oxidation potentials \( E_{\text{ox}} \) correspond to the highest occupied molecular orbitals (HOMO). The lowest unoccupied molecular orbitals (LUMO) were obtained from the values of \( E_{\text{ox}} \) and the zero-zero band gaps \( E_{0-0} \) estimated from the onset of the UV-visible absorption spectra (Table 3.1). The HOMO levels of all dyes are more positive than iodide/tri-iodide redox potential value (0.4 V vs. NHE), which indicates the
oxidized dyes could be efficiently regenerated by the electrolyte. It is found that increasing the length and steric hindrance of the alkyl chain at N(10) can lift the HOMO energy levels from 0.61 V of PT-C2 to 0.70 V of PT-C12 and 0.70 V of PT-C8, 0.72 V of PT-C6.2. The larger difference between iodide/tri-iodide potential and the HOMO level, the more efficient the dye regeneration, which can effectively avoid the geminate charge recombination between oxidized dye molecules and photo-injected electrons in the TiO2 film, and may result in a higher short-circuit photocurrent ($J_{sc}$) and open-circuit photovoltage ($V_{oc}$). On the other hand, the LUMO levels of all dyes are more negative than the conduction band edge (CB) of TiO2 (-0.5 V vs. NHE), providing the possibility of electron injection from the excited dye molecules to the conduction band of TiO2. Specifically, the higher LUMOs of dyes PT-C2 and PT-C6 are favorable for faster electron injection into TiO2 and thus suppressing back reactions.

![Figure 3.4. Oxidation potential of dyes in CH2Cl2 solution.](image-url)
Table 3.1. Photophysical and Electrochemical properties of the organic dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}^a$/nm</th>
<th>$\lambda_{\text{max}}^b$/nm</th>
<th>$E_{\text{ox}}^c$/V</th>
<th>$E_{0-0}^d$/eV</th>
<th>$E_{\text{red}}^f$/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT-C$_2$</td>
<td>464 (1.82)</td>
<td>444</td>
<td>0.61</td>
<td>2.18</td>
<td>-1.57</td>
</tr>
<tr>
<td>PT-C$_6$</td>
<td>474 (2.06)</td>
<td>448</td>
<td>0.62</td>
<td>2.19</td>
<td>-1.57</td>
</tr>
<tr>
<td>PT-C$_{6.2}$</td>
<td>464 (1.68)</td>
<td>429</td>
<td>0.72</td>
<td>2.22</td>
<td>-1.50</td>
</tr>
<tr>
<td>PT-C$_8$</td>
<td>449 (1.90)</td>
<td>439</td>
<td>0.67</td>
<td>2.12</td>
<td>-1.45</td>
</tr>
<tr>
<td>PT-C$_{12}$</td>
<td>458 (1.77)</td>
<td>445</td>
<td>0.70</td>
<td>2.10</td>
<td>-1.40</td>
</tr>
</tbody>
</table>

$^a$ Absorption maximum in $1\times10^{-5}$ mol/L CH$_2$Cl$_2$ solution. $^b$ Absorption maximum on TiO$_2$ film. $^c$ Oxidation potential in CH$_2$Cl$_2$ solution containing 0.1 M (n-C$_4$H$_9$)$_4$NPF$_6$ with a scan rate 100 mV.s$^{-1}$ (vs. NHE). $^d$ $E_{0-0}$ was determined from the onset of absorption spectra. $^f$ $E_{\text{red}} = E_{\text{ox}} - E_{0-0}$.

3.2.4 Theoretical Calculation

The structures of dyes have been further analyzed by using B3LYP/6-31G(d)* hybrid functional for full geometrical optimization (Figure 3.5). In the ground state, the geometry of phenothiazine is not totally planar, but is rather slightly bent in the middle to give a butterfly shape. That is, the angle between the two terminal phenyl rings is 146 ° from the nitrogen side, while the cyanoacrylic acid functionality is in-plane with the substituted phenyl ring of phenothiazine. The non-planar shape of the phenothiazine reveals the non-aromatic character of the central heterocycle, which can suppress dye-aggregation and reduce the rate of internal charge recombination, thus increasing the efficiency of solar cells. The
charge distribution in the frontier molecular orbitals can be depicted in Figure 3.5 (right). Due to a relatively smaller dihedral angle of about 35° between the phenothiazine core and the (4-hexyloxy)phenyl group, the HOMO levels are delocalized throughout the entire system, while the LUMO lies mainly on cyanoacrylic acid acceptor and partly on the neighboring phenothiazine core, which would have a favorable effect on the electronic transition from the HOMO to the LUMO. The sufficient orbital overlap between donor and acceptor suggests a fast charge transition. When these dyes are adsorbed on nanocrystalline TiO₂ surface, the photoinduced electron can be effectively injected into the conduction band of TiO₂ semiconductor from the donor unit via the terminal cyanoacrylic acid acceptor. This further demonstrates that cyanoacrylic acid group attached directly to the C(3) atom of phenothiazine as an electron acceptor, can effectively drive electron injection from the LUMO state of the dye to the TiO₂ conduction band.

![Figure 3.5. Optimized ground state geometry (left) and frontier molecular orbitals of the HOMO and LUMO (right) calculated by DFT on a B3LYP/6-31 t G (d)* level.](image)

Figure 3.5. Optimized ground state geometry (left) and frontier molecular orbitals of the HOMO and LUMO (right) calculated by DFT on a B3LYP/6-31 t G (d)* level.
3.2.5 Photovoltaic Performance

A series of DSSCs have been fabricated as described in the experimental section and tested under standard conditions (AM 1.5G, 100 mW cm\(^{-2}\)) in order to investigate the photovoltaic performance of the dyes. The parameters of DSSCs fabricated with these dyes, i.e., short-circuit current density \((J_{sc})\), open-circuit photovoltage \((V_{oc})\), fill factor \((FF)\), and total power conversion efficiency \((\eta)\), measured under AM 1.5 solar light (100 mW cm\(^{-2}\)) are summarized in Table 2.2, and the photocurrent–voltage \((J–V)\) plots are shown in Figure 3.6. Among these dyes, the cell based on \textbf{PT-C\textsubscript{6}} exhibits the highest PCE of 8.18\% \((J_{sc} = 15.32\) mA cm\(^{-2}\), \(V_{oc} = 0.775\) V, \(FF = 0.689\)), which exceeds the efficiency of an \textbf{N719}-based device (7.73\%) fabricated under the same working conditions. To the best of our knowledge, the PCE of 8.18\% is the highest value among previously reported DSSCs based on phenothiazine-type dyes, which can be mainly attributed to the enhanced light harvesting capacity, electron lifetime and resistance to recombination of electrons (vide infra), arising from a more compact and balanced structure of the dye with a bilateral conjugation of 1-hexyloxybenzene substituent and N-hexyl chain.\textsuperscript{[15]} And other cells sensitized with the dyes \textbf{PT-C\textsubscript{2}}, \textbf{PT-C\textsubscript{6,2}}, \textbf{PT-C\textsubscript{8}} and \textbf{PT-C\textsubscript{12}} also showed attractive performances with \(J_{sc}\) of 14.97, 10.61, 14.75 and 13.31 mA cm\(^{-2}\), \(V_{oc}\) of 0.723, 0.779, 0.797 and 0.799 V, and \(FF\) of 0.635, 0.714, 0.687 and 0.712, corresponding to \(\eta\) values of 6.87\%, 5.90\%, 8.08\% and 7.57\%, respectively. It is found that the \(V_{oc}\) increases from 0.723 V to 0.799 V when the chain lengths increased from ethyl (\textbf{PT-C\textsubscript{2}}) to 1-dodecyl (\textbf{PT-C\textsubscript{12}}) unit. This was assigned to the reduced recombination ability at the TiO\textsubscript{2}/dye/electrolyte.
interface by insulating the alkyl chains on the dyes. However, further increase in chain length resulted in decreasing PCEs (from PT-C$_6$ to PT-C$_{6.2}$, PT-C$_8$ and PT-C$_{12}$). One reason for this evolution is that the 1-dodecyl chain is soft and twisted, and this can create hindrance for the hole transportation which retards the dye regeneration. Apparently, another consequence of the steric hindrance is that the dye loading capacity may become smaller.$^{[32]}$ On the other hand, the progressively reduced LUMO level usually causes the charge injection kinetics to become slower, which also contributes to the reducing trend in PCE.

![Figure 3.6](image)

**Figure 3.6** Photocurrent–voltage ($J$–$V$) plots obtained with the new dyes and N719.

The incident photon-current conversion efficiencies (IPCEs) for these dyes in DSSCs are plotted in Figure 3.7. The IPCEs of PT-C$_2$, PT-C$_{6.2}$, PT-C$_6$, PT-C$_8$ and PT-C$_{12}$ dyes display a broad band in the region of 400–600 nm with values mostly $> 70$ to $80\%$, and show considerably higher maximum IPCE values in the range of
300–600 nm than that of N719, implying that the structural optimization of these phenothiazine-based dyes is effective for DSSC application. It is worth noting that the IPCE spectrum of PT-C₆ based cell shows an obvious shift to a longer wavelength, which is consistent with the absorption of the dye in solution and on the TiO₂ film. Therefore, the higher and broader IPCE of the cell based on PT-C₆ leads to a higher $J_{sc}$, which is conducive to improve the photovoltaic performance of DSSCs. The aforementioned results further demonstrate that the addition of donor groups on the opposite side to the acceptor group can effectively increase the $\pi$-conjugation system and broaden the visible absorption spectrum in both solution and on the TiO₂ film, leading to significant performance enhancement of the DSSCs. Moreover, both the 1-hexyloxy unit of donor group and N(10)-alkyl substituents are not only beneficial to improving the film morphology, but also can help suppress dye aggregation and the dark current upon reducing the recombination of conduction-band electrons with the electrolyte. Furthermore, the N(10)-alkyl chains with different length and structure are applied to rationalize their influences on the cell performance.
Figure 3.7 Incident photon-to-current efficiency (IPCE) curves of DSSCs based on the new dyes and N719.

Electrochemical Impedance Spectroscopy (EIS) has been performed to elucidate the interfacial charge recombination process in DSSCs based on these dyes under the dark conditions. As shown in Figure 3.8, a major semicircle for each dye was observed in the EIS Nyquist plot, which is related to the resistance of electron transport at the TiO$_2$/dye/electrolyte interface, i.e. the resistance of the recombination between electrons on TiO$_2$ conduction band and I$_3^-$ species in the electrolyte.$^{[33,34]}$ The calculated resistance values ($R_{\text{rec}}$) are listed in Table 3.2. The larger the $R_{\text{rec}}$, the slower the recombination kinetics. It is clear that with the increase of chain length, from PT-C$_2$, PT-C$_6$, PT-C$_{6.2}$, PC-C$_8$ to PT-C$_{12}$, the recombination resistance is gradually increased, which is most likely due to the increased chain length that more efficiently closes up the area for direct contact between TiO$_2$ and the electrolytes. On the other hand, the $R_{\text{rec}}$ of all synthesized
molecules are larger than that of **N719**. It can be understood as small molecules adopt dense packing on the nanoparticle surface, while large molecules, such as **N719**, lead to more available areas for the I$_3^-$ species diffusing onto the TiO$_2$ surface.$^{[35]}$

**Figure 3.8.** EIS Nyquist plots for DSSCs based on these dyes and **N719** under dark.

To further probe the recombination kinetics of the devices, open-circuit voltage decay (OCVD) was recorded to illustrate the lifetime of $V_{oc}$ from a steady state to dark equilibrium.$^{[36]}$ Figure 3.9 shows the OCVD profiles of devices based on these dyes. The correlation between Voc decay and electron lifetime ($\tau_n$) can be described by the following equation:

$$
\tau_n = -\frac{K_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1}
$$
where $K_B$ is the Boltzmann constant, $T$ is temperature, and $e$ is the electron charge.\cite{36, 37} Therefore, the electron lifetimes can be extracted from the slope of $V_{oc}$ decay curves. As a consequence, from devices sensitized with PT-C$_{12}$, PT-C$_8$, PT-C$_{6.2}$, PT-C$_6$ to PT-C$_2$, the slopes become steeper and steeper, indicating that the electron lifetimes are gradually reduced with decreased length of the alkyl chain, which are well consistent with the EIS spectra that a long alkyl chain can always retard the carrier recombination. With outstanding charge separation properties at the oxide solution interface, the structural features of these phenothiazine-based dyes match the requirements for current rectification: in analogy to the photo-field effect in transistors, and the gate for unidirectional electron flow from the electrolyte through the junction and into the oxide is opened by the photo-excitation of the sensitizer. The reverse charge flow, i.e. recapture of the electron by the electrolyte could be impaired by a judicious design of the sensitizer.

![Figure 3.9. open-circuit voltage decay of DSSCs based on PT-Cn dyes and N719](image-url)
Table 3.2 Photovoltaic parameters of the dyes in liquid based DSSCs at full sunlight (AM 1.5G, 100mW cm\(^{-2}\))

<table>
<thead>
<tr>
<th>Dye</th>
<th>(J_{sc}/\text{mA cm}^{-2})</th>
<th>(V_{oc}/\text{V})</th>
<th>FF</th>
<th>(\eta/%)</th>
<th>(R_{rec}/\Omega\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC(_2)</td>
<td>14.97</td>
<td>0.723</td>
<td>0.635</td>
<td>6.87</td>
<td>154.58</td>
</tr>
<tr>
<td>PC(_6)</td>
<td>15.32</td>
<td>0.775</td>
<td>0.689</td>
<td>8.18</td>
<td>468.11</td>
</tr>
<tr>
<td>PC(_{6,2})</td>
<td>10.61</td>
<td>0.779</td>
<td>0.714</td>
<td>5.90</td>
<td>474.33</td>
</tr>
<tr>
<td>PC(_8)</td>
<td>14.75</td>
<td>0.797</td>
<td>0.687</td>
<td>8.08</td>
<td>649.81</td>
</tr>
<tr>
<td>PC(_{12})</td>
<td>13.31</td>
<td>0.799</td>
<td>0.712</td>
<td>7.57</td>
<td>969.60</td>
</tr>
<tr>
<td>N719</td>
<td>15.98</td>
<td>0.741</td>
<td>0.653</td>
<td>7.73</td>
<td>121.84</td>
</tr>
</tbody>
</table>

Performance of DSSCs measured in a 0.24 cm\(^2\) working area on a FTO (8Ω/square) substrate at room temperature. Dyes were maintained at 0.5 mM in CH\(_2\)Cl\(_2\) solution for PC dyes series and in acetonitrile/tert-butyl alcohol (volume ratio, 1:1) for N719. Electrolyte: LiI (0.05 M), I\(_2\) (0.1 M), and DMPII (0.6 M) in acetonitrile:tert-butyl alcohol (1:1, v/v).

3.2.6 Photophysical, Photocurrent–Voltage Characteristics of Cosensitized DSSCs

As mentioned above, the narrow spectrum response (300–650 nm) limits the light absorption to the visible region leading to lower \(J_{sc}\) compared to the ruthenium complex N719. So the zinc porphyrin dye ZnP reported by our group earlier were selected as cosensitizers with PT-C\(_6\) to enhance the light harvesting efficiency in DSSCs applications. The structures of ZnP are shown in Figure 3.1. The absorption spectrum of ZnP, PT-C\(_6\), and the co-absorption of the two dyes on
TiO$_2$ films are shown in Figure 3.10. Dye **PT-C$_6$** has a strong absorption in the range of 400–500 nm, and ZnP shows intense absorption in 400-500 nm and 600-700 nm. A sequential dye soaking approach was applied to adsorb two types of dyes and the film display enhancement of light absorption in 400-700 nm regions when compared with the individually sensitized film by either porphyrin or phenothiazine.

![Absorption Spectra](image)

**Figure 3.10.** Absorption spectra of **PT-C$_6$**, **ZnP** and co-adsorption on TiO$_2$ films.

The IPCE spectra of devices sensitized by **PT-C$_6$**, **ZnP** and co-sensitization were plotted as a function of excitation wavelength and are presented in Figure 3.11. From the experiments, it was found that the IPCE of the co-sensitized devices depended greatly on the dipping time of the electrode in different dye solutions. The largest increase in the IPCE region was observed in the co-sensitized device 4, which was fabricated by the following steps: co-sensitization of TiO$_2$ films was first done by dipping the in the **ZnP** dye
solution (10 h), then by dipping in the PT-C₆ dye solution (4 h). The IPCE spectrum of the solar cell based on co-sensitization by device 4 exhibits an impressive panchromatic response from 300 to 750 nm.

**Figure 3.11.** IPCE spectra of DSSCs sensitized by ZnP, PT-C₆ and Co-sensitization (Device 4).

**Figure 3.12.** $J-V$ curves and photos of DSSCs sensitized by ZnP, PT-C₆ and Co-sensitization.
Table 3.3. Photovoltaic performances of DSSCs sensitized by ZnP, PT-C\textsubscript{6} and Co-sensitization.

<table>
<thead>
<tr>
<th>Device</th>
<th>Dye-loading strategy</th>
<th>( J_{sc} ) (mA/cm\textsuperscript{2})</th>
<th>( V_{oc} ) (V)</th>
<th>FF (%)</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10h in ZnP</td>
<td></td>
<td>15.78</td>
<td>0.699</td>
<td>67.5</td>
<td>7.44</td>
</tr>
<tr>
<td>10h in PT-C\textsubscript{6}</td>
<td></td>
<td>14.70</td>
<td>0.778</td>
<td>71.3</td>
<td>8.16</td>
</tr>
<tr>
<td>1</td>
<td>10h in ZnP + 1h in PT-C\textsubscript{6}</td>
<td>18.46</td>
<td>0.707</td>
<td>69.1</td>
<td>9.02</td>
</tr>
<tr>
<td>2</td>
<td>10h in ZnP + 2h in PT-C\textsubscript{6}</td>
<td>18.93</td>
<td>0.715</td>
<td>72.1</td>
<td>9.76</td>
</tr>
<tr>
<td>3</td>
<td>10h in ZnP + 3h in PT-C\textsubscript{6}</td>
<td>19.20</td>
<td>0.726</td>
<td>72.0</td>
<td>10.04</td>
</tr>
<tr>
<td>4</td>
<td>10h in ZnP + 4h in PT-C\textsubscript{6}</td>
<td>19.36</td>
<td>0.735</td>
<td>71.0</td>
<td>10.10</td>
</tr>
<tr>
<td>5</td>
<td>10h in ZnP + 10h in PT-C\textsubscript{6}</td>
<td>19.61</td>
<td>0.739</td>
<td>69.6</td>
<td>10.08</td>
</tr>
</tbody>
</table>

Performance of DSSCs measured in a 0.24 cm\textsuperscript{2} working area on a FTO (8\,\textOmega/square) substrate at room temperature. PT-C\textsubscript{6} (0.5 mM) and ZnP (0.1 mM) were maintained in acetonitrile:tert-butyl alcohol solution (volume ratio, 1:1). Electrolyte: LiI (0.05 M), I\textsubscript{2} (0.1 M), and DMP\textsubscript{II} (0.6 M) in acetonitrile:tert-butyl alcohol (1:1, v/v).

The \textit{J–V} curves of solar cells with PT-C\textsubscript{6}, ZnP and co-sensitization of two dyes (device 4) are shown in Figure 3.12. The corresponding photovoltaic parameters of these solar cells are presented in Table 3.3. The power conversion efficiencies (at AM 1.5G illumination) of devices based on individual PT-C\textsubscript{6} and ZnP are 8.16 and 7.44 %, respectively. Importantly, the co-sensitized solar cell show much higher photo-current and efficiency than those of the individual dye-sensitized cells. The resulting photovoltaic parameters \( J_{sc} \), \( V_{oc} \), FF, and \( \eta \) are
19.36 mA cm$^{-2}$, 0.735 mV, 0.71, and 10.10 %, respectively. These results show a superior photovoltaic performance for the co-sensitization of two organic dyes compared to that of the individual dye-sensitized solar cells.

### 3.3 Conclusions

In summary, a series of new organic dyes based on phenothiazine have been synthesized through facile modifications, in which a cyanoacrylate acceptor directly attached to the C(3) position of phenothiazine, and an additional linear electron-rich (4-hexyloxy)phenyl group at C(7) on the opposite side of the acceptor, and an alkyl chain with different length and steric hindrance at N(10) of phenothiazine periphery are present. The structural features of (4-hexyloxy)phenyl donor moiety at the C(7) position of phenothiazine extends the $\pi$-conjugation of the chromophore, therefore enhancing the performance of DSSCs. Moreover, the alkyl substituents with different chain length at the N(10) atom of phenothiazine could further optimize the performance through completely shielding the surface of TiO$_2$ from the $I^-/I_3^-$ electrolyte and subsequently reducing the leakage of dark current. Under a standard 1.5G solar illumination, the PCE of 8.18% based on dye **PT-C$_6$**, which exceeds the reference Ru(II)-based **N719** with an efficiency of 7.73% under the same conditions, represents the highest PCE value when compared with the reported phenothiazine-derived dyes. The high efficiency achieved can mainly be attributed to the enhanced light harvesting capacity, electron lifetime and resistance to recombination of electrons, arising from a more compact and balanced structure of the dye with a bilateral conjugation of
1-hexyloxybenzene substituent and 1-hexyl chain at N(10). These findings will facilitate our understanding of the crucial importance of molecular engineering and shed light on optimizing phenothiazine-based metal-free organic dyes for highly efficient DSSCs. Upon exploration of PT-C₆ as co-sensitizer in combination with a porphyrin dye ZnP, a considerably improved efficiency of 10.10% is achieved ($J_{sc}=19.36$ mA cm$^{-2}$, $V_{oc}=0.735$ V, and FF=0.71). The co-sensitized device exhibits remarkable overall efficiency improvement of 36% or 24% compared with individually porphyrin-based dye or organic dye sensitized devices. More importantly, the co-sensitized devices having complementary spectral responses provides a remarkable increase in the photocurrent and hence enhances the power conversion efficiency. The IPCE spectra of cells based on co-sensitization show a panchromatic response with $>70\%$ efficiency over the entire visible spectral region (300–750 nm). Using this strategy, we can conveniently utilize a wide region of the solar spectrum by co-sensitizing dyes that have complementary spectral responses.

3.4 Experimental Section

3.4.1 Materials and Characterization

All solvents and reagents were purchased from Sigma-Aldrich Company and used as received without further purification. The starting material phenothiazine and 2-cyanoacetic acid were purchased commercially. Dye sensitizer cis-bis(isothicyanato)bis(2,2’-bipyridyl-4,4’-dis-carboxylato)-ruthenium(II)-bis-tetrabutylammonium (coded as N719), TiO$_2$ paste and iodide-based liquid electrolyte
(HL-HPE) were purchased from Dyesol company. The synthetic routes of phenothiazine-based dyes PT-Cn are outlined in Scheme 3.1 and the details are depicted as follows. $^1$H and $^{13}$C NMR spectra were recorded with a Bruker Ultrashield 400 Plus NMR spectrometer. The UV-visible absorption spectra of these dyes were measured in CH$_2$Cl$_2$ solution with a Varian Cary 100 UV-Vis spectrophotometer. Emission spectra were performed using a Photon Technology International (PTI) Alphascan spectrofluorimeter. High-resolution matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer. The cyclic voltammograms (CV) were measured with Versastat II electrochemical work station using a normal three-electrode cell with a Pt working electrode, a Pt wire counter electrode and a Ag/Ag$^+$ reference electrode. The supporting electrolyte was 0.1 M tetra-n-butylammonium hexafluorophosphate in DCM solution. The potential of the reference electrode was calibrated by ferrocene after each set of measurements, and all potentials mentioned in the work were against normal hydrogen electrode.

**10-Ethyl-10H-phenothiazine (1a)**

Phenothiazine (2 g, 10 mmol), NaOH (0.5g, 13 mmol) and 1-bromoethane (1.18 g, 11 mmol) were dissolved in 100 mL DMSO and stirred for overnight at room temperature. Then, the reaction mixture were poured into water and extracted with DCM. The organic phase was collected and dried with anhydrous MgSO$_4$. After removing the solvent, the residue was purified by column chromatography using silica gel and hexane as the eluent to give 1a colorless
liquid (1.93 g, 86%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.14 (d, $J = 8.0$ Hz, 4H), 6.85 (t, $J = 8.0$ Hz, 4H), 3.84 (t, $J = 6.9$ Hz, 2H), 1.39 (t, $J = 5.1$ Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 145.61, 127.83, 127.42, 125.35, 122.46, 115.77, 43.48, 14.03. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{14}$H$_{13}$NS) 227.0834; found, 227.0845.

10-Hexyl-10H-phenothiazine (1b)

Using a similar procedure with 1a. 1b colorless liquid (2.45 g, 88%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.18 (d, $J = 8.0$ Hz, 4H), 6.87 (t, $J = 8.0$ Hz, 4H), 3.89 (t, $J = 6.9$ Hz, 2H), 1.74–1.86 (m, 2H), 1.25–1.42 (m, 6H), 0.88 (t, $J = 5.1$ Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 145.69, 127.86, 127.45, 125.85, 122.47, 115.06, 43.89, 32.62, 29.26, 25.79, 22.64, 14.09. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{18}$H$_{21}$NS) 283.1445; found, 283.1456.

10-(2-Ethylhexyl)-10H-phenothiazine (1c)

Using a similar procedure with 1a. 1c colorless liquid (2.09 g, 76%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.23 (d, $J = 8.0$ Hz, 4H), 6.99 (t, $J = 8.0$ Hz, 4H), 3.74 (t, $J = 6.9$ Hz, 2H), 1.74-1.88 (m, 1H), 1.36-1.42 (m, 4H), 1.22-1.34 (m, 4H), 0.83-0.89 (m, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 151.69, 128.86, 127.95, 126.05, 123.79, 116.06, 51.33, 43.89, 32.62, 29.26, 25.67, 22.87, 14.19, 14.01. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{20}$H$_{25}$NS) 311.1788; found, 311.1766.

10-Octyl-10H-phenothiazine (1d)

Using a similar procedure with 1a. 1d colorless liquid (2.65 g, 79%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.43 (d, $J = 8.0$ Hz, 4H), 6.83 (t, $J = 8.0$ Hz, 4H), 3.78 (t, $J = 6.9$ Hz, 2H), 1.74-1.86 (m, 2H), 1.25–1.42 (m, 6H), 0.88 (t, $J = 5.1$ Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 145.61, 127.83, 127.42, 125.35, 122.46, 115.77, 43.48, 14.03. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{18}$H$_{21}$NS) 283.1445; found, 283.1456.
3.94 (t, J = 6.9 Hz, 2H), 1.76-1.83 (m, 2H), 1.39-1.42 (m, 2H), 1.25-1.32 (m, 8H),
0.83-0.89 (m, 3H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 150.69, 128.77, 127.63,

HRMS (MALDI-TOF, m/z): [M+] calcd for (C₂₀H₂₅NS) 311.1749; found, 311.1750.

10-Dodecyl-10H-phenothiazine (1e)

Using a similar procedure with 1a. 1e colorless liquid (2.09 g, 76%). ¹H NMR
(400 MHz, CDCl₃): δ (ppm) 7.23 (d, J = 8.0 Hz, 4H), 6.79 (t, J = 8.0 Hz, 4H),
3.90 (t, J = 6.9 Hz, 2H), 1.71–1.85 (m, 4H), 1.33-1.46 (m, 4H), 1.24–1.30 (m, 12H), 0.86 (t, J = 5.1 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 142.34,
128.87, 127.67, 126.85, 123.47, 114.06, 43.09, 31.69, 31.45, 29.78, 29.64, 29.54,
29.27, 26.36, 26.18, 25.79, 22.64, 14.09. HRMS (MALDI-TOF, m/z): [M+] calcd
for (C₂₄H₃₃NS) 367.2345; found, 367.2378.

10-Ethyl-10H-phenothiazine-3-carbaldehyde (2a)

10-Ethyl-10H-phenothiazine 1a (0.71g, 2.5mmol) and dry DMF (0.73g, 10mmol) was dissolved in 1,2-dichloroethane (20mL), phosphorous oxychloride (1.54g, 10mmol) was added slowly at 0 °C in an ice water bath. Then mixture was heated to reflux for overnight. The reaction mixture was quenched with water and extracted three times with chloroform. The combined organic fractions were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography using silica gel and n-hexane/DCM (8/2; v/v) as the eluent to give a yellow solid. Yield: 0.45 g (56%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.79 (s, 1H), 7.64 (d, J = 8.0
Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.49 (s, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.76 (t, J = 8.0 Hz, 1H), 3.85 (t, J = 6.9 Hz, 2H), 1.38 (t, J = 5.1 Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 189.97, 149.63, 142.45, 131.56, 130.78, 129.86, 128.83, 125.42, 123.65, 122.46, 116.35, 115.73, 114.12, 42.58, 14.23. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{15}$H$_{13}$NOS) 255.0712; found, 255.0719.

**10-Hexyl-10H-phenothiazine-3-carbaldehyde (2b)**

Using a similar procedure with 2a. 2b yellow solid (0.39 g, 58%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.82 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.43 (s, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 6.85 (t, J = 8.0 Hz, 1H), 3.89 (t, J = 6.4 Hz, 2H), 1.78-1.90 (m, 2H), 1.28-1.32 (m, 6H), 0.86 (t, J = 6.4 Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 189.91, 150.32, 142.63, 131.33, 130.35, 130.12, 129.38, 128.54, 126.61, 124.44, 117.41, 115.48, 115.20, 48.10, 31.43, 26.56, 26.64, 22.36, 14.01. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{19}$H$_{21}$NOS) 311.0413; found, 311.0422.

**10-(2-Ethylhexyl)-10H-phenothiazine-3-carbaldehyde (2c)**

Using a similar procedure with 2a. 2c yellow solid (0.42 g, 59%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.81 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.43 (s, 1H), 7.24 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.74 (t, J = 8.0 Hz, 1H), 3.72 (t, J = 8.2 Hz, 2H), 1.71-1.84 (m, 1H), 1.37-1.41 (m, 4H), 1.25-1.37 (m, 4H), 0.81-0.86 (m, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 189.96, 151.33, 143.61, 131.36, 130.56, 130.25, 130.17, 128.59, 127.64, 125.17, 117.44, 115.48, 115.20, 51.53, 35.89, 31.65, 30.26, 23.87, 22.67,
10-(2-Octyl)-10H-phenothiazine-3-carbaldehyde (2d)

Using a similar procedure with 2a. 2d yellow solid (0.38 g, 53%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 9.79 (s, 1H), 7.66 (d, \(J = 8.0\) Hz, 1H), 7.58 (d, \(J = 8.0\) Hz, 1H), 7.42 (s, 1H), 7.20 (t, \(J = 8.0\) Hz, 1H), 7.18 (d, \(J = 8.0\) Hz, 1H), 6.90 (d, \(J = 8.0\) Hz, 1H), 6.84 (t, \(J = 6.9\) Hz, 2H), 1.73-1.80 (m, 2H), 1.37-1.40 (m, 2H), 1.24-1.29 (m, 8H), 0.85-0.90 (m, 3H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 189.91, 150.32, 142.66, 131.26, 130.28, 130.26, 129.87, 128.34, 126.64, 124.97, 117.48, 115.40, 114.21, 48.12, 31.42, 29.18, 29.13, 26.99, 26.63, 22.61, 14.15. HRMS (MALDI-TOF, m/z): [M+] calced for (C\(_{21}\)H\(_{25}\)NOS) 399.1712; found, 399.1718.

10-(2-Dodecyl)-10H-phenothiazine-3-carbaldehyde (2e)

Using a similar procedure with 2a. 2e yellow solid (0.50 g, 49%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 9.80 (s, 1H), 7.64 (d, \(J = 8.0\) Hz, 1H), 7.54 (d, \(J = 8.0\) Hz, 1H), 7.42 (s, 1H), 7.19 (t, \(J = 8.0\) Hz, 1H), 7.16 (d, \(J = 8.0\) Hz, 1H), 6.88 (d, \(J = 8.0\) Hz, 1H), 6.76 (t, \(J = 8.0\) Hz, 1H), 3.85 (t, \(J = 6.9\) Hz, 2H), 1.73–1.79 (m, 2H), 1.37-1.42 (m, 2H), 1.22–1.31 (m, 16H), 0.86 (t, \(J = 5.1\) Hz, 3H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 189.90, 150.31, 143.61, 131.06, 130.57, 130.21, 129.77, 128.44, 126.23, 124.37, 117.12, 115.16, 115.01, 48.01, 31.77, 31.12, 29.48, 29.04, 29.00, 28.28, 26.31, 26.08, 25.39, 22.12, 14.00. HRMS (MALDI-TOF, m/z): [M+] calcd for (C\(_{25}\)H\(_{33}\)NOS) 395.2319; found, 395.2357.

7-Bromo-10-ethyl-10H-phenothiazine-3-carbaldehyde (3a)
NBS (411 mg, 2.31 mmol) was added in one portion to the solution of 2a (510 mg, 2.0 mmol) in THF (50 mL) at 0 °C. The mixture was allowed to warm to room temperature and continued the stirring for 1.5 h. Then the reaction was quenched by addition of water (50 mL), and extracted with DCM. The collected organic layer was evaporated under vacuum and the residue was purified by column chromatography on silica gel with CH₂Cl₂ as eluent to give a yellow solid. Yield: 568 mg, (85%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.76 (s, 1H), 7.58-7.61 (m, 1H), 7.49 (d, J = 2.0 Hz, 1H), 7.18-7.21 (m, 1H), 7.14 (d, J = 8.4 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 3.90 (t, J = 6.4 Hz, 2H), 1.39 (t, J = 6.4 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 189.87, 149.74, 142.20, 131.16, 130.46, 130.25, 129.60, 128.12, 125.45, 123.66, 116.69, 115.75, 114.55, 43.56, 14.20. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₁₅H₁₂BrNOS) 332.9813; found, 332.9834.

7-Bromo-10-hexyl-10H-phenothiazine-3-carbaldehyde (3b)

Using a similar procedure with 3a. 3b yellow solid (0.56 g, 89%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.80 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 6.85 (t, J = 8.0 Hz, 1H), 3.89 (t, J = 6.4 Hz, 2H), 1.78-1.90 (m, 2H), 1.28-1.32 (m, 6H), 0.86 (t, J = 6.4 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 189.91, 150.32, 142.63, 131.33, 130.35, 130.12, 129.38, 128.54, 126.61, 124.44, 117.41, 115.48, 115.20, 48.10, 31.43, 26.56, 26.64, 22.36, 14.01. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₁₉H₂₀BrNOS) 389.0413; found, 389.0422.
7-Bromo-10-(2-ethylhexyl)-10H-phenothiazine-3-carbaldehyde (3c)

Using a similar procedure with 3a. 3c yellow solid (0.47 g, 81%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.79 (s, 1H), 7.63-7.66 (m, 1H), 7.57 (d, $J = 2.0$ Hz, 1H), 7.23-7.26 (m, 1H), 7.22 (d, $J = 2.0$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 1H), 3.72 (t, $J = 8.8$ Hz, 2H), 1.72-1.74 (m, 1H), 1.38-1.43 (m, 4H), 1.22-1.35 (m, 4H), 0.83-0.87 (m, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 189.97, 151.03, 143.22, 131.37, 130.24, 130.10, 130.00, 128.75, 127.16, 125.49, 117.73, 115.85, 115.69, 51.56, 35.92, 31.60, 30.51, 28.47, 23.85, 22.69, 14.18. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{21}$H$_{24}$BrNOS) 417.0812; found, 417.0814.

7-Bromo-10-octyl -10H-phenothiazine-3-carbaldehyde (3d)

Using a similar procedure with 3a. 3d yellow solid (0.44 g, 87%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.78 (s, 1H), 7.62-7.64 (m, 1H), 7.54 (d, $J = 2.0$ Hz, 1H), 7.22-7.24 (m, 1H), 7.20 (d, $J = 2.0$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 1H), 6.68 (d, $J = 8.0$ Hz, 1H), 3.82 (t, $J = 8.8$ Hz, 2H), 1.65-1.80 (m, 2H), 1.31-1.47 (m, 2H), 1.24-1.28 (m, 8H), 0.87 (t, $J = 8.4$ Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 189.90, 150.34, 142.62, 131.24, 130.27, 130.23, 129.76, 128.42, 126.10, 124.34, 117.09, 115.79, 114.99, 48.09, 31.72, 29.18, 29.12, 26.75, 26.62, 22.63, 14.13. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{21}$H$_{24}$BrNOS) 417.0812; found, 417.0814.

7-Bromo-10-dodecyl -10H-phenothiazine-3-carbaldehyde (3e)

Using a similar procedure with 3a. 3e yellow solid (0.36 g, 82%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.79 (s, 1H), 7.62-7.65 (m, 1H), 7.55 (d, $J = 2.0$ Hz,
1H), 7.22-7.25 (m, 1H), 7.20 (d, J = 2.0 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 3.83 (t, J = 8.8 Hz, 2H), 1.73-1.79 (m, 2H), 1.37-1.42 (m, 2H), 1.23-1.29 (m, 16H), 0.85 (t, J = 8.4 Hz, 3H). 13C NMR (400 MHz, CDCl3): δ (ppm) 189.90, 150.34, 142.62, 131.24, 130.27, 130.23, 129.76, 128.42, 126.10, 124.34, 117.09, 115.79, 114.99, 48.09, 31.72, 29.18, 29.12, 26.75, 26.62, 22.63, 14.13. HRMS (MALDI-TOF, m/z): [M+] calcd for (C25H32BrNOS) 473.1412; found, 473.1476.

10-Ethyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (4a)

The mixture of 7-bromo-10-ethyl-10H-phenothiazine-3-carbaldehyde (100 mg, 0.30 mmol), (4-(hexyloxy)phenyl)boronic acid (89 mg, 0.40 mmol), Pd(PPh3)4 (25 mg, 0.04 mmol) and 2N aqueous solution of K2CO3 (2 mL) in THF (10 mL) under N2 atmosphere was heated to reflux for about 12h. Then the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 1:4 mixture of hexane and CH2Cl2 as eluent to afford the red compound. Yield: 100 mg, (77%). 1H NMR (400 MHz, CDCl3): δ (ppm) 9.72 (s, 1H), 7.55-7.58 (m, 1H), 7.49 (d, J = 2.0 Hz, 1H), 7.40 (t, J = 2.0 Hz, 1H), 7.39 (t, J = 2.0 Hz, 1H), 7.32-7.35 (m, 2H), 6.95 (t, J = 2.0 Hz, 2H), 6.93 (t, J = 2.0 Hz, 2H), 3.97 (t, J = 6.8 Hz, 2H), 3.95 (t, J = 6.8 Hz, 2H), 1.70–1.75 (m, 2H), 1.36–1.42 (m, 2H), 1.31-1.34 (m, 7H), 0.88 (t, J = 7.2 Hz, 3H). 13C NMR (400 MHz, CDCl3): δ (ppm) 190.03, 158.72, 151.52, 142.42, 136.57, 131.95, 130.97, 129.10, 128.45, 127.50, 126.89, 125.87, 125.60, 125.35, 116.89, 115.46, 114.77, 51.49, 36.01, 31.64, 30.28, 25.74, 23.55, 14.19, 14.07. HRMS (MALDI-TOF, m/z): [M+] calcd for (C27H29NO2S) 431.1934; found, 431.1937.
10-hexyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (4b)

Using a similar procedure with 4a. 4b A red solid. Yield: 115 mg, (78%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 9.71 (s, 1H), 7.54-7.57 (m, 1H), 7.51 (d, \(J = 2.0\) Hz, 1H), 7.35-7.37 (m, 2H), 7.22-7.25 (m, 1H), 7.21 (d, \(J = 2.0\) Hz, 1H), 6.83-6.87 (m, 2H), 6.83 (d, \(J = 2.0\) Hz, 1H), 6.81 (d, \(J = 2.0\) Hz, 1H), 3.92 (t, \(J = 6.8\) Hz, 2H), 3.83 (t, \(J = 6.8\) Hz, 2H), 1.70–1.75 (m, 4H), 1.28–1.39 (m, 4H), 1.18-1.20 (m, 8H), 0.79-0.86 (m, 6H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 190.01, 158.75, 150.58, 141.92, 136.50, 131.91, 130.97, 130.16, 128.43, 127.52, 125.68, 125.47, 124.60, 124.03, 116.07, 114.86, 114.65, 48.09, 31.61, 31.41, 29.27, 26.73, 26.55, 25.75, 22.63, 22.60, 14.15, 14.06, 13.99. HRMS (MALDI-TOF, m/z): [M+] calcd for (C\(_{31}\)H\(_{37}\)NO\(_2\)S) 487.2599; found, 487.2587.

10-(2-ethylhexyl)-7-(4-(hexyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (4c)

Using a similar procedure with 4a. 4c A red solid. Yield: 112 mg, (76%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 9.80 (s, 1H), 7.65-7.67 (m, 1H), 7.63 (d, \(J = 2.0\) Hz, 1H), 7.45 (d, \(J = 2.0\) Hz, 1H), 7.42 (d, \(J = 2.0\) Hz, 1H), 7.33-7.36 (m, 2H), 6.95 (t, \(J = 2.0\) Hz, 2H), 6.93 (t, \(J = 2.0\) Hz, 2H), 3.98 (t, \(J = 7.2\) Hz, 2H), 3.80 (t, \(J = 7.2\) Hz, 2H), 1.82-1.85 (m, 1H), 1.28–1.39 (m, 4H), 1.21-1.27 (m, 12H), 0.85-0.90 (m, 9H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 190.07, 158.70, 151.41, 142.57, 136.55, 131.96, 131.08, 129.92, 128.81, 127.54, 126.87, 125.89, 125.69, 125.65, 116.73, 115.42, 114.83, 51.48, 36.04, 31.62, 30.61, 29.28, 25.75, 23.94, 23.05, 22.69, 22.64, 15.31, 14.16, 14.08, 14.03. HRMS (MALDI-TOF, m/z): [M+] calcd for (C\(_{33}\)H\(_{41}\)NO\(_2\)S) 515.2989; found, 515.2977.
7-(4-(hexyloxy)phenyl)-10-octyl-10H-phenothiazine-3-carbaldehyde (4d)

Using a similar procedure with 4a. 4d A red solid. Yield: 116 mg, (75%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.78 (s, 1H), 7.61-7.66 (m, 1H), 7.57 (d, $J = 2.0$ Hz, 1H), 7.42 (d, $J = 2.0$ Hz, 1H), 7.28-7.33 (m, 2H), 7.09-7.18 (m, 1H), 6.95 (t, $J = 2.0$ Hz, 2H), 6.86 (t, $J = 2.0$ Hz, 2H), 3.96 (t, $J = 6.8$ Hz, 2H), 3.88 (t, $J = 6.8$ Hz, 2H), 1.77-1.84 (m, 4H), 1.41-1.46 (m, 4H), 1.25-1.39 (m, 12H), 0.85-0.89 (m, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 190.01, 158.72, 150.54, 141.88, 131.88, 130.94, 130.16, 130.07, 128.38, 127.55, 127.50, 125.66, 124.00, 123.56, 116.06, 115.94, 114.64, 68.10, 48.07, 36.09, 31.74, 31.63, 29.28, 29.18, 26.85, 26.75, 25.77, 23.99, 22.64, 14.13, 14.09. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{33}$H$_{41}$NO$_2$S) 515.2989; found, 515.2977.

10-Dodecyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (4e)

Using a similar procedure with 4a. 4e A red solid. Yield: 124 mg, (68%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.78 (s, 1H), 7.62-7.64 (m, 1H), 7.58 (d, $J = 4.0$ Hz, 1H), 7.44 (d, $J = 4.0$ Hz, 1H), 7.42 (d, $J = 4.0$ Hz, 1H), 7.31-7.34 (m, 1H), 7.28 (d, $J = 4.0$ Hz, 1H), 6.92 (t, $J = 4.0$ Hz, 2H), 6.88 (t, $J = 4.0$ Hz, 2H), 3.98 (t, $J = 6.8$ Hz, 2H), 3.89 (t, $J = 6.8$ Hz, 2H), 1.79-1.87 (m, 4H), 1.45-1.59 (m, 4H), 1.37-1.42 (m, 4H), 1.29-1.35 (m, 16H), 0.85-0.89 (m, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 189.99, 158.72, 150.56, 141.89, 136.47, 131.88, 130.94, 130.16, 128.41, 127.50, 125.65, 125.45, 124.56, 124.01, 123.56, 116.06, 114.83, 68.12, 48.08, 31.94, 31.78, 31.65, 31.05, 29.65, 29.54, 29.37, 29.28, 29.22, 26.85, 26.74, 25.77, 22.72, 22.65, 14.17, 14.09. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{37}$H$_{49}$NO$_2$S) 571.3588; found, 571.3587.
(E)-2-cyano-3-(10-ethyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)acrylic acid (PT-C2)

A mixture of precursor 4a (100 mg, 0.23 mmol) with cyanoacetic acid (89 mg, 1.10 mmol) in acetic acid (20 mL) was refluxed in the presence of ammonium acetate (200 mg) overnight under N2 atmosphere. Then water was added and extracted with CH2Cl2. Next solvent was removed under vacuum and the crude compound was purified by column chromatography on silica gel eluted with CH2Cl2 and MeOH (20:1, v/v) to give a dark red solid. Yield: 74 mg (61.5%).

1H NMR (400 MHz, DMSO-d6): δ (ppm) 8.17 (s, 1H), 7.91-7.94 (m, 1H), 7.82 (d, J = 2.0 Hz, 1H), 7.57 (s, 2H), 7.55 (s, 2H), 7.15 (d, J = 8.8 Hz, 1H), 7.10 (d, J = 8.8 Hz, 1H), 6.96-7.00 (t, J = 8.8 Hz, 2H), 4.02 (t, J = 6.8 Hz, 2H), 3.97 (t, J = 6.8 Hz, 2H), 1.70–1.73 (m, 2H), 1.36–1.42 (m, 2H), 1.31–1.34 (m, 7H), 0.88 (t, J = 6.8 Hz, 3H).


(E)-2-cyano-3-(10-hexyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)acrylic acid (PT-C6)

Using a similar procedure with PT-C2. A dark red solid. Yield: 55 mg, (66%).

1H NMR (400 MHz, CDCl3): δ (ppm) 8.07 (s, 1H), 7.88-7.91 (m, 1H), 7.66 (d, J = 2.0 Hz, 1H), 7.42-7.44 (m, 2H), 7.30-7.32 (m, 1H), 7.25 (t, J = 2.0 Hz, 1H), 6.94 (d, J = 2.0 Hz, 1H), 6.93 (d, J = 2.0 Hz, 1H), 6.83-6.89 (m, 2H), 4.00 (t, J = 6.8 Hz, 2H).
Hz, 2H), 3.88 (t, J = 6.8 Hz, 2H), 1.75–1.86 (m, 4H), 1.45–1.47 (m, 4H), 1.32–1.37 (m, 8H), 0.92 (t, J = 6.8 Hz, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 168.18, 158.84, 154.63, 150.04, 141.15, 136.39, 132.01, 131.73, 130.50, 127.49, 125.70, 125.40, 124.25, 123.45, 116.04, 115.87, 114.92, 114.78, 97.28, 68.18, 48.22, 34.50, 31.60, 31.39, 29.26, 26.68, 26.52, 25.74, 22.61, 14.02, 13.96.

HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{34}$H$_{38}$N$_2$O$_3$S) 554.2598; found, 554.2580.

(E)-2-cyano-3-(10-(2-ethylhexyl)-7-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)acrylic acid (PT-C$_{6,2}$)

Using a similar procedure with PT-C$_2$. A dark red solid. Yield: 58 mg, (72%).

$^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.10 (s, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.71 (s, 1H), 7.44 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 7.6 Hz, 1H), 7.31 (s, 1H), 6.89-7.01 (m, 4H), 3.98 (t, J = 6.4 Hz, 2H), 3.79 (t, J = 6.4 Hz, 2H), 1.83–1.95 (m, 1H), 1.76–1.80 (m, 2H), 1.42-1.47 (m, 4H), 1.28-1.35 (m, 5H), 1.21–1.27 (m, 5H), 0.86-0.91 (m, 9H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 168.20, 158.75, 154.68, 151.03, 143.70, 142.03, 136.80, 131.80, 131.73, 130.95, 127.87, 127.55, 125.71, 125.38, 124.80, 116.84, 116.04, 115.71, 114.86, 97.73, 51.42, 36.19, 31.64, 30.56, 29.75, 29.28, 28.52, 25.78, 23.89, 23.07, 22.67, 15.09, 14.11, 14.06, 13.96. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{34}$H$_{38}$N$_2$O$_3$S) 583.2988; found, 583.2939.

(E)-2-cyano-3-(7-(4-(hexyloxy)phenyl)-10-octyl-10H-phenothiazin-3-yl)acrylic acid (PT-C$_{8}$)

Using a similar procedure with PT-C$_2$. A dark red solid. Yield: 59 mg, (74%).

$^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.04 (s, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.62
(d, J = 8.4 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.28-7.31 (m, 1H), 7.21 (d, J = 8.4 Hz, 1H), 6.92 (d, J = 8.4 Hz, 2H), 6.79-6.86 (m, 2H), 3.97 (t, J = 6.4 Hz, 2H), 3.83 (t, J = 6.4 Hz, 2H), 1.75–1.82 (m, 4H), 1.42–1.56 (m, 4H), 1.33-1.35 (m, 4H), 1.26-1.32 (m, 8H), 0.85-0.90 (m, 6H). 13C NMR (400 MHz, CDCl3): δ (ppm) 168.76, 158.80, 154.74, 150.24, 142.67, 141.00, 136.68, 132.16, 131.64, 130.40, 127.47, 125.67, 125.29, 124.01, 123.26, 116.02, 115.91, 114.89, 114.71, 97.71, 48.23, 48.15, 31.75, 31.63, 29.28, 29.25, 29.19, 26.85, 26.67, 26.62, 25.77, 22.65, 14.14, 14.10. HRMS (MALDI-TOF, m/z): [M+] calcd for (C36H42N2O3S) 583.2988; found, 583.2987.

(E)-2-cyano-3-(10-dodecyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)acrylic acid (PT-C12)

Using a similar procedure with PT-C2. A dark red solid. Yield: 62 mg, (77%).

1H NMR (400 MHz, CDCl3): δ (ppm) 8.07 (s, 1H), 7.89 (s, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 1H), 7.24 (d, J = 8.8 Hz, 1H), 6.89 (t, J = 8.8 Hz, 2H), 6.83-6.87 (m, 2H), 3.98 (t, J = 6.6 Hz, 2H), 3.87 (t, J = 6.4 Hz, 2H), 1.77–1.83 (m, 4H), 1.43–1.47 (m, 4H), 1.24-1.37 (m, 20H), 0.85-0.92 (m, 6H). 13C NMR (400 MHz, CDCl3): δ (ppm) 168.53, 158.81, 154.72, 150.06, 142.73, 141.98, 141.09, 136.77, 132.11, 130.50, 127.50, 125.71, 125.54, 123.92, 123.37, 116.18, 116.06, 115.16, 114.88, 97.14, 48.21, 31.94, 31.62, 29.63, 29.57, 29.54, 29.37, 29.27, 29.16, 26.83, 26.74, 26.66, 26.56, 25.76, 22.72, 22.64, 14.16, 14.08. HRMS (MALDI-TOF, m/z): [M+] calcd for (C40H50N2O3S) 638.3536; found, 638.3552.
3.4.2 Fabrication and Characterization of Cells

To make a reasonable comparison, all the anode films for the DSSCs were made under the same standard manner, which are composed of 12 μm thick of transparent layer (TiO₂ with diameter of 20 nm) and 6 μm thick of scattering layer (TiO₂ nanoparticles with diameter of 200 nm). In specific, a doctor-blade technique was utilized to prepare photoanode (TiO₂) films. Firstly, a layer of ca. 6 μm TiO₂ paste (20 nm) was doctor-bladed onto the FTO conducting glass and then relaxed at room temperature for 3 min before heating at 150 °C for 6 min, this procedure was repeated once to achieve a film thickness of ca. 12 μm and the resulting surface was finally coated by a scattering layer (ca. 6 μm) of TiO₂ paste (200 nm). The electrodes were gradually heated under an air flow at 275 °C for 5 min, 325 °C for 5 min, 375 °C for 5 min, 470 °C for 30 min to remove polymers and generate three-dimensional TiO₂ nanoparticle network. After that, the sintered films were soaked with 0.02 M TiF₄ aqueous solution for 45 min at 70°C, washed with deionized water, and further annealed at 450 °C for 30 min. After cooling down to ca. 80°C, the electrodes were immersed into a 5 × 10⁻⁴ M dye bath in CH₂Cl₂ solution for PT-Cₙ dye series or in acetonitrile/tert-butyl alcohol (volume ratio, 1:1) for N719 dye and maintained in the dark for 16 hrs. Afterwards, the electrodes were rinsed with ethanol to remove the non-adsorbed dyes and dried in air. Pt counter electrodes were prepared by sputtering method at 15 mA for 90 s at a power of 150 W. Two holes (0.75 mm in diameter) were pre-drilled in the FTO glass for introducing electrolyte. The dye-adsorbed TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt
parafilm at about 100 °C. The liquid electrolyte consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I₂ in a mixture of acetonitrile and tert-butyl alcohol (volume ratio, 1:1) was introduced into the cell through the drilled holes at the back of the counter electrode. At last, the holes were sealed by parafilm and covering glass (0.1 mm thickness) at elevated temperature. The effective areas of all the TiO₂ electrodes were 0.24 cm². The current-voltage (J-V) characteristics of the assembled DSSCs were measured by a semiconductor characterization system (Keithley 236) at room temperature in air under the spectral output from solar simulator (Newport) using an AM 1.5G filter with a light power of 100 mW/cm². IPCEs of DSSCs were recorded in Solar Cell QE/IPCE Measurement System (Zolix Solar Cell Scan 100) using DC mode. CHI 660D electrochemical workstation was used to characterize the electrochemical properties of the DSSCs. Electrochemical impedance spectroscopy (EIS) was recorded under dark condition over a frequency range of 0.1-10⁵ Hz with an AC amplitude of 10 mV and the parameters were calculated from Z-View software (v2.1b, Scribner AssociatNe, Inc.). For the open-circuit voltage decay measurements, the cell was first illuminated for 20 sec to a steady voltage, then the illumination was turned off for 80 sec and the open-circuit voltage decay curve was recorded.

3.4.3 Theoretical Calculation

Theoretical calculations: Gaussian 09 package was used for density functional theory (DFT) calculations. The geometries and energies of dyes PT-CN were
determined by TDDFT on B3LYP/6-31G(d) basis set. Importantly, none of the frequency calculations generated negative frequencies, being consistent with an energy minimum for the optimized geometry.

3.5 References


Chapter 4 Molecular Engineering of Simple Phenothiazine-based Dyes to Modulate Dye Aggregation, Charge Recombination and Dye Regeneration in Highly Efficient Dye-Sensitized Solar Cells

4.1 Introduction

Currently available fossil fuel resources are limited and depleted rapidly during the last decades. Hence, there is a increased global awareness concerning the crisis to find alternative renewable energy sources such as solar energy to meet the requirements and developments of the modern society. Since O’Regan and Grätzel first reported the efficient DSSCs system with polypyridyl ruthenium(II) complex adsorbed on a nanocrystalline semiconductor TiO$_2$ electrode in 1991,[1] DSSCs as promising alternatives to conventional silicon-based photovoltaic device have received considerable research excitements due to their low cost, easy manufacturing processes and high power conversion efficiency (PCE).[2] The advancement of PCE is always depended on the development of new photosensitizers, as well as new electrolytes,[3] which leads to the ever recording PCE of 12.3% based on a porphyrin dye in a cobalt(II/III)-based redox electrolyte under the simulated AM 1.5 irradiation.[4] In recent years, tons of metal-free organic dyes as alternatives to the noble Ru complex sensitizers have obtained impressive efficiencies.[5] These sensitizers exhibit many advantages, such as lower material cost, higher molar extinction coefficients, and various molecular structure. However, the metal-free organic dyes-based DSSCs are known to generate lower PCE than that of Ru(II)-based
polypyridyl complexes, which is probably a result of the formation of dye aggregates on the semiconductor surface, which leads to the self-quenching of excited states and the reduction in the yield of electron injection from the dye into the conduction band of TiO$_2$. Another disadvantage of organic dyes in DSSCs is the fast interfacial charge recombination between the injected electron and I$_3^-$ ions in the electrolyte or dye cations formed in DSSCs, resulting in a reduced $V_{oc}$ value. Thus, to improve the photovoltaic performance, two fundamental aspects need to be considered: (i) the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the dye are required to suit the I$^-$/I$_3^-$ redox potential and the conduction band (CB) edge level of the TiO$_2$ semiconductor. (ii) fine tuning of structures of the organic sensitizers to regulate the dye aggregation, electron injection and charge recombination processes in DSSCs. The rational option of electron donor and $\pi$–conjugated moiety to construct organic sensitizers is of profound importance in the cell photovoltaic performance control. In this respect, thiophene and its analogue EDOT have been widely introduced into the the $\pi$-bridge conjugated skeletons of organic sensitizers in DSSCs application. The various thiophene derivatives-based dyes can furnish a flexible molecular structural optimization of photosensitizers correlated to photovoltaic performance. It is well known that the phenothiazine is a good electron-donating group owing to it contains electron-rich nitrogen and sulfur heteroatoms in the central ring, and also its non-planar butterfly conformation can sufficiently inhibit molecular aggregation, moreover, the substituents such as alkyl chains on N(10) atom of the phenothiazine core can impede the dark current
upon retarding charge recombination.\cite{5c} These advantages make phenothiazine derivatives a potential candidate for highly efficient DSSCs. As is well known, the open-circuit photocurrent ($J_{sc}$) and photovoltage ($V_{oc}$) of a well-functioning DSSCs are mainly dependent upon on the optimized molecular arrangement. Therefore, the further molecular engineering is desirable for improving the $J_{sc}$ and $V_{oc}$ in DSSCs device.

In this chapter, we present five new organic dyes (Figure 4.1), namely, T, TT, E, ET, and EE, in which thiophene analogues at the C(7) atom of phenothiazine core acted as an electron donors, the electron-rich phenothiazine featuring a hexyl chain at the N(10) atom as \pi-conjugated segment, and cyanoacrylic acid at the C(3) position of the phenothiazine ring as electron acceptor. Furthermore, through quantum calculation, electrical impedance analysis and transient photovoltage decay measurement, we have systematically studied the effects of subtle structural change upon the photophysical, photochemical and photovoltaic properties for cell devices. To the best of our knowledge, there are no systemic reports on the introduction of thiophene and its derivatives into metal-free organic dyes as electron donors for DSSCs.
4.2 Results and Discussion

4.2.1 Synthesis and Characterization

The structures of these new dyes TP-EEP are illustrated in Figure 4.1. The synthetic routes for these phenothiazine-based dyes are shown in Scheme 4.1. The alkyl chain attached to the N(10) of phenothiazine group can improve the solubility, forming a tightly packed insulating monolayer blocking the I$_3^-$ or cations from approaching the TiO$_2$ and enhancing the open circuit voltage. The synthesis of TP-EEP was started from a commercially available phenothiazine precursor. The N-alkylation of phenothiazine gave 1. Compound 2 was obtained by the followed Vilsmeier reaction, in which the bromination of 2 with N-bromosuccinimide (NBS) provided compound 3 in good yield. Step by step, 7-bromo-N-hexyl-10H-phenothiazine-3-carbaldehyde with a stille coupling or a Suzuki cross coupling of appropriate stannyl reagents of thiophene analogues,
respectively, followed by the Knoevenagel condensation afforded the target dyes. The chemical structures of these aldehyde intermediates and target dyes were fully characterized by their $^1$H NMR, $^{13}$C NMR and MALDI-TOF mass spectral data.

**Scheme 4.1.** Synthetic routes for phenothiazine-based dyes TP-EEP. (a) KOH, 1-bromohexane, DMSO, room temperature; (b) DMF, POCl$_3$, CICH$_2$CH$_2$Cl, reflux; (c) NBS, THF, 0°C; (d) Pd(PPh$_3$)$_4$, n-Bu$_3$SnR, toluene, reflux; (e) cyanoacetic acid, CH$_3$COOH, CH$_3$COONH$_4$, 120°C.

4.2.2 Spectroscopic Studies

The UV-Vis absorption spectra of the phenothiazine-based dyes have been recorded in CH$_2$Cl$_2$ solutions (Figure. 4.2), and the detailed spectroscopic data are collected in Table 4.1. All of these dyes exhibit two major distinct broad
absorption bands in the range of 300~600 nm with the molar extinction coefficient ($\varepsilon$) ranging from $2.24 - 2.60 \times 10^4$ M$^{-1}$ cm$^{-1}$). The absorptions at 300~380 nm are ascribed to the aromatic $\pi$-$\pi^*$ electronic transitions of the chromophores, while the absorptions at 400~600 nm are attributed to the intramolecular charge transfer (ICT) from the donor to the acceptor. The absorption maximum of the TP and EP dye is at 457 nm and 466 nm, respectively. The slight red-shift for EP compared to TP can be ascribed to the greater electron-donating ability of the EDOT unit. Similarly, the ICT band of dye ETP (481 nm) containing EDOT and thiophene mix-up as the electron donor displays a large red-shift of 11 nm compared with the analogous bithiophene unit based dye TTP (470 nm). For the same reason, the appended bi-EDOT (EE) unit in dye EEP ($\lambda_{\text{max}}$ =489 nm) leads to a larger red-shift of 19 nm in comparison with TTP ($\lambda_{\text{max}}$ =470 nm). In addition, the large bathochromic shift also due to the fact that the appending bi-EDOT or the combination of EDOT and thiophene (EDOT-thiophene) unit causes a large degree of molecular self-planarity through the intramolecular O···S interaction between the oxygen atom of EDOT and the sulfur atom of thiophene or EDOT in the $\pi$-conjugated system.$^9$ When adsorbed on transparent TiO$_2$ films (Figure 4.3), the absorption spectra of the dyes exhibited slight hypsochromic shifts with respect to their solutions, which may be mainly attributed to the deprotonation of the carboxylic acid.$^{10}$ Specifically, the absorption bands of ETP (14 nm) and EEP (17 nm) adsorbed on TiO$_2$ films display larger blue-shifts compared with TP (5 nm), EP (6 nm), and TTP (4 nm), indicating that the bi-EDOT or the EDOT-thiophene unit is more liable to form $\pi$-stacked aggregations on TiO$_2$
film.\(^{6b}\) Notably, all these dyes exhibit apparent red-shifted absorption thresholds of above 650 nm on TiO\(_2\) films compared to those in solutions, which are beneficial for harvesting the solar light and thus increasing photocurrent response region.

**Figure 4.2.** The UV-Vis absorption spectra of phenothiazine-based dyes.
4.2.3 Electrochemical Properties.

To evaluate the thermodynamic possibility of electron injection and sensitizer regeneration, the cyclic voltammograms were recorded in dichloromethane solutions to determine the oxidation potentials ($E_{ox}$) (Figure 4.4). The oxidation potentials ($E_{ox}$) correspond to the highest occupied molecular orbitals (HOMO). The lowest unoccupied molecular orbitals (LUMO) were obtained from the values of $E_{ox}$ and the zero-zero band gaps ($E_{0-0}$) estimated from the onset of the UV-visible absorption spectra. As listed in Table 4.1, the HOMO levels of all dyes were determined to be 0.64, 0.57, 0.62, 0.51, and 0.42 V, respectively, which are more positive than iodide/tri-iodide redox potential value (0.4 V vs. NHE),
indicating that the oxidized dyes could be efficiently regenerated by the electrolyte. Estimated from the onset of the UV-visible absorption spectra of these dyes, the resulting $E_{0\theta}$ are 2.27, 2.19, 2.23, 2.12, and 2.04 eV. Subsequently, The LUMO levels of all dyes were calculated to be $-1.63$, $-1.62$, $-1.61$, $-1.61$, and $-1.62$ V, respectively, which are more negative than the conduction band edge (CB) of TiO$_2$ ($-0.5$ V vs. NHE), providing the thermodynamic feasibility of electron injection from the excited dye molecules into the conduction band of TiO$_2$. According to literatures, a stronger electron-donating group results in a higher HOMO energy level. As expected, the HOMO level of TTP is higher than that of TP, because bithiophene group is more inclined to give an electron than a single thiophene unit. For the same reason, replacing the thiophene unit with EDOT for EP and ETP further pushes their HOMO levels to higher levels due to the stronger electron-donating ability of the EDOT group. Notably, the dye EEP appended with bi-EDOT unit exhibits the highest HOMO level of 0.42 V. Although the significant upgrade of the HOMO level for EEP can narrow the HOMO–LUMO bandgap and produce a red shifted absorption spectrum in solution, the resulted less difference between the HOMO level of the dye and the redox potential of the $\Gamma^-/I_3^-$ is unfavorable for the fast dye regeneration.$^{[11]}$ As a result, the slower dye regeneration would lead to the potential back reactions at the TiO$_2$/dye/electrolyte interface, which was demonstrated by the lowest charge recombination resistance in DSSC based on EEP (vide infra).
Figure 4.4. Cyclic voltammograms of sensitizers based on TP-EEP.

Figure 4.5. Energy diagram of the dyes.
### Table 4.1. Photophysical and electrochemical properties of dyes TP-EEP.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}^{[a]}$ (nm)</th>
<th>$\lambda_{\text{max}}^{[b]}$ (nm)</th>
<th>$E_{\text{ox}}^{[c]}$ (V)</th>
<th>$E_{0-0}^{[d]}$ (eV)</th>
<th>$E_{\text{red}}^{[e]}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP</td>
<td>457 (2.57)</td>
<td>452</td>
<td>0.64</td>
<td>2.27</td>
<td>-1.63</td>
</tr>
<tr>
<td>EP</td>
<td>466 (2.60)</td>
<td>460</td>
<td>0.57</td>
<td>2.19</td>
<td>-1.62</td>
</tr>
<tr>
<td>TTP</td>
<td>470 (2.24)</td>
<td>466</td>
<td>0.62</td>
<td>2.23</td>
<td>-1.61</td>
</tr>
<tr>
<td>ETP</td>
<td>481 (2.39)</td>
<td>467</td>
<td>0.51</td>
<td>2.12</td>
<td>-1.61</td>
</tr>
<tr>
<td>EEP</td>
<td>489 (2.52)</td>
<td>472</td>
<td>0.42</td>
<td>2.04</td>
<td>-1.62</td>
</tr>
</tbody>
</table>

[a] Absorption maximum measured in CH$_2$Cl$_2$ solution (1 × 10$^{-5}$ M). [b] Absorption maximum of dye adsorbed on TiO$_2$. [c] Oxidation potential measured in CH$_2$Cl$_2$ solution containing 0.1 M (n-C$_4$H$_9$)$_4$NPF$_6$ with a scan rate of 100 mV s$^{-1}$ (vs. NHE). [d] Zero-zero band gap determined from the onset of absorption spectrum. [e] $E_{\text{red}} = E_{\text{ox}} - E_{0-0}$.

#### 4.2.4 Theoretical Studies

To understand the electronic distribution in the frontier molecular orbitals and electronic processes upon photoexcitation, the density functional theory (DFT) calculations were performed using Gaussian 03 program package at the B3LYP/6-31 G(d)* hybrid functional for full geometrical optimization (Figure 4.6). The electron density distributions of the HOMO orbitals for the five phenothiazine-based dyes are delocalized through the entire molecular systems from the donor to the cyanoacrylic acid acceptor, while the electron density distributions of the LUMO orbitals are mainly located on the cyanoacrylic acid.
segment and partly on the phenothiazine core. The sufficient orbital overlap between donor and acceptor suggests a fast charge transition. When these dyes are adsorbed on nanocrystalline TiO$_2$ surface, the photoinduced electron can be effectively injected into the conduction band of TiO$_2$ semiconductor from the donor unit via the terminal cyanoacrylic acid acceptor. At the same time, the fast charge transfer could avoid the geminate charge recombination between the oxidized dye molecules and the photoinjected electrons at the TiO$_2$/dye/electrolyte interface.

In the optimized ground-state geometries shown in Figure 4.6, the dihedral angles between the donor units of thiophene and EDOT and the phenothiazine core are computed to be 22.1° and 20.1° for TP and EP, respectively. The ground state geometry of TTP possesses a 10.5° twist between the two adjacent thiophene units, while the much smaller dihedral angles of 2.3° and 1.1° were observed for ETP and EEP, respectively. This results indicate that the EDOT-thiophene or bi-EDOT unit tends to produce a higher degree of molecular coplanarity through the intramolecular S···O interaction between the oxygen atom of EDOT and the sulfur atom of thiophene or EDOT. Specifically, the intramolecular S···O interactions are maximized when two EDOT groups are adjacent, resulting in a big coplanarity comprised of bi-EDOD and phenyl ring of phenothiazine core. The results are consistent with the UV-vis absorption spectra observed in the solutions. When compared with TP, the dyes of TTP ($\lambda_{\text{max}}$ = 470 nm), ETP ($\lambda_{\text{max}}$ = 481 nm) and EEP ($\lambda_{\text{max}}$ = 489 nm) show gradually increase in
red-shifted of CT bands of 13, 24 and 32 nm, respectively, due to the continuously strengthened π-conjugation in the chromophores.

<table>
<thead>
<tr>
<th>Dye</th>
<th>HOMO</th>
<th>LUMO</th>
<th>Optimized structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>EP</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>TTP</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td>ETP</td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
<tr>
<td>EEP</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
</tr>
</tbody>
</table>

**Figure 4.6.** Calculated frontier orbitals and Optimized geometries.

4.2.5 Photovoltaic Performance

The performance parameters of DSSCs fabricated with these phenothiazine-based dyes on nanocrystalline titania films in conjunction with $\Gamma/I_3^-$ electrolyte, namely, short-circuit current density ($J_{sc}$), open-circuit photovoltage ($V_{oc}$), fill factor (FF), and total power conversion efficiency ($\eta$), were measured under standard AM 1.5 solar light (100 mW cm$^{-2}$) and are summarized in Table 4.2. The photocurrent–voltage ($J–V$) plots are shown in Figure 4.7. The $\eta$ values are strongly depended on the arrangement of substituents.
of thiophene analogues in these organic dyes. The cell based on the dye TP appended with thiophene monomer as the electron donor exhibits the highest $\eta$ of 8.07% with a $J_{sc}$ of 15.18 mA cm$^{-2}$ and $V_{oc}$ of 0.783 V. And the cell based on EP shows a similar performance with a higher $J_{sc}$ of 16.65 mA cm$^{-2}$, a lower $V_{oc}$ of 0.746 V and the $\eta$ of 7.98%. Under the same condition, the cell based on dye TTP containing two thiophene units as the donor gives an efficiency of 7.87% with a higher $J_{sc}$ of 16.13 mA cm$^{-2}$ relative to TP due to the extension of the $\pi$-conjugated system. On the other side, the dye ETP with the mix-up of EDOT and thiophene as the donor shows a much lower $\eta$ value of 5.62% with a lower $J_{sc}$ of 12.01 mA cm$^{-2}$ and $V_{oc}$ of 0.672 V. Remarkably, the cell sensitized with the dye EEP with the bi-EDOT units shows a greater inferior $J_{sc}$ of 5.93 mA cm$^{-2}$ and $V_{oc}$ of 0.559 V, corresponding to the lowest $\eta$ of 2.24%, regardless of its higher molar extinction coefficient and broader absorption spectral response in solution. Obviously, the subtle structural difference among these phenothiazine-based dyes led to much differential performances in DSSCs based on these dyes. These results demonstrate that the replacement of thiophene with electron-rich EDOT in these phenothiazine-based dyes results in deleterious effect on the $J_{sc}$. The dramatically reduced $J_{sc}$ values for cells based on ETP and EEP can also be predicted by the low incident photo-current conversion (IPCE) spectra (Figure 4.8) with 65% and 40% at 475nm, respectively, in contrast to the IPCE of 72% at 470 nm for dye TTP. The main reason for the low $J_{sc}$ value is that the dyes ETP and EEP with a well coplanarity arising from the S···O interactions are liable to the formation of $\pi$-stacked aggregation on TiO$_2$ films which would quench the excited
photoinjected electron, resulting in low efficiency of electron injection.\cite{5a, 6b, 12}

As aforementioned above the up-shift of the HOMO energy levels for \textbf{ETP} and \textbf{EEP} led to the weak driving force for the oxidized dye to be regenerated by I\textsuperscript{–}, which also contributed to the low photocurrent in DSSCs. In addition, the adsorbed amount of dyes \textbf{TTP} and \textbf{EEP} on the TiO\textsubscript{2} films are found to be $6.39 \times 10^{-8}$ and $11.9 \times 10^{-8}$ mol/cm\textsuperscript{2}, respectively. It indicates that the resulting absorptivity is not the reason for the lower short circuit current of the device based on dye \textbf{EEP}.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{current_voltage_curves.png}
\caption{Current-voltage curves of sensitizers based on TP-EEP.}
\end{figure}
Figure 4.8. Incident photo-to-current efficiency (IPCE) curves of DSSCs based on the new dyes.

4.2.6 Electrochemical Impedance Spectroscopy

To understand the significant decrease of $V_{oc}$ from TP to EEP based DSSCs, Electrochemical Impedance Spectroscopy (EIS) was performed to analyze the interfacial charge recombination and carrier transportation process under the dark conditions. The interfacial charge recombination reaction of electron with the $I_3^-$ ions can be described by a charge recombination resistance ($R_{rec}$). As shown in Figure 4.9, a major intermediated semicircle for each dye is observed in the EIS Nyquist plot, which is related to the charge recombination resistance on the TiO$_2$/dye/electrolyte interface ($R_{rec}$). The calculated $R_{rec}$ values were listed in Table 4.2 and a smaller $R_{rec}$ value means a larger charge recombination rate.$^{[13]}$ It is found that the $R_{rec}$ values are in the order of $\text{TP} (262.3\Omega) > \text{EP} (252.8\Omega) > \text{TTP}$
(121.8Ω) > ETP (92.34Ω) > EEP (45.8Ω). The larger $R_{\text{rec}}$ value implies a less facile injected charge recombination with $\text{I}_3^-$ in the electrolyte and can be reflected in the better performance in DSSCs. The results are well consistent with the order of in the photovoltage ($V_{\text{oc}}$) values in DSSCs based on these dyes. Notably, both the cells based on the dyes ETP and EEP with at least one EDOT unit show a greatly inferior $V_{\text{oc}}$ compared to that of dye TTP containing bi-thiophene. As to the ground-state optimized geometries, TTP possesses a 18.9° twist angles between the phenyl ring of phenothiazine core and the adjacent thiophene unit, while the dihedral angle of the two thiophene units is 10.5°. In contrast, the corresponding dihedral angles were determined to be 11.6° and 2.3° in ETP, and 4.3° and 1.1° in EEP, respectively. In other words, the appending of the bi-EDOT or EDOT-thiophene unit led to an enhancement of molecular coplanarity, which may facilitate the approach of $\text{I}_3^-$ ions to the TiO$_2$ surface, resulting in faster charge recombination and lower $V_{\text{oc}}$. More importantly, the dye aggregation arising from the coplanar structure should be accounted as the main reason for the low $V_{\text{oc}}$. 
**Figure 4.9.** EIS Nyquist plots for DSSCs based on the new dyes.

**Table 4.2.** Photovoltaic parameters in DSSCs based on TP-EEP and N719 at full sunlight (AM 1.5G, 100 mW cm$^{-2}$).[a]

<table>
<thead>
<tr>
<th>Dye</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$R_{sc}$ (Ω cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP</td>
<td>15.18</td>
<td>0.783</td>
<td>0.679</td>
<td>8.07</td>
<td>262.3</td>
</tr>
<tr>
<td>EP</td>
<td>16.65</td>
<td>0.746</td>
<td>0.642</td>
<td>7.98</td>
<td>252.8</td>
</tr>
<tr>
<td>TTP</td>
<td>16.13</td>
<td>0.717</td>
<td>0.681</td>
<td>7.87</td>
<td>121.8</td>
</tr>
<tr>
<td>ETP</td>
<td>12.01</td>
<td>0.672</td>
<td>0.696</td>
<td>5.62</td>
<td>92.34</td>
</tr>
<tr>
<td>EEP</td>
<td>5.93</td>
<td>0.559</td>
<td>0.676</td>
<td>2.24</td>
<td>45.8</td>
</tr>
<tr>
<td>N719</td>
<td>16.28</td>
<td>0.731</td>
<td>0.614</td>
<td>7.31</td>
<td>/</td>
</tr>
</tbody>
</table>

[a] the effective areas of all the DSSCs are 0.24 cm$^2$. Dyes and N719 were maintained at 0.5 mM in acetonitrile/tert-butyl alcohol (1/1, v/v) solutions. Electrolyte: LiI (0.05 M), I$_2$ (0.1 M), and DMPII (0.6 M) in acetonitrile/tert-butyl alcohol (1/1, v/v).

4.2.7 Transient Photovoltage Measurement.
To further confirm the electron recombination kinetics between the photoinjected electrons at TiO$_2$ and the oxidized electrolyte in DSSCs, open-circuit voltage decay (OCVD) was recorded to illustrate the recombination lifetime of $V_{oc}$ from illuminated quasiequilibrium state for 20 seconds under open-circuit condition to dark equilibrium decaying for 80 seconds in dark equilibrium. Figure 4.10 shows the OCVD profiles of devices based on these dyes. The correlation between $V_{oc}$ decay and electron lifetime ($\tau_n$) can be described by the following equation:

$$\tau_n = -\frac{K_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1}$$

where $K_B$ is the Boltzmann constant, $T$ is temperature, and $e$ is the electron charge.$^{[14]}$ Therefore, the electron lifetimes can be derived from the slope of $V_{oc}$ decay curves. Following the sequence of the cells based on TP, EP, TTP, ETP and EEP, the slopes become steeper and steeper, indicating that the electron lifetimes are gradually reduced in the dark measurement, showing the order of the charge recombination in the electrolyte, which are well consistent with the EIS spectra. As illustrated, the $V_{oc}$ of the DSSCs based on the dyes of ETP and EEP show faster decay rates than that based on TTP, which indicates the higher electron recombination rate and shorter electron lifetime for the former cell. It is clear that the electron lifetimes are in the order of $\text{TP} > \text{EP} > \text{TTP} > \text{ETP} > \text{EEP}$, implying that expanding the $\pi$-conjugation by appending the EDOT unit is disadvantageous to suppress the charge recombination. Specifically, the two adjacent EDOT units can facilitate the charge recombination between the injected
electrons and the oxidized electrolyte species, which is attributed to a stable complex formation by means of the Columbic interaction between the hydrophilic oxygen atoms of EDOT and the oxidized electrolyte species (I$_3^-$ or I$_2$)$^{[15]}$ which can rapidly bring the oxidized electrolyte species close to the TiO$_2$ surface and promote the photoexcited electron recombination, resulting in a faster open-circuit voltage decay and lower $V_{oc}$ value. The rate of the oxidized electrolyte species approaching the TiO$_2$ surface can be speeded up with the increasing number of EDOT units, thus enhancing the charge recombination rate and penalizing the overall conversion efficiency.
**Figure 4.10.** Open-circuit voltage decay profiles of (a) device based on the new dyes and (b) enlarged from 20 to 90 seconds.

### 4.3 Conclusions

In summary, we have designed and synthesized a series of simple phenothiazine-based dyes featuring different numbers of thiophene and/or EDOT units as the donor, and cyanoacrylic acid as the acceptor, aiming to investigate the structure-property relationship in DSSC applications. The dyes of TP, EP, TTP, ETP, and EEP, were engineered by the thiophene, EDOT, the dimer of thiophene, the mix-up of EDOT and thiophene and the dimer of EDOT, respectively. The stepwise incorporation of electron-rich EDOT group resulted in a lift of the ground-state redox potential and a red-shift of the ICT absorption peak, accompanying with dye aggregation, faster interfacial charge recombination and slower dye regeneration. The devices sensitized by dyes TP and TTP display high
power conversion efficiency of 8.07% and 7.87%, respectively, measured under the simulated AM 1.5 sunlight in conjunction with a $I^-/I_3^-$ redox couple, which are attributed to fast dye regeneration dynamics and slow charge recombination kinetics. When replacing the thiophene group with EDOT unit, the dye EP based DSSCs shows a good PCE (7.98%) with a much higher short circuit current of 16.65 mA cm$^{-2}$ due to the broader IPCE absorption response. The dye ETP with the mix-up of EDOT and thiophene shows an even lower PCE value of 5.62% compared with dye TTP. Specially, the cell sensitized with the dye EEP having a bi-EDOT unit displays a greatly inferior $J_{sc}$ and $V_{oc}$, leading to a significantly reduced PCE of 2.24% than that of TTP. The primary results shed a light on the principle and strategy of design and synthesis of phenothiazine-based organic dyes with a balance between the dye aggregation and interfacial charge recombination and enhancing the absorption spectrum response.

4.4 Experimental Section

Materials. All solvents and reagents were purchased from Sigma-Aldrich Company and used as received without further purification. The starting material phenothiazine and 2-cyanoacetic acid were purchased commercially. Dye sensitizer cis-bis(isothicyanato)bis(2,2',bipyridyl-4,4'-disacarboxylato)ruthenium-(II)bistetrabutyl ammonium (coded as N719), TiO$_2$ paste and iodide-based liquid electrolyte (HL-HPE) were purchased from Dyesol company. Tributyl(thiophen-2-yl)stannane, tributyl-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane, tributyl(5-hexylthiophen-2-yl)stannane, and tributyl(7-hexyl-2,3-
dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane were synthesized according to the corresponding literature methods. The synthetic routes of phenothiazine-based dyes TP-EEP are outlined in Scheme 4.1 and the details are depicted as follows.

**10-hexyl-10H-phenothiazine (1)**

Phenothiazine (2 g, 10 mmol), NaOH (0.5 g, 13 mmol) and 1-bromohexane (11 mmol) were dissolved in 100 mL DMSO and the mixture was stirred overnight at room temperature. Then, the reaction mixture was poured into water and extracted with dichloromethane. The organic phase was collected and dried with anhydrous MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel using hexane as the eluent to give the product as a colorless liquid. 2.45 g, 88% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.18 (d, J = 8.0 Hz, 4H), 6.87 (t, J = 8.0 Hz, 4H), 3.89 (t, J = 6.9 Hz, 2H), 1.74–1.86 (m, 2H), 1.25–1.42 (m, 6H), 0.88 (t, J = 5.1 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 145.69, 127.86, 127.45, 125.85, 122.47, 115.06, 43.89, 31.62, 29.27, 25.79, 22.64, 14.09. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₁₈H₂₁NS) 283.1445; found, 283.1456.

**10-hexyl-10H-phenothiazine-3-carbaldehyde (2)**

1 (0.71 g, 2.5 mmol) and dry DMF (0.73 g, 10 mmol) were dissolved in 1,2-dichloroethane (20 mL), and phosphorus oxychloride (1.54 g, 10 mmol) was added slowly at 0 °C in an ice water bath. Then, the mixture was heated to reflux overnight. The reaction mixture was quenched with water and extracted three times with chloroform. The combined organic fractions were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the
residue was purified by column chromatography on silica gel using n-hexane/dichloromethane (8/2; v/v) as the eluent to give a yellow solid. 0.39 g, 58% yield. 1H NMR (400 MHz, CDCl₃): δ (ppm) 9.82 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.43 (s, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 6.85 (t, J = 8.0 Hz, 1H), 3.89 (t, J = 6.4 Hz, 2H), 1.78-1.90 (m, 2H), 1.28–1.32 (m, 6H), 0.86 (t, J = 6.4 Hz, 3H). 13C NMR (400 MHz, CDCl₃): δ (ppm) 189.91, 150.32, 142.63, 131.33, 130.35, 130.12, 129.38, 128.54, 126.61, 124.44, 117.41, 115.48, 115.20, 48.10, 31.43, 26.56, 26.64, 22.36, 14.01. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₁₉H₂₁NOS) 311.0413; found, 311.0422.

**General synthetic procedure for 3, 7 and 11.**

NBS (411 mg, 2.31 mmol) was added in one portion to the solution of 2 or 6 or 10 (2.0 mmol) in THF (50 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirring was continued for 1.5 h. Then, the reaction was quenched by addition of water (50 mL), and extracted with dichloromethane. The collected organic layer was evaporated under vacuum and the residue was purified by column chromatography on silica gel with CH₂Cl₂ as eluent to give 3, 7 and 11 respectively.

**7-Bromo-10-hexyl-10H-phenothiazine-3-carbaldehyde (3).**

A yellow solid, 89% yield. 1H NMR (400 MHz, CDCl₃): δ (ppm) 9.80 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 6.85 (t, J = 8.0 Hz, 1H), 3.89 (t, J = 6.4 Hz, 2H), 1.78-1.90 (m, 2H), 1.28–1.32 (m, 6H), 0.86 (t, J = 6.4 Hz, 3H). 13C NMR (400 MHz, CDCl₃): δ (ppm) 189.91, 150.32, 142.63, 131.33, 130.35, 130.12, 129.38, 128.54, 126.61,
7-(5-bromothiophen-2-yl)-10-hexyl-10H-phenothiazine-3-carbaldehyde (7).

A dark yellow solid, 77% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.76 (s, 1H), 7.59-7.62 (m, 1H), 7.53 (d, J = 2.0 Hz, 1H), 7.21-7.24 (m, 1H), 7.17 (d, J = 2.0 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.90 (d, J = 2.0 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H), 3.83 (t, J = 7.2 Hz, 2H), 1.74-1.78 (m, 2H), 1.38-1.43 (m, 2H), 1.25-1.30 (m, 4H), 0.86 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 189.93, 150.05, 144.38, 142.83, 131.15, 130.91, 130.30, 129.23, 128.31, 124.83, 124.40, 124.23, 124.15, 122.74, 116.06, 114.79, 110.99, 48.13, 31.63, 26.63, 22.62, 14.20, 14.04. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{19}$H$_{20}$BrNOS) 389.0413; found, 389.0422.

7-(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-10-hexyl-10H-phenothiazine-3-carbaldehyde (11).

A dark yellow solid, 80% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.78 (s, 1H), 7.61-7.64 (m, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.34-7.36 (m, 1H), 6.81 (m, 2H), 4.30 (d, J = 4.0 Hz, 4H), 3.86 (t, J = 7.2 Hz, 2H), 1.78-1.82 (m, 2H), 1.41-1.45 (m, 2H), 1.26–1.32 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 190.00, 150.26, 141.82, 140.46, 137.17, 131.05, 130.25, 128.10, 124.96, 124.73, 124.36, 124.05, 116.35, 115.89, 114.68, 114.29, 110.89, 64.92, 64.71, 48.08, 31.61, 26.66, 22.68, 14.15, 14.00. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{23}$H$_{22}$BrNOS$_2$) 471.0316; found, 471.0323.
General synthetic procedure for 4, 5, 6, 8, 9, 10 and 12.

A mixture of 3 or 7 or 11 (0.30 mmol), tributyl(5-hexylthiophen-2-yl)stannane or tributyl(7-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane or tributyl(thiophen-2-yl)stannane or tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (0.40 mmol), Pd(PPh₃)₄ (10 mg, 0.0016 mmol) in toluene (20 mL) was heated to reflux under a N₂ atmosphere for about 12 hrs. Then, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 1:4 mixture of hexane and CH₂Cl₂ as eluent to afford relative product, respectively.

10-hexyl-7-(5-hexylthiophen-2-yl)-10H-phenothiazine-3-carbaldehyde (4).

A red solid, 89% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.77 (s, 1H), 7.61-7.63 (m, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.32-7.38 (m, 1H), 7.30 (d, J = 2.0 Hz, 1H), 7.20-7.23 (m, 1H), 7.14-7.19 (m, 1H), 7.05-7.07 (m, 1H), 6.83-6.88 (m, 1H), 3.84 (t, J = 7.2 Hz, 2H), 2.79 (t, J = 6.4 Hz, 2H), 1.75-1.87 (m, 2H), 1.64-1.70 (m, 2H), 1.28-1.42 (m, 12H), 0.86-0.92 (m, 6H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 190.01, 150.51, 145.63, 141.18, 139.83, 132.23, 130.82, 130.35, 125.14, 125.00, 124.62, 124.00, 123.34, 123.09, 122.32, 115.95, 114.34, 48.22, 31.63, 31.62, 31.40, 31.12, 30.29, 28.84, 26.54, 26.51, 22.69, 14.15, 14.02. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₂₉H₃₅NOS₂) 477.2215; found, 477.2234.

10-hexyl-7-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-10H-phenothiazine-3-carbaldehyde (5).

A red solid, 86% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.78 (s, 1H), 7.61-7.64 (m, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.44-7.48 (m, 2H), 6.82-6.89 (m, 2H),
<math>6.26 \text{ (s, 1H)}, 4.31 \text{ (s, 2H)}, 4.24 \text{ (s, 2H)}, 3.87 \text{ (t, } J = 7.2 \text{ Hz, 2H)}, 2.63 \text{ (t, } J = 7.2 \text{ Hz, 2H)}, 1.79-1.83 \text{ (m, 2H)}, 1.42-1.45 \text{ (m, 2H)}, 1.26-1.31 \text{ (m, 12H)}, 0.86-0.92 \text{ (m, 6H)}.
</math>

<math>13^\text{C} \text{ NMR (400 MHz, CDCl}_3\text{): } \delta \text{ (ppm) 190.02, 154.52, 148.72, 139.83, 137.65, 137.23, 132.15, 130.29, 129.59, 125.03, 124.57, 123.41, 122.92, 116.71, 115.73, 114.54, 111.43, 64.89, 64.45, 48.18, 31.59, 31.23, 30.11, 29.17, 28.88, 26.51, 25.79, 24.54, 22.63, 14.13, 14.01. \text{ HRMS (MALDI-TOF, m/z): } [M+] \text{ calcd for } (C_{31}H_{37}NO_3S_2) 535.2235; \text{ found, 535.2239.}
</math>

10-hexyl-7-(thiophen-2-yl)-10H-phenothiazine-3-carbaldehyde (6).

A red solid, 79% yield. \text{ } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta \text{ (ppm) 9.77 (s, 1H), 7.61-7.63 \text{ (m, 1H)}, 7.55 \text{ (d, } J = 2.0 \text{ Hz, 1H)}, 7.34-7.37 \text{ (m, 1H)}, 7.30 \text{ (d, } J = 2.0 \text{ Hz, 1H)}, 7.20-7.24 \text{ (m, 1H)}, 7.19-7.20 \text{ (m, 1H)}, 7.03-7.05 \text{ (m, 1H)}, 6.81-6.87 \text{ (m, 2H)}, 3.84 \text{ (t, } J = 7.2 \text{ Hz, 2H)}, 1.31-1.43 \text{ (m, 2H)}, 1.27-1.30 \text{ (m, 4H)}, 0.87 \text{ (d, } J = 2.0 \text{ Hz, 3H)}. \text{ } ^{13}\text{C NMR (400 MHz, CDCl}_3\text{): } \delta \text{ (ppm) 190.00, 150.25, 142.94, 142.47, 131.06, 130.26, 130.12, 128.37, 128.10, 126.67, 125.13, 124.65, 124.54, 124.29, 124.22, 116.05, 114.73, 48.11, 31.40, 26.66, 26.52, 22.62, 14.04. \text{ HRMS (MALDI-TOF, m/z): } [M+] \text{ calcd for } (C_{23}H_{23}NOS_2) 393.1236; \text{ found, 393.1249.}

10-hexyl-7-(5'-hexyl-[2,2'-bithiophen]-5-yl)-10H-phenothiazine-3-carbaldehyde (8).

A red solid, 74% yield. \text{ } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta \text{ (ppm) 9.70 (s, 1H), 7.53-7.56 \text{ (m, 1H)}, 7.49 \text{ (d, } J = 4.0 \text{ Hz, 1H)}, 7.24-7.27 \text{ (m, 1H)}, 7.21 \text{ (d, } J = 4.0 \text{ Hz, 1H)}, 7.00 \text{ (d, } J = 4.0 \text{ Hz, 1H)}, 6.94 \text{ (d, } J = 4.0 \text{ Hz, 1H)}, 6.90 \text{ (d, } J = 4.0 \text{ Hz, 1H)}, 6.78 \text{ (d, } J = 4.0 \text{ Hz, 1H)}, 6.73 \text{ (d, } J = 4.0 \text{ Hz, 1H)}, 6.59-6.60 \text{ (m, 1H)}, 3.78 \text{ (t, } J = 7.2 \text{ Hz, 2H)}, 2.71 \text{ (t, } J = 7.2 \text{ Hz, 2H)}, 1.69-1.76 \text{ (m, 2H)}, 1.54-1.63 \text{ (m, 2H)}, 150
1.29-1.38 (m, 4H), 1.16-1.27 (m, 8H), 0.79-0.87 (m, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 189.98, 150.27, 150.20, 145.56, 142.42, 140.85, 137.05, 134.67, 131.09, 130.22, 129.90, 128.41, 125.14, 124.84, 124.54, 124.21, 123.83, 123.30, 123.19, 116.05, 114.74, 48.13, 31.60, 31.58, 31.40, 30.22, 28.79, 26.67, 26.52, 22.69, 22.61, 14.13, 14.04. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{33}$H$_{37}$NOS$_3$) 559.2033; found, 559.2039.

10-hexyl-7-(5-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)-10H-pheno-thiazine-3-carbaldehyde (9).

A red solid, 72% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.76 (s, 1H), 7.58-7.61 (m, 1H), 7.54 (d, J = 4.0 Hz, 1H), 7.31-7.34 (m, 1H), 7.28 (d, J = 4.0 Hz, 1H), 7.08 (d, J = 4.0 Hz, 1H), 7.04 (d, J = 4.0 Hz, 1H), 6.77-6.85 (m, 2H), 4.31 (t, J = 7.2 Hz, 2H), 4.21 (t, J = 7.2 Hz, 2H), 3.82 (t, J = 6.4 Hz, 2H), 2.61-2.65 (d, J = 4.0 Hz, 2H), 1.60-1.68 (m, 2H), 1.40-1.45 (m, 2H), 1.27-1.33 (m, 12H), 0.85-0.93 (m, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 189.98, 150.22, 142.06, 139.92, 137.62, 137.49, 134.48, 130.99, 130.22, 130.17, 128.34, 124.51, 124.25, 124.14, 124.04, 122.81, 122.66, 116.53, 116.02, 114.67, 107.99, 65.18, 64.53, 48.08, 31.59, 31.40, 30.42, 28.85, 26.65, 26.52, 25.79, 22.64, 22.62, 17.35, 14.16, 14.03. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{35}$H$_{39}$NO$_3$S$_3$) 617.2146; found, 617.2148.

7-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-10-hexyl-10H-pheno-thiazine-3-carbaldehyde (10).

A red solid, 70% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.78 (s, 1H), 7.61-7.64 (m, 1H), 7.57 (d, J = 6.4 Hz, 1H), 7.44-7.48 (m, 2H), 6.82-6.89 (m, 2H),
6.26 (s, 1H), 4.30 (t, J = 7.2 Hz, 2H), 4.25 (t, J = 7.2 Hz, 2H), 3.87 (t, J = 4.0 Hz, 2H), 1.79-1.83 (m, 2H), 1.42-1.45 (m, 2H), 1.26-1.31 (m, 4H), 0.88 (t, J = 4.0 Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 190.01, 150.23, 141.84, 140.23, 137.23, 131.12, 130.25, 128.13, 124.86, 124.67, 124.55, 124.89, 116.36, 115.87, 114.68, 114.23, 64.55, 64.12, 48.07, 31.62, 26.68, 22.78, 14.16, 14.04. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{25}$H$_{25}$NO$_3$S$_2$) 451.1344; found, 451.1346.

10-hexyl-7-(7'-hexyl-2,2',3,3'-tetrahydro-[5,5'-bithieno[3,4-b][1,4]dioxin]-7-yl)-10H-phenothiazine-3-carbaldehyde (12).

A red solid, 73% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.77 (s, 1H), 7.61-7.63 (m, 1H), 7.57 (d, J = 6.4 Hz, 1H), 7.44-7.50 (m, 2H), 7.15-7.18 (m, 1H), 6.80-6.88 (m, 2H), 4.30-4.36 (m, 6H), 4.22-4.29 (m, 2H), 3.86 (t, J = 7.0 Hz, 2H), 2.64 (t, J = 6.4 Hz, 2H), 1.77-1.82 (m, 2H), 1.59-1.65 (m, 2H), 1.22-1.34 (m, 12H), 0.86-0.90 (m, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 190.01, 150.29, 142.13, 139.12, 137.44, 137.48, 134.46, 130.34, 130.22, 130.16, 128.38, 124.57, 124.65, 124.78, 124.08, 122.83, 122.64, 116.23, 116.01, 114.65, 107.55, 65.47, 65.15, 64.54, 64.18, 48.05, 31.55, 31.44, 30.40, 28.89, 26.64, 26.12, 25.45, 22.78, 22.61, 17.33, 14.13, 14.02. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{37}$H$_{41}$NO$_5$S$_3$) 675.2153; found, 675.2146.

**General synthetic procedure for these dyes TP, EP, TTP, ETP and EEP.**

A mixture of the precursor carbaldehyde (0.20 mmol) and cyanoacetic acid (100 mg, 1.30 mmol) in acetic acid (20 mL) was refluxed in the presence of ammonium acetate (200 mg) overnight under a N$_2$ atmosphere. Then, water was...
added and extracted with CH₂Cl₂. Next, the solvent was removed under vacuum and the crude compound was purified by column chromatography on silica gel eluting with CH₂Cl₂/MeOH (20:1, v/v) to give these dyes.

**TP.**

A dark red solid, 61% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.04 (s, 1H), 7.86-7.89 (m, 1H), 7.61 (d, J = 2.0 Hz, 1H), 7.27-7.29 (m, 1H), 7.21 (d, J = 2.0 Hz, 1H), 7.00 (d, J = 2.0 Hz, 1H), 6.79 (t, J = 2.0 Hz, 2H), 6.70 (d, J = 2.0 Hz, 1H), 3.61 (s, 2H), 2.76 (t, J = 7.6 Hz, 2H), 1.63-1.70 (m, 4H), 1.24-1.35 (m, 12H), 0.84–0.91 (m, 6H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 168.57, 154.55, 149.64, 145.68, 141.08, 139.88, 132.13, 130.82, 130.37, 125.18, 125.07, 124.61, 124.03, 123.78, 123.35, 123.22, 122.36, 115.92, 114.72, 97.24, 48.26, 31.63, 31.62, 31.40, 31.24, 30.29, 28.83, 26.57, 26.52, 22.63, 14.14, 14.03. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₃₂H₃₆N₂O₂S₂) 545.2290; found, 545.2312.

**EP.**

A dark red solid, 64% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.01 (s, 1H), 7.82 (d, J = 4.8 Hz, 1H), 7.59 (s, 1H), 7.35 (d, J = 4.8 Hz, 2H), 6.74-6.77 (m, 2H), 4.27 (d, J = 2.0 Hz, 2H), 4.21 (d, J = 2.0 Hz, 2H), 3.79 (t, J = 7.2 Hz, 2H), 2.62 (t, J = 7.2 Hz, 2H), 1.76-1.79 (m, 2H), 1.56-1.64 (m, 2H), 1.31-1.42 (m, 12H), 0.87–0.90 (m, 6H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 168.61, 154.52, 149.72, 139.87, 137.95, 137.91, 132.15, 130.29, 129.59, 125.03, 124.57, 124.20, 123.81, 122.92, 116.71, 116.00, 115.73, 114.54, 111.43, 96.95, 64.89, 64.39, 48.19, 31.58,
31.39, 30.41, 29.17, 28.88, 26.51, 25.79, 24.54, 22.63, 14.13, 14.01. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{34}H_{38}N_{2}O_{4}S_{2}) 603.2346; found, 603.2324. (E)-2-cyano-3-(10-hexyl-7-(5'-hexyl-[2,2'-bithiophen]-5-yl)-10H-phenothiazin-3-yl)acrylic acid (TTP).

A dark red solid, 68% yield. $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.97 (s, 1H), 7.73 (d, $J = 7.2$ Hz, 1H), 7.43 (d, $J = 7.2$ Hz, 1H), 7.09-7.22 (m, 2H), 6.97-7.01 (m, 1H), 6.92-6.94 (m, 2H), 6.30 (d, $J = 7.2$ Hz, 2H), 6.56 (d, $J = 8.0$ Hz, 1H), 3.61 (s, 2H), 2.76 (t, $J = 7.2$ Hz, 2H), 1.63-1.70 (m, 4H), 1.24-1.39 (m, 12H), 0.84–0.91 (m, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 168.18, 153.49, 148.20, 145.30, 141.14, 140.65, 136.78, 134.74, 131.92, 129.51, 128.06, 125.41, 124.77, 124.33, 123.80, 123.49, 123.18, 123.10, 122.73, 122.53, 116.92, 115.39, 114.36, 98.94, 48.24, 31.62, 31.59, 31.39, 30.23, 28.86, 26.54, 26.25, 22.69, 22.64, 14.15, 14.05. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{36}H_{38}N_{2}O_{2}S_{3}) 627.2168; found, 627.2194.

(E)-2-cyano-3-(10-hexyl-7-(5-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-y)thiophen-2-yl)-10H-phenothiazin-3-yl)acrylic acid (ETP).

A dark red solid, 61% yield. $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.01 (s, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.59 (s, 1H), 7.29-7.32 (m, 1H), 7.23 (d, $J = 2.0$ Hz, 1H), 7.08 (d, $J = 2.0$ Hz, 1H), 7.04 (d, $J = 2.0$ Hz, 1H), 6.76-6.79 (m, 2H), 4.32 (t, $J = 7.6$ Hz, 2H), 4.23 (t, $J = 7.6$ Hz, 2H), 3.81 (t, $J = 7.6$ Hz, 2H), 2.62 (t, $J = 7.6$ Hz, 2H), 1.77-1.80 (m, 2H), 1.58-1.62 (m, 2H), 1.30-1.43 (m, 12H), 0.87-0.90 (m, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 168.04, 154.32, 149.40, 141.19, 139.72, 137.60, 137.53, 134.61, 131.97, 130.41, 130.35, 125.28, 124.50, 123.89,

HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{38}H_{40}N_{2}O_{4}S_{3}) 684.2145; found, 684.2117.

(E)-2-cyano-3-(10-hexyl-7-(7'-hexyl-2,2',3,3'-tetrahydro-[5,5'-bithieno[3,4-b][1,4]dioxin]-7-yl)-10H-phenothiazin-3-yl)acrylic acid (EEP).

A dark red solid, 58% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.98 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.42-7.46 (m, 2H), 6.74-6.78 (m, 2H), 4.23-4.34 (m, 8H), 3.80 (t, J = 6.4 Hz, 2H), 2.62 (t, J = 7.6 Hz, 2H), 1.76 (d, J = 7.4 Hz, 2H), 1.58-1.62 (m, 2H), 1.29-1.42 (m, 12H), 0.86-0.91 (m, 6H).$^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 168.25, 154.27, 139.99, 137.80, 137.10, 137.04, 136.79, 136.61, 131.97, 130.28, 129.34, 125.10, 124.65, 124.14, 123.65, 122.93, 117.15, 116.13, 115.69, 114.51, 112.49, 108.55, 105.57, 97.41, 65.21, 65.07, 64.79, 64.56, 48.19, 31.60, 31.41, 30.49, 29.74, 29.21, 28.92, 26.53, 25.85, 22.64, 14.16, 14.04. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{40}H_{42}N_{2}O_{6}S_{3}) 743.2277; found, 743.2240.

**Measurement and Characterizations.** $^1$H and $^{13}$C NMR spectra were recorded with a Bruker Ultrashield 400 Plus NMR spectrometer. The UV-visible absorption spectra of these dyes were measured in CH$_2$Cl$_2$ solution with a Varian Cary 100 UV-Vis spectrophotometer. Emission spectra were performed using a Photon Technology International (PTI) Alphascan spectrofluorimeter. High-resolution matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF.
mass spectrometer. The cyclic voltammograms (CV) were measured with Versastat II electrochemical work station using a normal three-electrode cell with a Pt working electrode, a Pt wire counter electrode and a Ag/Ag⁺ reference electrode. The supporting electrolyte was 0.1 M tetra-n-butylammonium hexafluorophosphate in DCM solution. The potential of the reference electrode was calibrated by ferrocene after each set of measurements, and all potentials mentioned in the work were against normal hydrogen electrode.

**Fabrication and characterization of cells.** To make a reasonable comparison, all the anode films for the DSSC were made under the same standard manner, which are composed of 12 μm thick of transparent layer (TiO₂ with diameter of 20 nm) and 6 μm thick of scattering layer (TiO₂ nanoparticles with diameter of 200 nm). In specific, a doctor-blade technique was utilized to prepare photoanode (TiO₂) films. Firstly, a layer of ca. 6 μm TiO₂ paste (20 nm) was doctor-bladed onto the FTO conducting glass and then relaxed at room temperature for 3 min before heating at 150 °C for 6 min, this procedure was repeated once to achieve a film thickness of ca. 12 μm and the resulting surface was finally coated by a scattering layer (ca. 6 μm) of TiO₂ paste (200 nm). The electrodes were gradually heated under an air flow at 275 °C for 5 min, 325 °C for 5 min, 375 °C for 5 min, 470 °C for 30 min to remove polymers and generate three-dimensional TiO₂ nanoparticle network. After that, the sintered films were soaked with 0.02 M TiF₄ aqueous solution for 45 min at 70°C, washed with deionized water, and further annealed at 450 °C for 30 min. After cooling down to ca. 80°C, the electrodes were immersed into a 5 × 10⁻⁴ M dye bath in CH₂Cl₂ solution for TP-EEP dye series or in
acetonitrile/tert-butyl alcohol (volume ratio, 1:1) for N719 dye and maintained in the dark for 16 hrs. Afterwards, the electrodes were rinsed with ethanol to remove the non-adsorbed dyes and dried in air. Pt counter electrodes were prepared by sputtering method at 15 mA for 90 s at a power of 150 W. Two holes (0.75 mm in diameter) were pre-drilled in the FTO glass for introducing electrolyte. The dye-adsorbed TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt parafilm at about 100 °C. The liquid electrolyte consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I₂ in a mixture of acetonitrile and tert-butyl alcohol (volume ratio, 1:1) was introduced into the cell through the drilled holes at the back of the counter electrode. At last, the holes were sealed by parafilm and covering glass (0.1 mm thickness) at elevated temperature. The effective areas of all the TiO₂ electrodes were 0.24 cm². The current-voltage (J-V) characteristics of the assembled DSSCs were measured by a semiconductor characterization system (Keithley 236) at room temperature in air under the spectral output from solar simulator (Newport) using an AM 1.5G filter with a light power of 100 mW/cm². IPCEs of DSSCs were recorded in Solar Cell QE/IPCE Measurement System (Zolix Solar Cell Scan 100) using DC mode. CHI 660D electrochemical workstation was used to characterize the electrochemical properties of the DSSCs. Electrochemical impedance spectroscopy (EIS) was recorded under dark condition over a frequency range of 0.1-105 Hz with an AC amplitude of 10 mV and the parameters were calculated from Z-View software (v2.1b, Scribner Associates, Inc.). For the open-circuit voltage decay measurements, the cell was
first illuminated for 20 sec to a steady voltage, then the illumination was turned off for 80 sec and the open-circuit voltage decay curve was recorded.

4.5 References


18830.


Chapter 5 Simple 3D Bulky Organic Phenothiazine Dyes for Highly Efficient Co-Sensitized Solar cells

5.1 Introduction

Dye-sensitized solar cells (DSSCs) have been considered to be a promising alternative photovoltaic technology to the traditional costly inorganic silicon-based solar cells due to their cost-efficient fabrication and resource-unlimited.[1] A typical DSSCs includes three main ingredients: nanocrystalline semiconductor, redox electrolyte, and photosensitizer. Among the key components, the photosensitizer plays a vital role for improving the light conversion efficiency and the device stability in DSSCs. Up to date, DSSCs sensitized by ruthenium(II)-polypyridyl complexes have achieved high energy conversion efficiencies exceeding 11% measured at the AM 1.5G simulated sunlight.[2] Apart from the precious metal complexes, various D-π-A configured organic sensitizers featuring substituted triphenylamine,[3] indoline,[4] and phenothiazine[5] have been widely investigated and successfully applied in DSSCs owing to their low material costs, various structures and potential large-scale industrial application. However, the performances of DSSCs based on metal-free organic dyes are somewhat lower in comparison to the ruthenium(II) complexes-based sensitizers.[6-8] The major reasons are the relatively lower open-circuit photocurrent ($J_{sc}$) and photovoltage ($V_{oc}$) for DSSCs based on metal-free organic dyes. Therefore, there is still a need to further improve photovoltaic performances by structural-engineering of the metal-free organic
dyes. Aside from the electron donor and acceptor moieties in the general D-$\pi$-A structured organic sensitizers, the $\pi$-conjugated bridge between the donor and acceptor is of paramount importance in tuning the absorption spectral coverage, molecular energy levels and some dynamic processes such as dye regeneration and charge recombination. Thus, a large amount of versatile electron-rich thiophene and its derivatives based organic sensitizers have been developed with good performances.[9,10] In order to further boost the conversion efficiency, it is critical to improve the photocurrent ($J_{sc}$) and photovoltage ($V_{oc}$). And a strategic way of improving the $J_{sc}$ value is to introduce more planar $\pi$-conjugated segments between the donor and the acceptor, so that the organic dye can harvest more solar photos. Unfortunately, expansion of the length of the $\pi$-conjugated system often facilitate the recombination of the electrons to the I$_3^-$ ion and dye aggregation on TiO$_2$ films, resulting in a low $V_{oc}$.[11] The high $V_{oc}$ value can be increased by suppressing the charge recombination and dye aggregation. Incorporation of steric hindered groups in the organic sensitizer molecular structure is an effective way to slow the charge recombination rate and prevent dye aggregation. Tian et al. reported a series of starburst triphenylamine-based organic dyes, which showed a high $V_{oc}$ value by blocking charge recombination.[12] In our previous works, we have designed a series of simple non-planar phenothiazine-based dyes linked with different alkyl chain length as block groups for DSSCs, which displayed the high photocurrent and photovoltage as the results of slower charge recombination and weaker dye aggregation.[4d] In this chapter, we try to extend our works by using phenothiazine as a building block to construct 3D bulky organic dyes, in which
the cyanoacrylate acceptor directly attached to the C(3) position of phenothiazine, and the triphenylamine (TPA) donor group at C(7) on the opposite side of the acceptor, and different size of bulky substituents, i.e., hexyl, hexyloxybenzene, hexylcarbazole, and dihexylfluorene at N(10) of the phenothiazine periphery as the π-conjugated linker are presented (Figure. 5.1). We have systematically investigated the influence of 3D bulky substituents on the suppression of dye aggregation and charge recombination as well as photovoltaic performance of DSSCs. The molecular design strategy demonstrated that high $V_{oc}$ can be realized by employing 3D-phenothiazine dyes featuring with bulky substituents, such as hexylcarbazole and dihexylfluorene units. Impressively, the co-adsorbent-free DSSCs based on dye TP3 exhibits the photovoltaic performance with the best efficiency up to 8.00 % in combination with liquid electrolyte under standard global AM 1.5 solar light illumination. However, it is necessary to further improve the energy conversion efficiency of DSSCs to enable successful commercialization. To achieve this goal, the photosensitizer needs to capture broad absorption covering most of the visible to near-infrared (NIR) region of solar spectrum. Co-sensitized DSSCs using two and more dyes have been proved to be a successful strategy to extend the absorption into the red to NIR region. To further improve the PCE of TP3, we designed a stepwise approach for co-adsorption of the organic dye TP3 with a NIR dye YR6$^{[13]}$ for DSSCs. The co-sensitized TP3 + YR6 device showed significantly enhanced $J_{sc}$ relative to its individual single-dye sensitized devices. Upon optimization, the device made of the TP3 + YR6 system yielded $J_{sc} = 19.18$ mA cm$^{-2}$, $V_{oc} = 0.721$ V, FF = 0.712
and $\eta = 9.84\%$; The performance is superior to that of single-dye device made from either TP3 (8.00\%) or YR6 (2.16\%) under the same conditions of fabrication. The PCE of 9.84\% is the highest reported efficiency for a squaraine dye-based co-sensitized DSSCs.

![Figure 5.1. Structures of dyes TP1–TP4 and YR6.](image)

### 5.2 Results and Discussion

#### 5.2.1 Synthesis and Characterization

The structures of these new dyes TP1-TP4 are illustrated in Figure 5.1. The synthetic routes for these phenothiazine-based dyes are shown in Scheme 5.1. The bulky groups attached to the N(10) of phenothiazine group can improve the solubility, forming a tightly packed insulating monolayer blocking the $\Gamma^-$ or cations from approaching the TiO$_2$ and enhancing the open circuit voltage. The synthesis of TP1-TP4 were started from a commercially available phenothiazine precursor. The N-substitution of phenothiazine gave 1a-1d. Compound 2a-2d was obtained by the followed Vilsmeier reaction, in which the bromination of
2a-2d with N-bromosuccinimide (NBS) provided compound 3a-3d in good yield. The synthesis of TP1-TP4 dyes follow the previously reported strategy of the Suzuki cross coupling of (4-(diphenylamino)phenyl)boronic acid with 7-bromo-N-hexyl-10H-phenothiazine-3-carbaldehyde and its analogues, respectively, then followed by the widely employed Knoevenagel condensation with cyanoacetic acid to construct the target dyes. The chemical structures of these aldehyde intermediates and target dyes were fully characterized by their \(^1\)H NMR, \(^{13}\)C NMR and MALDI-TOF mass spectral data.

### 5.2.2 UV-Vis Absorption Properties

The UV-Vis absorption spectra of all dyes in CH\(_2\)Cl\(_2\) solutions are displayed in Figure 5.2, and the detailed spectroscopic data are summarized in Table 5.1. These dyes display two prominent distinct absorption bands, appearing at 300–400 nm and 400–600 nm. The shorter wavelengths are ascribed to the localized aromatic \(\pi-\pi^*\) electronic transitions of the chromophores, while the longer wavelengths are attributed to the intramolecular charge transfer (ICT) from the TPA donor to the cyanoacetic acid acceptor. The ICT peaks (\(\lambda_{\text{max}}\)) for TP1, TP2, TP3 and TP4 are located at 469, 485, 491 and 487 nm, respectively. By comparison with TP1, the ICT peaks of TP2, TP3 and TP4 are red-shifted by 16, 22, and 18 nm, respectively, indicating that the incorporation of stronger electron-donating groups onto the nitrogen atom of phenothiazine core can promote red-shifting in the absorption peaks, which is beneficial to harvest more solar photons. Also, the corresponding molar extinction coefficients of these dyes TP1–TP4 for the visible
absorption peaks are 2.17, 1.99, 2.28 and 1.89 × 10^4 M\(^{-1}\) cm\(^{-1}\), respectively. The results indicate that TP3 featuring with hexylcarbazole unit possesses excellent light-harvesting propety, which favors a higher photocurrent generation in DSSC. When these dyes are adsorbed onto nanocrystalline TiO\(_2\) surface, the absorption bands are located at 446, 490, 504 and 497 nm (Figure 5.3), respectively. The absorption band of TP1 displays a large blue-shift with respect to that in solution, which can be ascribed to the deprotonation of carboxylic acid, as well as to the formation of H-aggregation on the semiconductor surface for most organic dyes of this type.\(^{[5d, 11c]}\) Interestingly, the maximum absorption peaks and threshold of TP2, TP3 and TP4 exhibit little red-shifts relative to those in solutions, which demonstrate that the intermolecular \(\pi\)-stacked aggregations on TiO\(_2\) films may be effectively suppressed by the presence of these auxiliary large bulky substituents on the nitrogen atom of phenothiazine core.

![Absorption spectra](image)

**Figure 5.2.** Absorption spectra of these new dyes TP1–TP4 in CH\(_2\)Cl\(_2\) solutions.
5.2.3 Electrochemical Properties.

To study the possibilities of electron injection from the excited state of sensitizers into the conduction band (CB) of TiO$_2$ semiconductor and dye regeneration by redox electrolytes, the electrochemical behaviors of these dyes were measured by cyclic voltammetry in CH$_2$Cl$_2$ solutions (Figure 5.4). The oxidation potentials ($E_{ox}$) correspond to HOMOs, while the LUMOs are calculated from the values of $E_{ox}$ and the zero-zero band gaps ($E_{0-0}$) estimated from the onset of the UV-visible absorption spectra. The electrochemical data of the four dyes are listed in Table 5.1. The HOMO levels decrease slightly in the order of TP1 (0.70 V) > TP2 (0.68 V) > TP4 (0.66 V) > TP3 (0.60 V), which suggest that the introduction of electron-donating substituents on the nitrogen atom of phenothiazine core can lower the HOMO levels. The estimated HOMO levels of
the four dyes are sufficiently lower than the electrolyte iodide/tri-iodide redox potential value (0.4 V vs. NHE), thus ensuring the oxidized dyes could be efficiently regenerated by the electrolyte. On the other hand, the LUMO levels of all dyes are more negative than the conduction band edge (CB) of TiO$_2$ (−0.5 V vs. NHE), indicating that the electron injection from the excited dye molecules into the conduction band of TiO$_2$ is energetically permitted. Among them, TP3 gives the most negative LUMO value, meaning that TP3 is much easier to give electron than the other dyes, due to the strongest electron-donating ability of carbazole unit.

![Cyclic voltammograms of dyes TP1–TP4 in CH$_2$Cl$_2$ solution.](image)

**Figure. 5.4.** Cyclic voltammograms of dyes TP1–TP4 in CH$_2$Cl$_2$ solution.
Figure 5.5. Energy diagram of these dyes TP1–TP4.

Table 5.1. Absorption and electrochemical parameters for these new dyes TP1–TP4.

<table>
<thead>
<tr>
<th>dye</th>
<th>$\lambda_{\text{max}} (\varepsilon \times 10^4 \text{M}^{-1} \text{cm}^{-1})/\text{nm}$</th>
<th>$\lambda_{\text{max}}^b$/nm</th>
<th>$E_{\text{ox}}^c$/V</th>
<th>$E_{0-0}^d$/eV</th>
<th>$E_{\text{red}}^e$/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP1</td>
<td>469 (2.17)</td>
<td>446</td>
<td>0.70</td>
<td>2.21</td>
<td>-1.51</td>
</tr>
<tr>
<td>TP2</td>
<td>485 (1.99)</td>
<td>490</td>
<td>0.68</td>
<td>2.15</td>
<td>-1.47</td>
</tr>
<tr>
<td>TP3</td>
<td>491 (2.28)</td>
<td>504</td>
<td>0.60</td>
<td>2.14</td>
<td>-1.54</td>
</tr>
<tr>
<td>TP4</td>
<td>487 (1.89)</td>
<td>497</td>
<td>0.66</td>
<td>2.11</td>
<td>-1.45</td>
</tr>
</tbody>
</table>

[a] Absorption maximum in $1\times10^{-5}$ mol L$^{-1}$ CH$_2$Cl$_2$ solution. [b] Absorption maximum on TiO$_2$ film. [c] Oxidation potential in CH$_2$Cl$_2$ solution containing 0.1 M $(n$-$C_4H_9)_4$NPF$_6$ with a scan rate of 100 mV s$^{-1}$ (vs. NHE). [d] $E_{0-0}$ was determined from the onset of absorption spectrum. [e] $E_{\text{red}} = E_{\text{ox}} - E_{0-0}$
5.2.4 Theoretical Calculation.

To understand the electronic distribution in the frontier molecular orbitals and electronic processes upon photoexcitation, the density functional theory (DFT) calculations were performed using Gaussian 03 program package at the B3LYP/6-31 G(d)* hybrid functional for full geometrical optimization (Figure 5.6).

<table>
<thead>
<tr>
<th>Dye</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP1</td>
<td><img src="image1" alt="HOMO" /></td>
<td><img src="image2" alt="LUMO" /></td>
</tr>
<tr>
<td>TP2</td>
<td><img src="image3" alt="HOMO" /></td>
<td><img src="image4" alt="LUMO" /></td>
</tr>
<tr>
<td>TP3</td>
<td><img src="image5" alt="HOMO" /></td>
<td><img src="image6" alt="LUMO" /></td>
</tr>
<tr>
<td>TP4</td>
<td><img src="image7" alt="HOMO" /></td>
<td><img src="image8" alt="LUMO" /></td>
</tr>
</tbody>
</table>

**Figure 5.6.** Calculated frontier orbitals of these dyes TP1–TP4.
The electron density distribution of the HOMO orbitals of TP1–TP4 are delocalized throughout the entire molecular sensitizers from the donor to the cyanoacrylic acid acceptor, while, the electron density distribution of the LUMO orbitals of all dyes are primarily located over the cyanoacrylic acid segment and partly on the phenothiazine core. Hence, the well-overlapped HOMO and LUMO orbitals on the phenothiazine core guarantee a fast charge transition between donor and acceptor. Thus, excitation from the HOMO to the LUMO should lead to efficient photoinduced electron transfer from the electron donating triphenylamine moiety to the terminal cyanoacrylic acid, and finally into the conduction band of TiO$_2$.

In the optimized ground-state geometries shown in Figure 5.7, the dihedral angles formed between the different size of bulky substituents (hexyl, hexyloxybenzene, hexylcarbazole, and dihexylfluorene) at N(10) of the phenothiazine periphery and the phenothiazine core are computed to 90° for TP1–TP4. Obviously, the whole molecular skeleton of the four dyes show out-of-plane twist conformation. Thus, the 3D twisted structure of these dyes is favorable for suppressing dye aggregation, charge recombination, and back-electron transfer.
5.2.5 Photovoltaic Performance.

The action spectra of incident photon-current conversion efficiencies (IPCEs) for DSSCs based on these dyes are plotted in Figure 5.8. The IPCEs of the four dyes display broad bands in the region of 300–650 nm with values mostly > 60 to 70%. It is worth noting that the IPCE spectra of the cells based on these dyes show obvious red-shifts to longer wavelength, which is conducive to improve the photovoltaic performance of DSSCs. The aforementioned results further demonstrate that the 3D constructed organic dyes can effectively broaden the

\[\text{Figure 5.7. The optimized ground-state geometries of these dyes TP1–TP4.}\]
visible absorption spectrum to get good IPCE, leading to significant performance enhancement of the DSSCs.

**Figure 5.8.** IPCE action spectra of DSSCs sensitized by dyes TP1–TP4.

The performance parameters of DSSCs fabricated with these dyes, i.e., short-circuit current density ($J_{sc}$), open-circuit photovoltage ($V_{oc}$), fill factor (FF), and total power conversion efficiency ($\eta$), measured under AM 1.5 solar light (100 mW cm$^{-2}$) are summarized in Table 5.2, and the photocurrent–voltage ($J$–$V$) plots are shown in Figure 5.9. All of them show favorable photovoltaic responses and exhibit relatively high PCE. Among these dyes, the DSSCs based on TP3 exhibits the best photovoltaic performance with $J_{sc} = 14.06$ mA cm$^{-2}$, $V_{oc} = 0.791$ V, FF = 0.719, corresponding to the PCE of 8.00%. Under the same conditions, other cells sensitized with the dyes TP1, TP2 and TP4 also showed attractive performances with $J_{sc}$ of 14.87, 14.21 and 12.68 mA cm$^{-2}$, $V_{oc}$ of 0.778, 0.790 and 0.801 V, and FF of 0.666, 0.686 and 0.693, corresponding to the $\eta$ values of 7.71%, 7.70% and
7.05%, respectively. Though the four sensitizers have the similar chemical structures, their photovoltaic performances behave somewhat different. The four sensitizers give the relatively high $V_{oc}$ values, in the range of 0.778-0.801 V. Compared to TP1, 3D structured TP2, TP3 and TP4 show higher $V_{oc}$ value, which should be attributed to the suppression of the charge recombination at the TiO$_2$/dye/electrolyte interface by incorporating the 3D bulky conjugated substituents on the N-atom of phenothiazine core.$^{[14]}$ The results illustrate that the introduction of the bulky substituents in π-conjugated spacer on the orthogonal direction could suppress dye aggregation and retard charge recombination in DSSCs more effectively than the linear alkyl chain.

![Graph showing photocurrent density vs. voltage for TP1–TP4](image)

**Figure 5.9.** $J - V$ curves for DSSCs sensitized by dyes TP1–TP4.
Table 5.2. Photovoltaic Parameters of DSSCs under Full Sunlight Illumination (AM 1.5G, 100 mW cm⁻²) 

<table>
<thead>
<tr>
<th>dye</th>
<th>( J_{sc}/\text{mA cm}^{-2} )</th>
<th>( V_{oc}/\text{V} )</th>
<th>FF</th>
<th>( \eta/% )</th>
<th>( R_{rec}/\Omega \text{ cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP1</td>
<td>14.87</td>
<td>0.778</td>
<td>0.666</td>
<td>7.71</td>
<td>695.43</td>
</tr>
<tr>
<td>TP2</td>
<td>14.21</td>
<td>0.790</td>
<td>0.686</td>
<td>7.70</td>
<td>710.37</td>
</tr>
<tr>
<td>TP3</td>
<td>14.06</td>
<td>0.791</td>
<td>0.719</td>
<td>8.00</td>
<td>914.63</td>
</tr>
<tr>
<td>TP4</td>
<td>12.68</td>
<td>0.801</td>
<td>0.693</td>
<td>7.05</td>
<td>984.75</td>
</tr>
</tbody>
</table>

[a] Performance of DSSCs measured in a 0.24 cm² working area on a FTO substrate at room temperature. Dyes were maintained at 0.5 mM in acetonitrile/tert-butyl alcohol (volume ratio, 1:1) for TPn dyes. Electrolyte: LiI (0.05 M), I₂ (0.1 M), and DMPII (0.6 M) in acetonitrile/tert-butyl alcohol (1:1, v/v).

5.2.6 Electrochemical Impedance Spectroscopy (EIS)

The generation of \( V_{oc} \) is related to the charge recombination rate in DSSC. Electrochemical impedance spectroscopy (EIS) was performed to analyse the interfacial charge recombination and carrier transportation process in DSSCs based on these dyes in the dark under a forward of ~0.70 V with a frequency range of 0.1 Hz to 100 kHz. The interfacial charge recombination reaction of electron with the \( \text{I}_3^- \) ions can be described by a charge recombination resistance \( (R_{rec}) \). As shown in Figure 5.10, a major intermediate semicircle is observed for each dye in the EIS Nyquist plots, which is regarded as the charge recombination resistance on the TiO₂/dye/electrolyte interface \( (R_{rec}) \). The calculated resistance
values ($R_{rec}$) using Z-view software are listed in Table 5.2, and a smaller $R_{rec}$ value means a larger charge recombination rate.\textsuperscript{[5d]} It is clear that the $R_{rec}$ values are in the order of TP4 (984.75\,$\Omega$) $>$ TP3 (914.63\,$\Omega$) $>$ TP2 (710.37\,$\Omega$) $>$ TP1 (695.43). The larger $R_{rec}$ value implies a less facile injected charge recombination with I$_3^-$ in the electrolyte and this can be reflected by the high photocurrent or photovoltage values. The results are well consistent with the observed order of the photovoltage ($V_{oc}$) values of the cells based on these dyes TP1–TP4, suggesting the same order of enhanced charge recombination rate. Nishida et al. proposed that attaching of unit with steric hindrance to the $\pi$-conjugation spacer can increase the intermolecular distance between the $\pi$-linker and acceptor species (I$_3^-$ or I$_2$) in electrolytes, causing long electron lifetime and thus high $V_{oc}$.\textsuperscript{[16]} Compared to TP1, TP2–TP4 with twisted 3-dimensional structure could be more efficient to reduce the charge recombination with acceptor species at the titania/electrolyte interface. In particular, the TP4 shows the highest $V_{oc}$ of 0.801 V, proving that the dihexylfluorene unit is the most effective to retard the charge recombination.

![Figure 5.10. EIS Nyquist plots for DSSCs based on the new dyes TP1–TP4.](image)
5.2.7 Photophysical, Photocurrent–Voltage Characteristics of Cosensitized DSSCs

Despite the promising results obtained in the single dye based DSSCs, a key drawback of the TP1–TP4 dye is the limited light absorption response in the near-infrared region (NIR), leading to lower $J_{sc}$ values compared to the ruthenium complex N719. It’s still a challenge for a small molecule sensitizer to realize a broad absorption extending to NIR region of the solar spectrum. In order to realize a panchromatic absorption in DSSC, the reported NIR dye YR6 was selected to co-sensitize with TP3 to enhance the light harvesting efficiency in DSSC. The structure of YR6 is shown in Figure 5.1. The absorption spectra of TP3, YR6, and the co-adsorption of the two dyes on TiO$_2$ films are shown in Figure 5.11. Dye TP3 has a strong absorption in the range of 400–650 nm, and YR6 shows intense absorption in the region of 600–750 nm. A sequential dye soaking approach was applied to adsorb two types of dyes and the film displayed an enhancement of light absorption in a fairly broad region (400-750 nm) when compared with the individually sensitized film by either TP3 or YR6.
Figure 5.11. Absorption spectra of TP3, YR6 and co-adsorption on TiO$_2$ films.

The IPCE spectra of devices sensitized by TP3, YR6 and co-sensitization were plotted as a function of excitation wavelength and presented in Figure 5.12. From the experiments, it was found that the IPCE of the co-sensitized devices depended greatly on the ratio of the two dye in solutions. The largest increase in the IPCE region was observed in the co-sensitized device 4 at the TP3/YR6 molar ratio of 25:1. The IPCE spectrum of the device 4 exhibits an impressive panchromatic response from 300 to 750 nm.
**Figure 5.12.** IPCE spectra of DSSCs sensitized by TP3, YR6 and co-sensitization of the two dyes.

**Figure 5.13.** $J$–$V$ curves of DSSCs sensitized by TP3, YR6 and the co-sensitization of the two dyes.
The $J-V$ curves of solar cells with TP3, YR6 and co-sensitization of the two dyes are shown in Figure 5.13. The corresponding photovoltaic parameters of these solar cells are presented in Table 5.3. The PCE (at AM 1.5G illumination) of the devices based on individual TP3 and YR6 are 8.00 and 2.16 %, respectively. Importantly, the co-sensitized solar cell shows much higher photocurrent and efficiency than those of the individual dye-sensitized cells. The optimized cell gives a short circuit current density of 19.18 mA cm$^{-2}$, an open circuit voltage of 0.721 V and a fill factor of 0.712, corresponding to an overall conversion efficiency of 9.84% under solar simulated light irradiation. These results show a superior photovoltaic performance for the co-sensitization of two organic dyes compared to that of the individual dye-sensitized solar cells.
Table 5.3. Photovoltaic performances of DSSCs sensitized by TP3, YR6 and the co-sensitization of the two dyes.

<table>
<thead>
<tr>
<th>Device</th>
<th>Dye-loading strategy</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP3</td>
<td>0.5 mM</td>
<td>14.06</td>
<td>0.791</td>
<td>0.719</td>
<td>8.00</td>
</tr>
<tr>
<td>YR6</td>
<td>0.1 mM</td>
<td>6.47</td>
<td>0.572</td>
<td>0.584</td>
<td>2.16</td>
</tr>
<tr>
<td>1</td>
<td>TP3/YR6(500:1)</td>
<td>15.12</td>
<td>0.780</td>
<td>0.728</td>
<td>8.58</td>
</tr>
<tr>
<td>2</td>
<td>TP3/YR6(100:1)</td>
<td>16.31</td>
<td>0.771</td>
<td>0.729</td>
<td>9.17</td>
</tr>
<tr>
<td>3</td>
<td>TP3/YR6(50:1)</td>
<td>17.27</td>
<td>0.743</td>
<td>0.723</td>
<td>9.28</td>
</tr>
<tr>
<td>4</td>
<td>TP3/YR6(25:1)</td>
<td>19.18</td>
<td>0.721</td>
<td>0.712</td>
<td>9.84</td>
</tr>
<tr>
<td>5</td>
<td>TP3/YR6(10:1)</td>
<td>16.63</td>
<td>0.741</td>
<td>0.699</td>
<td>8.82</td>
</tr>
</tbody>
</table>

Performance of DSSCs measured in a 0.24 cm² working area on a FTO (8Ω/square) substrate at room temperature. TP3 (0.5 mM) and YR6 (0.1 mM) were maintained in acetonitrile:tert-butyl alcohol solution (volume ratio, 1:1). Electrolyte: LiI (0.05 M), I₂ (0.1 M), and DMPII (0.6 M) in acetonitrile/tert-butyl alcohol (1:1, v/v).

5.3 Conclusions

In summary, we have successfully synthesized a series of new 3D bulky organic sensitizers by exploiting the phenothiazine as π-conjugated linker, in which the cyanoacrylate acceptor directly attached to the C(3) position, TPA donor group at C(7) on the opposite side of the acceptor, and different size bulky substituents, i.e., hexyl, hexyloxybenzene, hexylcarbazole, and dihexylfluorene at N(10) of the phenothiazine periphery. By comparison with TP1, the twisted
3-dimensional bulky structure make the three sensitizers (TP2–TP4) exhibit somewhat bathochromic shifts on TiO₂ films, and suppress dye aggregation and charge recombination, corresponding to better photovoltaic performance in DSSCs. Impressively, the coadsorbent-free DSSCs based on dye TP3 exhibits the best efficiency up to 8.00% in combination with liquid electrolyte under standard global AM 1.5 solar light illumination. To further improve the PCE of TP3, we designed a stepwise approach for co-sensitization of the organic dye TP3 with the NIR dye YR6 for dye-sensitized solar cells. Highly efficient co-sensitized DSSC with a conversion efficiency up to 9.84% has been achieved. To our knowledge, the PCE of 9.84% is the highest reported efficiency for a squaraine dye-based co-sensitized DSSCs. These findings will facilitate our understanding of the crucial importance of molecular engineering and shed light on optimizing phenothiazine-based metal-free organic dyes for highly efficient DSSCs.

5.4 Experimental Section

Materials and Reagents. All solvents and reagents were purchased from Sigma-Aldrich Company and used as received without further purification. The starting material phenothiazine and 2-cyanoacetic acid were purchased commercially. TiO₂ paste and iodide-based liquid electrolyte (HL-HPE) were purchased from Dyesol company. The intermediates 1a-1d, 2a-2d, and 3a-3d were synthesized according to the corresponding literature methods. The reported dye YR6 was synthesized by the literature methods. The synthetic routes of phenothiazine-based dyes TP1-TP4 are outlined in Scheme 5.1 and the
details are depicted as follows.

![Scheme 5.1](image)

**Scheme 5.1.** Synthetic routes for these dyes TP1–TP4. (a) KOH, RBr, DMSO, rt; (b) Cu, K₂CO₃, 18-crown-6, RBr, o-dichlorobenzene, reflux; (c) DMF, POCl₃, ClCH₂CH₂Cl, reflux; (d) NBS, THF, 0°C; (e) Pd(PPh₃)₄, 4-(diphenylamino)phenylboronic acid, 2N K₂CO₃, THF, reflux; (f) cyanoacetic acid, CH₃COOH, CH₃COONH₄, 120°C.

**10-hexyl-10H-phenothiazine (1a)**

Phenothiazine (5.0 g, 25.1 mmol) and 1-bromohexane (8.7 g, 26 mmol) were dissolved in 50 mL DMSO and stirred for 30 min at room temperature. Potassium hydroxide (2.8 g, 50 mmol) was slowly added and stirred for overnight at room temperature. The reaction mixture was poured into water and extracted with chloroform. The organic layer was separated and dried with anhydrous magnesium sulfate. The product was purified using column chromatography with hexane as the solvent. The product was obtained as light yellow oil. Yield: 6.0 g
(85%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.118–7.148 (m, 4H), 6.828–6.855 (m, 4H), 3.340 (t, $J = 6.9$ Hz, 2H), 1.741–1.869 (m, 2H), 1.255–1.426 (m, 6H), 0.867 (t, $J = 5.1$ Hz, 3H). HRMS (MALDI-TOF, m/z): [M$^+$] calcd for (C$_{18}$H$_{21}$NS) 283.1445; found, 283.1456.

**General procedures for the preparation of compounds 1b-1d.**

A mixture of 10H-phenothiazine (2.0 g, 10 mmol), 1-(hexyloxy)-4-iodobenzene (or 9-hexyl-3-iodo-9H-carbazole or 9,9-dihexyl-2-iodo-9H-fluorene) (11 mmol), K$_2$CO$_3$ (1.7 g, 12.5 mmol), copper powder (0.4 g, 6.2 mmol) and 18-crown-6 (0.08 g, 0.3 mmol) in o-dichlorobenzene (20 mL) was heated to reflux overnight under a N$_2$ atmosphere. Then, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 4:1 mixture of hexane and CH$_2$Cl$_2$ as eluent to afford the products as white solid.

**10-(4-(hexyloxy)phenyl)-10H-phenothiazine (1b) Yield: 2.43g, (65%).** $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.30 (t, $J = 2.8$ Hz, 1H), 7.28 (t, $J = 2.8$ Hz, 1H), 7.10 (t, $J = 2.8$ Hz, 1H), 7.08 (t, $J = 2.8$ Hz, 1H), 6.99 (d, $J = 1.6$ Hz, 1H), 6.97 (d, $J = 1.6$ Hz, 1H), 6.76-6.85 (m, 4H), 4.03 (t, $J = 1.6$ Hz, 2H), 1.82-1.86 (m, 2H), 1.40-1.53 (m, 2H), 1.36–1.39 (m, 4H), 0.86 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 158.87, 144.70, 132.21, 126.81, 126.59, 122.21, 119.62, 116.37, 115.65, 68.34, 31.62, 29.27, 25.79, 22.64, 14.07. HRMS (MALDI-TOF, m/z): [M$^+$] calcd for (C$_{24}$H$_{25}$NOS) 375.1717; found, 375.1720.

**10-(9-hexyl-9H-carbazol-2-yl)-10H-phenothiazine (1c) Yield: 2.77g, (62%).** $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.25 (s, 1H), 8.21 (d, $J = 8.0$ Hz, 2H), 7.88 (t, $J = 8.0$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 2H), 7.45-7.50 (m, 2H),
7.17 (t, $J = 8.0$ Hz, 2H), 6.77-6.85 (m, 4H), 4.44 (t, $J = 7.2$ Hz, 2H), 1.74–1.86 (m, 2H), 1.24–1.25 (m, 6H), 0.82 (t, $J = 7.2$ Hz, 3H) ppm. $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta = 146.43, 140.55, 139.01, 132.66, 131.44, 130.09, 129.08, 128.98, 127.10, 126.24, 126.00, 125.33, 124.55, 122.89, 121.84, 119.09, 114.66, 111.40, 43.34, 31.95, 28.50, 26.14, 22.09, 13.87 ppm.

HRMS (MALDI-TOF, m/z): [M$^+$] calcd for (C$_{30}$H$_{28}$N$_2$S) 448.2067; found, 448.2069.

10-(9,9-dihexyl-9H-fluoren-2-yl)-10H-phenothiazine (1d)

Yield: 3.77g, (71%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.12$ (s, 1H), 7.90-7.94 (m, 1H), 7.67 (d, $J = 8.0$ Hz, 2H), 7.18-7.22 (m, 4H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.86-6.97 (m, 4H), 6.76 (s, 1H), 3.45 (t, $J = 8.8$ Hz, 4H), 1.45–1.47 (m, 4H), 1.28–1.37 (m, 12H), 0.88 (t, $J = 8.8$ Hz, 6H) ppm. $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta = 154.76, 150.35, 142.77, 136.77, 135.89, 133.45, 131.96, 130.51, 127.65, 127.59, 125.27, 124.73, 123.90, 123.23, 115.92, 115.86, 114.95, 93.5, 65.78, 48.16, 31.39, 26.71, 26.52, 22.60, 14.00 ppm. HRMS (MALDI-TOF, m/z): [M$^+$] calcd for (C$_{37}$H$_{41}$NS) 531.3087; found, 531.3090.

**General procedures for the preparation of 2a-2d.**

1a-1d (10mmol) and dry DMF (0.73g, 10mmol) was dissolved in 1,2-dichloroethane (20mL), then phosphorous oxychloride (1.54g, 10mmol) was added slowly at 0 $^\circ$C in an ice water bath. The mixture was heated to reflux for overnight was and quenched with water and extracted three times with chloroform. The combined organic fraction was washed with brine and dried over MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography using silica gel and n-hexane/ethylacetate (8/2; v/v) as
the eluent to give yellow solids, respectively.

10-hexyl-10H-phenothiazine-3-carbaldehyde (2a)

Yield: 1.71 g (55%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.78 (s, 1H), 7.63 (d, $J$ = 8.0 Hz, 1H), 7.56 (s, 1H), 7.11 (t, $J$ = 8.0 Hz, 1H), 7.10 (d, $J$ = 8.0 Hz, 1H), 6.95 (d, $J$ = 8.0 Hz, 1H), 6.86 (t, $J$ = 8.0 Hz, 1H), 3.87 (t, $J$ = 6.4 Hz, 2H), 1.27–1.32 (m, 6H), 0.85 (t, $J$ = 6.4 Hz, 3H). HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{19}$H$_{21}$NOS) 311.1355; found, 311.1366.

10-(4-(hexyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (2b)

Yield: 1.82 g, (70%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.80 (s, 1H), 7.33 (t, $J$ = 8.0 Hz, 1H), 7.30 (t, $J$ = 8.0 Hz, 1H), 7.25 (t, $J$ = 8.0 Hz, 1H), 7.13 (t, $J$ = 8.0 Hz, 1H), 7.01 (d, $J$ = 8.0 Hz, 1H), 6.97 (d, $J$ = 8.0 Hz, 2H), 6.67–6.78 (m, 4H), 4.13 (t, $J$ = 7.2 Hz, 2H), 1.83–1.86 (m, 2H), 1.42–1.56 (m, 2H), 1.34–1.38 (m, 4H), 0.88 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 188.98, 162.87, 145.75, 134.21, 129.38, 127.81, 126.57, 122.27, 119.68, 116.77, 115.69, 68.64, 30.45, 29.28, 25.77, 22.66, 14.03. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{25}$H$_{33}$NO$_2$S) 403.1677; found, 403.1686.

10-(9-hexyl-9H-carbazol-2-yl)-10H-phenothiazine-3-carbaldehyde (2c)

Yield: 1.67 g, (56%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.85 (s, 1H), 8.17 (d, $J$ = 8.0 Hz, 1H), 8.09 (d, $J$ = 8.0 Hz, 1H), 7.84 (d, $J$ = 8.0 Hz, 2H), 7.65 (s, 1H), 7.45–7.48 (m, 2H), 7.29–7.31 (m, 2H), 7.16 (d, $J$ = 8.0 Hz, 1H), 6.77–6.85 (m, 4H), 4.47 (t, $J$ = 7.2 Hz, 2H), 1.79–1.85 (m, 2H), 1.26–1.28 (m, 6H), 0.82 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 187.89, 144.41, 140.53, 139.21, 130.96, 127.98, 127.14, 126.38, 126.30, 122.54, 121.82, 120.88, 119.03, 118.40,
187
115.68, 111.40, 19.55, 42.38, 30.94, 28.55, 26.16, 22.03, 13.83. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{31}H_{28}N_{2}O_{5}S) 476.1984; found, 476.1986.

10-(9,9-dihexyl-9H-fluoren-2-yl)-10H-phenothiazine-3-carbaldehyde (2d)

Yield: 1.83 g, (67%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) (ppm) 9.87 (s, 1H), 7.87 (d, \( J = 6.4 \) Hz, 1H), 7.55 (d, \( J = 6.4 \) Hz, 2H), 7.47 (s, 1H), 7.39-7.43 (m, 2H), 7.32-7.38 (m, 2H), 7.28 (t, \( J = 6.4 \) Hz, 2H), 6.83-6.90 (m, 2H), 6.27-6.29 (m, 2H), 4.35 (t, \( J = 7.6 \) Hz, 4H), 1.94-1.99 (m, 4H), 1.37-1.41 (m, 4H), 1.32-1.35 (m, 8H) 0.87-0.89 (t, \( J = 5.2 \) Hz, 6H). \textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) (ppm) 188.04, 154.39, 148.65, 143.47, 141.23, 139.97, 132.18, 131.31, 129.86, 128.89, 127.15, 126.78, 125.13, 124.56, 123.86, 122.29, 121.43, 120.11, 119.58, 118.89, 117.93, 115.96, 110.96, 109.23, 92.38, 44.48, 31.98, 29.03, 27.65, 22.76, 14.03. HRMS (MALDI-TOF, m/z): [M'] calcd for (C_{38}H_{41}N_{5}O_{5}S) 559.2912; found, 559.2916.

General procedures for the preparation of 3a-3d.

NBS (411 mg, 2.31 mmol) was added in one portion to the solution of 2a-2d (2.0 mmol) in THF (50 mL) at 0 °C. The mixture was allowed to warm to room temperature and continued the stirring for 1.5 h. Then the reaction was quenched by addition of water (50 mL), and extracted with DCM. The collected organic layer was evaporated under vacuum and the residue was purified by column chromatography on silica gel with CH\textsubscript{2}Cl\textsubscript{2} as eluent to give the products as yellow solid.

7-bromo-10-hexyl-10H-phenothiazine-3-carbaldehyde (3a)

Yield: 700 mg, (90%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) (ppm) 9.80 (s, 1H), 7.64 (d, \( J = 8.0 \) Hz, 1H), 7.13 (t, \( J = 8.0 \) Hz, 1H), 7.10 (d, \( J = 8.0 \) Hz, 1H), 6.91 (d, \( J = 8.0 \) Hz, 1H).
Hz, 1H), 6.85 (t, J = 8.0 Hz, 1H), 3.89 (t, J = 6.4 Hz, 2H), 1.78-1.90 (m, 2H), 1.28–1.32 (m, 6H), 0.86 (t, J = 6.4 Hz, 3H). 13C NMR (400 MHz, CDCl3): δ (ppm) 189.91, 150.32, 142.63, 131.33, 130.35, 130.12, 129.38, 128.54, 126.61, 124.44, 117.41, 115.48, 115.20, 48.10, 31.43, 26.56, 26.64, 22.36, 14.01. HRMS (MALDI-TOF, m/z): [M+] calcd for (C19H20BrNOS) 389.0413; found, 389.0422.

7-bromo-10-(4-(hexyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (3b)

Yield: 580 mg, (89%). 1H NMR (400 MHz, CDCl3): δ (ppm) 9.69 (s, 1H), 7.27-7.29 (m, 1H), 7.21-7.23 (m, 2H), 7.10-7.14 (m, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.88-6.91 (m, 1H), 6.18 (d, J = 8.0 Hz, 1H), 5.99 (d, J = 8.0 Hz, 1H), 4.03 (t, J = 6.4 Hz, 2H), 1.78-1.84 (m, 2H), 1.50-1.61 (m, 2H), 1.36-1.38 (m, 4H), 0.93 (t, J = 6.4 Hz, 3H). 13C NMR (400 MHz, CDCl3): δ (ppm) 189.65, 159.45, 149.13, 142.19, 131.69, 131.45, 131.13, 130.09, 129.75, 128.75, 127.49, 121.20, 119.31, 117.61, 116.48, 115.70, 115.20, 68.45, 31.60, 29.21, 25.77, 22.63, 14.06. HRMS (MALDI-TOF, m/z): [M+] calcd for (C25H28BrNO2S) 481.0713; found, 481.0721.

7-bromo-10-(9-hexyl-9H-carbazol-3-yl)-10H-phenothiazine-3-carbaldehyde (3c)

Yield: 500 mg, (87%). 1H NMR (400 MHz, CDCl3): δ (ppm) 9.68 (s, 1H), 8.05-8.07 (m, 2H), 7.62-7.65 (m, 2H), 7.48-7.54 (m, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.35-7.38 (m, 2H), 7.29 (d, J = 7.2 Hz, 1H), 7.22-7.25 (m, 1H), 6.83-6.86 (m, 1H), 4.38 (t, J = 6.4 Hz, 2H), 1.91-1.97 (m, 2H), 1.41-1.49 (m, 2H), 1.28–1.37 (m, 4H), 0.94 (t, J = 6.4 Hz, 3H). 13C NMR (400 MHz, CDCl3): δ (ppm) 189.65, 149.54, 142.60, 142.48, 141.06, 139.94, 131.08, 131.00, 130.39, 130.14, 129.70, 129.43, 128.71, 128.62, 127.36, 126.74, 124.80, 122.25, 121.16, 115.60, 115.45, 115.40,
111.36, 111.06, 109.27, 43.50, 31.63, 29.05, 27.07, 22.62, 14.08. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₃₁H₂₇BrN₂O₅S) 554.1012; found, 554.1025.

**7-bromo-10-(9,9-dihexyl-9H-fluoren-2-yl)-10H-phenothiazine-3-carbaldehyde (3d)**

Yield: 460 mg, (91%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.69 (s, 1H), 7.94 (d, J = 6.4 Hz, 1H), 7.76-7.78 (m, 1H), 7.46 (d, J = 6.4 Hz, 1H), 7.39-7.40 (m, 3H), 7.29-7.31 (m, 2H), 7.24-7.28 (m, 2H), 7.09 (d, J = 7.2 Hz, 1H), 6.85-6.88 (m, 2H), 2.01 (t, J = 6.4 Hz, 4H), 1.31-1.37 (m, 4H), 1.17-1.25 (m, 4H), 0.78 (t, J = 6.4 Hz, 6H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 189.67, 148.56, 143.61, 141.43, 141.02, 139.95, 131.01, 131.00, 130.27, 130.15, 129.76, 129.41, 128.73, 128.34, 127.37, 126.75, 124.90, 123.23, 121.16, 115.61, 115.40, 114.40, 112.36, 111.15, 109.29, 65.78, 43.51, 31.77, 29.01, 27.08, 22.34, 14.00. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₃₈H₄₀BrN₂O₅S) 637.2011; found, 637.1921.

**General procedures for the preparation of 4a-4d.**

A mixture of 3a-3d (0.30 mmol), (4-(diphenylamino)phenyl)boronic acid (115 mg, 0.40 mmol), Pd(PPh₃)₄ (25 mg, 0.04 mmol) and 2N aqueous solution of K₂CO₃ (2 mL) in THF (10 mL) was heated to reflux under a N₂ atmosphere for about 12 hrs. Then, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 1:4 mixture of hexane and CH₂Cl₂ as eluent to afford 4a–4d as red solids, respectively.

**7-(4-(diphenylamino)phenyl)-10-hexyl-10H-phenothiazine-3-carbaldehyde (4a)**

Yield: 120 mg, (71%). ¹H NMR (400 MHz, CDCl₃):
δ (ppm) 9.65 (s, 1H), 7.90-7.93 (m, 1H), 7.79 (d, J = 2.0 Hz, 1H), 7.56 (d, J = 2.0 Hz, 2H), 7.41-7.46 (m, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.32 (t, J = 7.6 Hz, 4H), 7.11 (d, J = 7.6 Hz, 1H), 6.87-6.94 (m, 10H), 3.94 (t, J = 6.8 Hz, 4H), 1.67-1.70 (m, 2H), 1.34-1.40 (m, 2H), 1.24-1.26 (m, 4H), 0.84 (t, J = 6.8 Hz, 3H). 13C NMR (400 MHz, CDCl3): δ (ppm) 189.77, 148.40, 146.88, 141.12, 134.95, 132.43, 130.09, 129.51, 129.00, 128.02, 125.44, 124.19, 123.88, 123.13, 122.98, 122.65, 122.54, 116.88, 116.23, 115.45, 99.60, 46.94, 30.69, 26.01, 25.68, 22.06, 14.01. HRMS (MALDI-TOF, m/z): [M+] calcd for (C37H34N2S) 554.2419; found, 554.2422.

7-(4-(diphenylamino)phenyl)-10-(4-(hexyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (4b)

Yield: 100 mg, (68%). 1H NMR (400 MHz, CDCl3): δ (ppm) 9.67 (s, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.22-7.25 (m, 2H), 7.18-7.22 (m, 7H), 7.07-7.11 (m, 2H), 6.99-7.06 (m, 6H), 6.95-6.97 (m, 2H), 6.10-6.13 (m, 2H), 3.97 (t, J = 7.6 Hz, 2H), 1.75-1.79 (m, 2H), 1.44-1.50 (m, 2H), 1.20-1.31 (m, 4H), 0.84 (t, J = 4.0 Hz, 3H). 13C NMR (400 MHz, CDCl3): δ (ppm) 189.75, 159.33, 149.36, 147.60, 141.61, 136.18, 133.27, 132.06, 131.60, 130.86, 129.98, 129.30, 128.83, 127.50, 126.99, 126.37, 125.09, 124.53, 124.46, 123.81, 123.01, 119.73, 119.33, 116.76, 115.00, 68.44, 31.61, 29.24, 25.79, 22.64, 14.08. HRMS (MALDI-TOF, m/z): [M+] calcd for (C43H38N2O2S) 646.2712; found, 646.2713.

7-(4-(diphenylamino)phenyl)-10-(9-hexyl-9H-carbazol-3-yl)-10H-phenothiazine-3-carbaldehyde (4c)

Yield: 112 mg, (66%). 1H NMR (400 MHz, CDCl3): δ (ppm) 9.68 (s, 1H),
7.61-7.68 (m, 1H), 7.50 (d, J = 8.8 Hz, 2H), 7.33-7.45 (m, 5H), 7.27-7.29 (m, 2H),
7.16-7.20 (m, 12H), 7.00-7.14 (m, 2H), 6.22-6.24 (m, 2H), 4.39 (t, J = 6.0 Hz,
2H), 1.81-1.87 (m, 2H), 1.33-1.40 (m, 2H), 1.20-1.26 (m, 4H), 0.84 (t, J = 6.8 Hz,
3H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 189.78, 159.97, 148.66, 146.14,
146.09, 145.89, 141.88, 141.25, 140.77, 139.95, 139.23, 134.98, 132.28, 131.34,
129.78, 127.99, 127.55, 127.10, 126.67, 125.09, 124.13, 124.00, 123.93, 123.75,
123.28, 123.10, 122.78, 122.47, 119.20, 118.40, 118.12, 116.12, 115.52, 30.95,
30.68, 28.57, 26.16, 22.13, 14.02. HRMS (MALDI-TOF, m/z): [M+] calcd for
(C$_{49}$H$_{41}$N$_3$O$_5$) 719.3017; found, 719.3025.

10-(9,9-diheyl-9H-fluoren-2-yl)-7-(4-(diphenylamino)phenyl)-10H-phenothia
zeine-3-carbaldehyde (4d)

Yield: 130 mg, (72%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.60 (s, 1H),
7.85-7.88 (m, 1H), 7.68-7.69 (m, 1H), 7.39-7.41 (m, 1H), 7.27 (d, J = 6.0 Hz, 2H),
7.21-7.24 (m, 4H), 7.14-7.17 (m, 4H), 6.93-7.00 (m, 5H), 6.89-6.92 (m, 4H),
6.69-6.77 (m, 3H), 6.07-6.11 (m, 2H), 1.91 (t, J = 6.0 Hz, 4H), 0.88-1.00 (m,
12H), 0.67 (t, J = 7.6 Hz, 6H), 0.59 (m, 4H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ
(ppm) 189.65, 154.08, 152.44, 151.09, 149.43, 147.61, 147.23, 142.06, 141.51,
139.87, 138.44, 136.27, 133.20, 130.94, 129.31, 129.06, 127.97, 126.97, 125.92,
125.69, 125.06, 124.68, 124.48, 123.97, 123.81, 123.65, 123.01, 122.19, 119.90,
119.22, 118.83, 116.62, 114.82, 55.57, 31.62, 29.55, 23.88, 22.69, 22.49, 14.05.
HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{56}$H$_{54}$N$_2$O$_5$) 802.4045; found,
802.4039.
General procedures for the preparation of TP1–TP4.

A mixture of precursor 4a-4d (0.20 mmol) and cyanoacetic acid (89 mg, 1.10 mmol) in acetic acid (20 mL) was refluxed in the presence of ammonium acetate (200 mg) overnight under a N₂ atmosphere. Then, water was added and extracted with CH₂Cl₂. Next, the solvent was removed under vacuum and the crude compound was purified by column chromatography on silica gel eluting with CH₂Cl₂/MeOH (20:1, v/v) to give TP1-TP4 as a dark red solid.

(E)-2-cyano-3-(7-(4-(diphenylamino)phenyl)-10-hexyl-10H-phenothiazin-3-yl) acrylic acid (TP1)

Yield: 80 mg, (62%). ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 8.15 (s, 1H), 7.90-7.93 (m, 1H), 7.81 (d, J = 2.0 Hz, 1H), 7.54 (d, J = 2.0 Hz, 2H), 7.44-7.47 (m, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 6.98-7.09 (m, 10H), 3.93 (t, J = 6.8 Hz, 4H), 1.66-1.71 (m, 2H), 1.36-1.41 (m, 2H), 1.24-1.26 (m, 4H), 0.83 (t, J = 6.8 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 163.77, 152.34, 148.44, 146.98, 146.55, 141.32, 134.95, 132.41, 131.59, 129.54, 129.03, 127.01, 125.49, 124.49, 124.08, 123.99, 123.23, 123.18, 122.65, 122.51, 116.84, 116.60, 115.46, 99.61, 46.95, 30.77, 26.00, 25.68, 22.06, 13.81. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₄₀H₃₅N₃O₂S) 621.2444; found, 621.2440.

(E)-2-cyano-3-(7-(4-(diphenylamino)phenyl)-10-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl) acrylic acid (TP2)

Yield: 76 mg, (59%). ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 8.00 (s, 1H), 7.70 (s, 1H), 7.51 (d, J = 8.8 Hz, 1H), 7.44-7.46 (m, 2H), 7.27-7.32 (m, 7H), 7.13-7.18
(m, 3H), 6.98-7.04 (m, 6H), 6.93 (d, J = 8.8 Hz, 2H), 6.08 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.0 Hz, 2H), 1.70-1.73 (m, 2H), 1.21-1.41 (m, 6H), 0.85 (t, J = 4.0 Hz, 3H).  
$^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 163.70, 158.77, 151.74, 147.13, 146.92, 146.55, 140.80, 135.00, 134.86, 132.24, 131.46, 131.31, 131.15, 129.52, 128.00, 126.90, 125.55, 125.06, 124.03, 123.85, 123.22, 123.15, 118.63, 118.41, 116.82, 116.63, 115.09, 99.89, 67.82, 31.01, 28.63, 25.23, 22.09, 13.93. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{46}$H$_{39}$N$_3$O$_5$S) 713.2707; found, 713.2739.

(E)-2-cyano-3-(7-(4-(diphenylamino)phenyl)-10-(9-hexyl-9H-carbazol-3-yl)-10H-phenothiazin-3-yl)acrylic acid (TP3)

Yield: 82 mg, (68%). $^1$H NMR (400 MHz, DMSO-$d_6$): δ (ppm) 8.03 (s, 1H), 7.69 (t, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.27-7.34 (m, 7H), 6.99-7.09 (m, 12H), 6.94 (d, J = 8.0 Hz, 2H), 6.11-6.18 (m, 2H), 4.46 (t, J = 6.0 Hz, 2H), 1.80-1.88 (m, 2H), 1.35-1.42 (m, 2H), 1.21-1.28 (m, 4H), 0.82 (t, J = 6.8 Hz, 3H).

$^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 163.76, 162.27, 151.97, 147.66, 147.15, 146.99, 146.94, 146.56, 145.89, 141.24, 140.71, 139.98, 139.53, 134.98, 132.28, 131.10, 129.52, 127.54, 127.11, 126.88, 125.01, 124.29, 124.03, 123.93, 123.75, 123.43, 123.25, 123.15, 122.89, 122.47, 119.22, 118.60, 118.32, 116.77, 115.52, 100.10, 30.94, 30.67, 28.57, 26.16, 22.03, 13.82. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{52}$H$_{42}$N$_4$O$_2$S) 786.3023; found, 786.2978.

(E)-2-cyano-3-(10-(9,9-dihexyl-9H-fluoren-2-yl)-7-(4-(diphenylamino)phenyl)-10H-phenothiazin-3-yl)acrylic acid (TP4)

Yield: 82 mg, (68%). $^1$H NMR (400 MHz, DMSO-$d_6$): δ (ppm) 8.08 (d, J = 8.0 Hz, 1H), 8.00 (s, 1H), 7.87-7.89 (m, 1H), 7.70 (d, J = 2.0 Hz, 1H), 7.52-7.54 (m, 2H),
7.43-7.45 (m, 3H), 7.32-7.36 (m, 4H), 7.24-7.28 (m, 4H), 6.92-7.08 (m, 9H), 6.07-6.11 (m, 2H), 1.97 (t, J = 6.0 Hz, 4H), 0.94-1.02 (m, 12H), 0.64 (t, J = 6.8 Hz, 6H), 0.52 (t, J = 6.8 Hz, 4H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 163.64, 153.59, 152.44, 151.49, 150.56, 146.90, 146.82, 146.59, 141.46, 140.67, 139.50, 137.73, 135.07, 132.11, 130.68, 129.52, 128.86, 128.56, 127.92, 127.13, 126.82, 125.68, 124.90, 124.20, 124.06, 123.93, 123.18, 122.87, 122.45, 120.37, 118.50, 118.38, 116.82, 116.38, 114.78, 101.84, 55.14, 30.83, 30.68, 28.78, 23.37, 21.79, 13.74. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{59}$H$_{55}$N$_3$O$_2$S) 869.4009; found, 869.4047.

**Characterizations.** $^1$H and $^{13}$C NMR spectra were recorded with a Bruker Ultrashield 400 Plus NMR spectrometer. The High-resolution matrix-assisted laser desorption/ ionization time of flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer. The UV-visible absorption spectra of these dyes were measured in CH$_2$Cl$_2$ solution with a Varian Cary 100 UV-Vis spectrophotometer. The cyclic voltammograms (CV) were measured with Versastat II electrochemical work station using a normal three-electrode cell with a Pt working electrode, a Pt wire auxiliary electrode and a saturated Ag/Ag$^+$ reference electrode in KNO$_3$ aqueous solution, 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF$_4$) was used a supporting electrolyte in DCM solution. The potential of the reference electrode was calibrated by ferrocene after each set of measurements, and all potentials mentioned in the work were against normal hydrogen electrode.
Fabrication and characterization of cells. To make a reasonable comparison, all the anode films for the DSSC were made under the same standard manner, which are composed of 12 μm thick of transparent layer (TiO$_2$ with diameter of 20 nm) and 6 μm thick of scattering layer (TiO$_2$ nanoparticles with diameter of 200 nm). In specific, a doctor-blade technique was utilized to prepare photoanode (TiO$_2$) films. Firstly, a layer of ca. 6 μm TiO$_2$ paste (20 nm) was doctor-bladed onto the FTO conducting glass and then relaxed at room temperature for 3 min before heating at 150 °C for 6 min, this procedure was repeated once to achieve a film thickness of ca. 12 μm and the resulting surface was finally coated by a scattering layer (ca. 6 μm) of TiO$_2$ paste (200 nm). The electrodes were gradually heated under an air flow at 275 °C for 5 min, 325 °C for 5 min, 375 °C for 5 min, 470 °C for 30 min to remove polymers and generate three-dimensional TiO$_2$ nanoparticle network. After that, the sintered films were soaked with 0.02 M TiF$_4$ aqueous solution for 45 min at 70°C, washed with deionized water, and further annealed at 450 °C for 30 min. After cooling down to ca. 80°C, the electrodes were immersed into a 5 × 10^{-4} M dye bath in acetonitrile/ tert-butyl alcohol (volume ratio, 1:1) solution for TPa dye series and maintained in the dark for 16 hrs. Afterwards, the electrodes were rinsed with ethanol to remove the non-adsorbed dyes and dried in air. Pt counter electrodes were prepared by sputtering method at 15 mA for 90 s at a power of 150 W. Two holes (0.75 mm in diameter) were pre-drilled in the FTO glass for introducing electrolyte. The dye-adsorbed TiO$_2$ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt parafilm at about 100°C. The liquid electrolyte consisting of 0.6 M
1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I\textsubscript{2} in a mixture of acetonitrile and \textit{tert}-butyl alcohol (volume ratio, 1:1) was introduced into the cell through the drilled holes at the back of the counter electrode. At last, the holes were sealed by parafilm and covering glass (0.1 mm thickness) at elevated temperature. The effective areas of all the TiO\textsubscript{2} electrodes were 0.24 cm\textsuperscript{2}.

The current-voltage (\textit{J-V}) characteristics of the assembled DSSCs were measured by a semiconductor characterization system (Keithley 236) at room temperature in air under the spectral output from solar simulator (Newport) using an AM 1.5G filter with a light power of 100 mW/cm\textsuperscript{2}. IPCEs of DSSCs were recorded in Solar Cell QE/IPCE Measurement System (Zolix Solar Cell Scan 100) using DC mode. CHI 660D electrochemical workstation was used to characterize the electrochemical properties of the DSSCs. Electrochemical impedance spectroscopy (EIS) was recorded under dark condition over a frequency range of 0.1-10\textsuperscript{5} Hz with an AC amplitude of 10 mV and the parameters were calculated from Z-View software (v2.1b, Scribner Associates, Inc.).

5.5 References


Chapter 6 New Simple Panchromatic Dyes Based on Thiadiazole[3,4-c]pyridine(PyT) for Dye-Sensitized Solar Cells Applications

6.1 Introduction

Dye-sensitized solar cells, referred to as the promising alternative to conventional semiconductor silicon-based solar, have been pioneered by Grätzel and co-workers in the last decade.[1] DSSC is composed of a wide band gap semiconductor deposited on a translucid conducting substrate, an anchored molecular sensitizer, and a redox electrolyte (usually the I\(^{-}/I_{3}^{-}\) couple is found in most of the “conventional” DSSCs). While the total efficiency of the dye-sensitized solar cell depends on the optimization and compatibility of each of its constituents, the initial requirement is for the device to be able to gather as many photons from sunlight as possible. Hence, photosensitizer with broad light harvesting characteristics is very crucial for efficient DSSCs. While the combination of multiple dyes appears to be a promising approach to obtain panchromatic systems, a judicious molecular engineering of the dye structure will directly allow for a further increase of the light harvesting in the longer wavelength region. To fulfil the requirement of panchromatic ruthenium complexes, “black dye” has ever been developed in which the ruthenium center is coordinated to a monoprotonated tricarboxyterpyridine ligand and three thiocyanate ligands. It is evident that the response of the “black dye” extends 100 nm further into the infrared than that of N719, and conversion efficiency of 11.1%
has been achieved with the dye using high-haze TiO₂ electrode.² Metallophthalocyanines (MPcs) show potential for near-infrared (NIR) photosensitizers because of their intense Q bands (λ = 600–700 nm), high molar extinction coefficients (ε > 100 000 M⁻¹cm⁻¹), and good thermal, chemical, and photolytic stabilities.³ However, MPc sensitizers displayed rather low conversion efficiencies in DSSCs. The major factors for the low efficiency of MPcs were the formation of aggregates on the surface of the TiO₂ crystal and the lack of electrontransfer directionality in the excited state. On the other hand, some metal-free organic sensitizers such as squaraine,⁴ cyanine,⁵ and bodipy⁶ have been applied in DSSCs for their good absorption bands in the near infrared region. Specifically, squaraine-based sensitizers absorb strongly in the NIR spectroscopic region and the most-efficient squaraine dye to date, YR6, shows a PCE of 6.7%, as well as a good IPCE (>50%) in the range 450–700 nm.⁷ Recently, the strong electron acceptor benzothiadiazole unit was incorporated between donor and anchor unit to propose a novel donor–acceptor–π-spacer–acceptor (D–A–π–A) configuration for metal-free organic sensitizers. The incorporated additional acceptor of benzothiadiazole unit in the π-conjugation can improve the distribution of donor electrons to enhance the photostability of indoline compounds, and red shift absorption spectra into the NIR region, resulting in high power-conversion efficiencies.⁸ Another electron-deficient unit, thiadiazolo[3,4-c]pyridine (PyT), has also been explored as a strong electron acceptor in the design of polymers and small molecules with relatively lower HOMO-LUMO bandgaps for efficient organic bulk heterojunction photovoltaic solar cells.⁹ It has been
shown that these molecules containing PyT unit have stronger intermolecular interactions to extend their optical absorption into the NIR region to maximize photon absorption. To the best of our knowledge, organic photosensitizers based on PyT have so far not been investigated in DSSC applications. In this chapter, three new organic D-A-π-A photosensitizers (Figure 6.1) with PyT moiety incorporated between nonplanar triarylamine and cyanoacrylic acid, have been developed and applied in DSSCs. As expected, the photoresponses of the DSSCs based on the three dyes reached even above 800 nm, which are comparable to the incident photon-to-current conversion efficiency (IPCE) onset of N719. Typically, different bulky triarylamine units such as triphenylamine (D1), N,N-bis(9,9-dimethylfluoren-2-yl)aniline (D2) and 4-(hexyloxy)-N-(4-(hexyloxy)-phenyl)-N-phenylaniline (D3) were utilized as donor units to investigated their influences on the photovoltaic performances of DSSCs. Though the conversion efficiency of 4.20% is low, the methodology of tuning the HOMO or LUMO energy levels by incorporation of PyT in such D–A–π–A dyes could be generally applied to design more efficient panchromatic sensitizers in DSSCs.

![Chemical structure of dyes H1–H3](image)

**Figure 6.1.** Chemical structure of dyes H1–H3.
6.2 Results and Discussion

6.2.1 Synthesis and Characterization

The synthetic procedures of the three dyes are depicted in Scheme 6.1. The key precursors of 4,7-dibromo-[1,2,5]thiadiazolo-[3,4-c]pyridine (BPyT),
(4-(diphenyl-amino)phenyl)boronic acid, (4-(bis(9,9-dimethyl-9H-fluoren-2-yl)-amino)phenyl)boronic acid and (4-(bis(4-(hexyloxy)phenyl)amino)phenyl)boronic acid were synthesized according to literature.\textsuperscript{[10]} Compounds 1, 2a, 2b and 2c were prepared through conventional Suzuki cross-coupling reaction in good yields. And three target sensitizers (H1, H2, H3) were separated after typical Knoevenagel reactions between cyanoacetic acid and formylated intermediates. All the new compounds were characterized with \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and MALDI-TOF mass spectra data.

\textbf{Scheme 6.1.} Synthetic rout for the dyes (H1, H2 and H3).
6.2.2 Photophysical Properties

The optical absorption spectra of three new dyes H1, H2 and H3 in dichloromethane solutions and adsorbed on TiO2 films are shown in figure 6.2 and figure 6.3, and the corresponding spectroscopic data are summarized in Table 6.1. The three dyes exhibited similar broad and strong absorption spectra covering a wide wavelength range of 300–750 nm. The shorter wavelength region corresponds to the π-π* transitions of the conjugated system and the longer wavelength region can be reasonably assigned to the efficient intramolecular charge transfer (ICT) between the donor and the acceptor. As expected, the introduction of PyT unit into the molecular frame distinctly decreases the bandgap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), thus extending the the ICT absorption peak into the NIR region. Obviously, in the three photosensitizers containing the same cyanoacetic acid unit, the ICT band is dependent upon the donor units and electron transport channels. As listed in Table 6.1, the donor effect on absorption peak is distinct. The bathochromic shift of 29 and 39 nm was observed by replacing D1 (H1) with D2 (H2) and D3 unit (H3) in the donor moiety, respectively. This definitely indicates that that the electron-donating capability is in the order of D3 > D2 > D1, which is consistent with the electrochemical properties (vide infra). In addition, the corresponding molar extinction coefficients of ICT peaks are in the order of H3 (585 nm, 2.87 × 10⁴ M⁻¹ cm⁻¹) > H2 (575 nm, 2.46 × 10⁴ M⁻¹ cm⁻¹) > H1 (546 nm, 2.14 × 10⁴ M⁻¹ cm⁻¹). The results clearly illustrate that the introduction of D3 donor group in H3 is favorable
for lowering the band gap and extending the responsive wavelength to the NIR region, as well as capturing more solar light for a higher photocurrent output. When adsorbed on a transparent thin TiO₂ film, the three dyes showed broad absorption spectra in agreement with those in solutions (Figure 2b), while the ICT absorption peaks displayed a slight blue-shift of 49, 31, and 27 nm for H₁, H₂, and H₃, respectively. Such a hypsochromic shift is mainly due to the deprotonation and H-aggregation between the carboxylate acid and the TiO₂ semiconductor.[¹¹] Notably, the maximum absorption band of H₃ is less blue-shifted than that of H₁ and H₂, indicating that the introduction of hexyloxy chain on the triarylamine moiety effectively inhibits H-aggregation.

Figure 6.2 Absorption spectra of dyes in CH₂Cl₂ solution.
6.2.3 Electrochemical Properties

To evaluate the possibility of photoelectron injection and sensitizer regeneration, the cyclic voltammograms have been performed in CH$_2$Cl$_2$ solution with ferrocene (0.4 V vs. NHE) as an external reference. The voltammograms of the three dyes (Figure 6.4) showed a well symmetrical and reversible behavior, indicative of high redox stability. The oxidation potentials correspond to the highest occupied molecular orbitals (HOMO), which are exclusively determined by the donors. As listed in Table 6.1, the HOMO levels of the three dyes are in the order of H1 (0.86 V) > H2 (0.64 V) > H3 (0.57 V). It can be rationalized that the donor groups with increasing electron-donating capability decrease the HOMO energy in the same order. Obviously, the HOMO values of the three dyes are more positive than $\Gamma^-/I_3^-$ redox potential value (0.4 V), indicating that the oxidized dyes
can be efficiently regenerated by the electrolyte. The lowest unoccupied molecular orbitals (LUMO) can be calculated by the values of $E_{ox}$ and the zero-zero bandgaps ($E_{0-0}$) determined from the onset of the UV-visible absorption spectra. The estimated $E_{0-0}$ is 1.99 eV, 1.78 eV and 1.72 eV for H1, H2 and H3, respectively. The values of the HOMO-LUMO bandgap for the three dyes are relatively low, indicating that the incorporation of PyT can effectively decrease the energy bandgap and redshift the absorption band to the NIR region. Subsequently, the LUMO values of the three dyes, calculated from $E_{HOMO} - E_{0-0}$ are $-1.13$, $-1.14$ V and $-1.15$ V for H1, H2 and H3, respectively, which are more negative than the conduction band edge (CB) of TiO$_2$ ($-0.5$ V vs. NHE), allowing the efficient electron injection from the oxidized organic dyes into the conduction band of TiO$_2$.

![Figure 6.4. Oxidation potential of dyes in CH$_2$Cl$_2$ solution.](image-url)
Table 6.1. Photophysical and Electrochemical properties of the organic dyes.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}$ (^a)/nm ((\varepsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}))</th>
<th>$\lambda_{\text{max}}$ (^b)/nm</th>
<th>$E_{\text{ox}}$ (^c)/V</th>
<th>$E_{0-0}$ (^d)/eV</th>
<th>$E_{\text{red}}$ (^e)/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>546 (2.14)</td>
<td>497</td>
<td>0.86</td>
<td>1.99</td>
<td>-1.13</td>
</tr>
<tr>
<td>H2</td>
<td>575 (2.46)</td>
<td>544</td>
<td>0.64</td>
<td>1.78</td>
<td>-1.14</td>
</tr>
<tr>
<td>H3</td>
<td>585 (2.87)</td>
<td>558</td>
<td>0.57</td>
<td>1.72</td>
<td>-1.15</td>
</tr>
</tbody>
</table>

[a] Absorption maximum in \(1 \times 10^{-5}\) mol/L CH\(_2\)Cl\(_2\) solution. [b] Absorption maximum on TiO\(_2\) film. [c] Oxidation potential in CH\(_2\)Cl\(_2\) solution containing 0.1 M (n-C\(_4\)H\(_9\))\(_4\)NPF\(_6\) with a scan rate 100 mV.s\(^{-1}\) (vs. NHE). [d] $E_{0-0}$ was determined from the onset of absorption spectra. [e] $E_{\text{red}} = E_{\text{ox}} - E_{0-0}$.

6.2.4 Molecular Calculations

To understand the geometrical and electronic properties of these dyes, density functional theory (DFT) calculations are performed using Gaussian 03 program package at the B3LYP/6-31 G(d) level. The electron distributions of the HOMOs and LUMOs of these dyes are shown in Figure 6.5. It is found that HOMOs of the three dyes are distributed mainly over the entire triarylamino donor part, while the LUMOs are mainly delocalized over cyanoacrylic acid, thiophene conjugated spacer and PyT acceptor. Generally, the HOMO orbitals are delocalized through the donor and $\pi$-bridge in traditional D-$\pi$-A type of dyes. However, in our D-A-$\pi$-A structural dyes, this connection might be somewhat blocked from the electron-withdrawing unit PyT in the bridge. Initially, in designing dyes of D-A-$\pi$-A configuration, the electrons on the donor subunit are not directly
transferred to the cyanoacetic acid subunit during the photo-excitation, but successively transferred to the electron-trap PyT subunit, then to the cyanoacetic acid subunit, and finally to TiO₂. Here, the insufficient overlapping of the HOMO and LUMO orbitals implies that strong acceptor PyT may retard a fast charge transition from the donor to the anchor group, which is partly ascribed to the relatively low PCE based on the three dyes, regardless of their panchromatic light response.

![Figure 6.5. Calculated HOMOs and LUMOs.](image)

6.2.5 Photovoltaic Properties of DSSCs

Figure 6.6 shows the IPCE spectra of DSSCs based on the three dyes as a function of light excitation wavelength. Notably, these DSSCs exhibited remarkably broad IPCE spectra covering the whole visible region and partial NIR region with the threshold wavelength over 850 nm, which matched well with the
threshold wavelength of the absorption spectra when adsorbed onto TiO₂ films. It means that incorporation of PyT unit in the three dyes with good delocalization between the donor and the acceptor can broaden the absorption spectrum to get a broad IPCE. From IPCE curves, the IPCE exceeded 50% in the spectral range of 300–850 nm for the three photosensitizers, and the solar cells based on H₃ showed the highest IPCE value of 65% at 583 nm. These results also indicate that H₃ dye possesses better light-harvesting ability and would generate a higher photocurrent among the three dyes.

![Graph of IPCE (%) vs Wavelength (nm)]

**Figure 6.6.** IPCE curves of organic dyes.

The photocurrent-voltage (J–V) characteristics of all devices are shown in Figure 6.7. The parameters of DSSCs fabricated with these dyes, i.e., short-circuit current (Jₛ𝑐), open-circuit photovoltage (Vₜₐₜ), fill factor (FF), and total power conversion efficiency (η), are summarized in Table 6.2. DSSC based on dye H₃ shows the highest PCE of 4.20% with a relatively higher Jₛ𝑐 = 14.19 mA cm⁻², Vₜₐₜ = 0.462 V, and FF = 0.64 under AM 1.5 irradiation. And the dyes H₁ and H₂
sensitized solar cells displayed relatively inferior photovoltaic performance ($\eta$) of 2.63 % and 3.58% due to the lower $J_{sc}$ and $V_{oc}$. Compared with dyes H1 and H2, the significant improvement of photovoltaic performances for H3 should be attributed to the more efficient light harvesting, effective electron injection and slower charge recombination rate (vide infra). For example, the LUMO energy levels of the three dyes are in the order of H3 (–1.15 V) < H2 (–1.14 V) < H1 (–1.13 V), indicating that DSSC based on H3 exhibited the most effective electron injection from the excited dye into the CB of TiO$_2$. As a result, DSSC based on H3 showed the highest $V_{oc}$ and $J_{sc}$ due to its better molar extinction coefficient, broad IPCE curve and high electron-injection efficiency. In addition, D3 appended with long hexyloxy chain in H3 can effectively suppress dye-aggregation and retard charge recombination in DSSC (vide infra). [12]

Figure 6.7. $J–V$ curves and IPCE of H1-H3-sensitized solar cells.
Table 6.2 Photovoltaic parameters of the dyes in liquid based DSSCs at full sunlight (AM 1.5G, 100mW cm\(^{-2}\))

<table>
<thead>
<tr>
<th>Dye</th>
<th>(J_{sc}/\text{mA cm}^{-2})</th>
<th>(V_{oc}/\text{V})</th>
<th>FF</th>
<th>(\eta/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>11.23</td>
<td>0.367</td>
<td>0.64</td>
<td>2.63</td>
</tr>
<tr>
<td>H2</td>
<td>12.00</td>
<td>0.432</td>
<td>0.69</td>
<td>3.58</td>
</tr>
<tr>
<td>H3</td>
<td>14.19</td>
<td>0.462</td>
<td>0.64</td>
<td>4.20</td>
</tr>
</tbody>
</table>

Performance of DSSCs measured in a 0.24 cm\(^2\) working area on a FTO (8Ω/square) substrate at room temperature. Dyes were maintained at 0.5 mM in CH\(_2\)Cl\(_2\) solution for Hn dyes series and in acetonitrile/tert-butyl alcohol (volume ratio, 1:1) for N719. Electrolyte: LiI (0.05 M), I\(_2\) (0.1 M), and DMPII (0.6 M) in acetonitrile:tert-butyl alcohol (1:1, v/v).

6.2.6 Electrochemical Impedance Spectroscopy Analysis

Electrochemical Impedance Spectroscopy (EIS) has been performed to elucidate the interfacial charge recombination process in DSSCs based on these dyes under the dark condition. As shown in Figure 6.8, a major semicircle for each dye was observed in the EIS Nyquist plot, which is related to the resistance of electron transport at the TiO\(_2\)/dye/electrolyte interface, i.e. the resistance of the recombination between electrons on TiO\(_2\) conduction band and I\(_3^-\) species in the electrolyte.\(^{[13]}\) The larger is the semicircle, the slower the recombination kinetics. It is clear that dye H3 exhibited the highest recombination resistance, which is most likely due to the long hexyloxy chain on D3 that more efficiently closes up the area for direct contact between TiO\(_2\) and the electrolytes.\(^{[10]}\) A high \(V_{oc}\) is
related to a low rate of charge recombination. The trend observed is definitely consistent with the \( V_{oc} \) values of the cells. As for dye H3, the introduction of a bulky electron-donating unit D3 appended with long hexyloxy chain can not only further extend absorption spectrum into the NIR region, but also efficiently provide a surface blocking layer on the TiO\(_2\) surface and impede a direct contact between the charge and oxidized species (I\(_3^-\)) in the electrolyte.\[^{10}\]

![EIS Nyquist plots for DSSCs based on the dyes under dark](image)

**Figure 6.8.** EIS Nyquist plots for DSSCs based on the dyes under dark

### 6.3 Conclusions

In conclusion, three new D-A-\( \pi \)-A photosensitizers incorporated with electron-withdrawing unit PyT as an additional acceptor have been synthesized and applied in DSSCs. It has been demonstrated that the incorporation of PyT unit can effectively tune the HOMO and LUMO energy levels, extend absorption spectra into the NIR region by decreasing the HOMO-LUMO bandgap. As expected, the photoresponses of DSSCs based on the three dyes reached even
above 800 nm, which are comparable to the incident IPCE onset of N719. Specifically for dye H3, the introduction of a bulky electron-donating unit D3 appended with hexyloxy chain results in a further red-shift of the ICT band and an enhanced light-harvesting property, as well as a retarded electron recombination between the charge and oxidized species (I$_3^-$) in the electrolyte. Though the conversion efficiency of 4.20% is still low, the approach of tuning the HOMO or LUMO energy level by incorporation of electron-withdrawing PyT unit in such D–A–π–A dyes could be generally applied in the design of more efficient panchromatic photosensitizers in DSSCs.

6.4 Experimental Section

Materials and Reagents. All solvents and reagents were purchased from Sigma-Aldrich Company and used as received without further purification. Optically transparent FTO-conducting glass electrodes (Nippon Sheet Glass Co., Japan) with a sheet resistance of 8-10 Ω$^{-2}$ per square and an optical transmission of greater than 80% in the visible-light range were used and cleaned by using a standard procedure. A main transparent layer (12 μm) with titania particles (about 20 nm) and a scattering layer (4 μm) with titania particles (about 400 nm) were screen-printed onto the fluorine-doped tin oxide (FTO)-conducting glass substrate.

Instruments and Characterization. $^1$H and $^{13}$C NMR spectra were recorded with a Bruker Ultrashield 400 Plus NMR spectrometer. The UV-visible absorption spectra of these dyes were measured in CH$_2$Cl$_2$ solution with a Varian Cary 100
UV-Vis spectrophotometer. Emission spectra were performed using a Photon Technology International (PTI) Alphascan spectrofluorimeter. High-resolution matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer. The cyclic voltammograms (CV) were measured with Versastat II electrochemical work station using a normal three-electrode cell with a Pt working electrode, a Pt wire counter electrode and a Ag/Ag+ reference electrode. The supporting electrolyte was 0.1 M tetra-n-butylammonium hexafluorophosphate in DCM solution. The potential of the reference electrode was calibrated by ferrocene after each set of measurements, and all potentials mentioned in the work were against normal hydrogen electrode. The photocurrent–voltage (J–V) curves of the DSSCs were measured by using a digital source meter (2400, Keithley) under standard air mass (AM 1.5) with simulated solar illumination at 100 mWcm\(^{-2}\) (WXS-90SL2, Wacom). Monochromatic incident-photon-to-current-conversion efficiency (IPCE) spectra were measured with monochromatic incident light of \(1 \times 10^{16} \text{ photons cm}^{-2}\) in DC mode (CEP-2000 BX, Bunko-Keiki). During the \(J-V\) and IPCE measurements, a black mask and edge were used with an aperture area of 0.25 cm\(^{-2}\). Charge-extraction from TiO\(_2\) was calculated by integration of the transient current that was detected when the laser illumination was turned off and the DSSC was simultaneously stepped from open-circuit to short-circuit. Intensity-modulated photovoltage spectroscopy of the open circuit was carried out by using a combination of sinusoidal low-intensity-modulated illumination from a green diode laser (Cobolt Co., Stockholm, Sweden, Samba, 532 nm, 50 mW) band
constant-bias light illumination from a Xe lamp (Ushio, Tokyo, Japan, UXL-500D-O), which was attenuated (if necessary) with a neutral-density filter. An acoustic optical modulator (Isomet Co., Springfield, VA, 1205 C^−1) was used to produce sinusoidal modulation of a laser beam. Electrochemical-impedance spectroscopy (EIS) measurements of all of the DSCs were performed on a Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany). The frequency range was 0.1 Hz–100 kHz. The magnitude of the alternative signal was 10 mV. The applied voltage bias was -0.68 V. **Fabrication of Dye-Sensitized Solar Cells.** A main transparent layer (12 μm) with titania particles (about 20 nm) and a scattering layer (4 μm) with titania particles (about 400 nm) were screen-printed onto the fluorine-doped tin oxide (FTO)-conducting glass substrate. The films were then sintered at 500 °C for 1 h. The thickness of the films was measured on a Surfcom 1400A surface profiler (Tokyo Seimitsu Co. Ltd.). The films were treated with a 0.1 M aqueous solution of HCl before examination. Coating of the titania films was carried out by immersion in a 3×10^−4 M solution of the sensitizers in MeCN/tBuOH (1:1, v/v) for 24 h. The dye-covered TiO_2 electrode and the Pt counter electrode were assembled into a sandwich-type cell and sealed with a hot-melt gasket (thickness: 25 μm) that was made of the ionomer Surlyn1702 (DuPont). Finally, the electrolyte, which consisted of 0.6M 1-methyl-3-propylimidazolium iodide (MPIImI), 0.1M LiI, 0.05M I_2, and 0.5M tert-butylpyridine in MeCN, was injected into the cell and sealed with a cover glass.
Synthesis

5-(7-bromo-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)thiophene-2-carbaldehyde (1):
The mixture of 4,7-dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine (1.17 g, 4 mmol),
(5-formylthiophen-2-yl)boronic acid (639 mg, 4.1 mmol), Pd(PPh₃)₄ (230 mg, 0.2 mmol)
and 2N aqueous solution of K₂CO₃ (2 mL) in THF (10 mL) under N₂ atmosphere was heated to reflux for about 48 h.
Then the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 1:4 mixture of hexane and CH₂Cl₂ as eluent to afford the red compound. Yield: 545.8 mg, (42%).

1H NMR (400 MHz, CDCl₃): δ (ppm) 9.87 (s, 1H), 8.64 (s, 1H), 8.52 (d, J = 1.2 Hz, 1H), 8.45 (d, J = 1.2 Hz, 1H).
3C NMR (400 MHz, CDCl₃): δ (ppm) 190.03, 156.32, 153.52, 147.92, 145.82, 139.80, 138.19, 133.15, 126.56, 117.56. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₁₀H₄BrN₃O₃S₂) 324.9034; found, 324.9137.

5-(7-(4-(diphenylamino)phenyl)-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)thiophene-2-carbaldehyde (2a):
The mixture of 1 (100 mg, 0.31 mmol),
(4-(diphenylamino)-phenyl)boronic acid (116 mg, 0.4 mmol), Pd(PPh₃)₄ (18 mg, 0.01 mmol)
and 2N aqueous solution of K₂CO₃ (2 mL) in THF (10 mL) under N₂ atmosphere was heated to reflux for about 24 h. Then the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 1:3 mixture of hexane and CH₂Cl₂ as eluent to afford the dark red compound. Yield: 114 mg, (75%).

1H NMR (400 MHz, CDCl₃): δ (ppm) 9.98 (s, 1H), 9.01 (s, 1H), 8.60 (t, J = 2.0 Hz, 2H), 8.18 (d, J = 2.0 Hz, 1H), 7.86 (d, J = 4.0 Hz, 1H), 7.30-7.35 (m, 4H), 7.19-7.22 (m, 5H), 7.17 (t, J = 2.0 Hz, 1H),
5-(7-(4-(bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)thiophene-2-carbaldehyde (2b): Using a similar procedure with 2a. 2b, a purple solid. Yield: 110 mg, (71%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.99 (s, 1H), 9.03 (s, 1H), 8.66 (d, J = 2.0 Hz, 1H), 8.64 (d, J = 2.0 Hz, 1H), 8.20 (d, J = 4.0 Hz, 1H), 7.86 (d, J = 4.0 Hz, 1H), 7.65-7.69 (m, 4H), 7.40 (t, J = 4.0 Hz, 2H), 7.27-7.36 (m, 9H), 7.23 (t, J = 2.0 Hz, 1H), 7.21 (t, J = 2.0 Hz, 1H), 1.25 (s, 12H).

13C NMR (400 MHz, CDCl₃): δ (ppm) 182.95, 155.29, 153.65, 152.66, 150.91, 146.27, 143.67, 142.85, 138.74, 137.09, 135.47, 134.37, 133.97, 131.32, 129.19, 127.90, 126.87, 124.43, 122.59, 121.53, 120.82, 119.86, 119.67, 118.00, 113.84. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₄₆H₃₄N₄O₃S) 722.2267; found, 722.2239.

5-(7-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)thiophene-2-carbaldehyde (2c): Using a similar procedure with 2a. 2c, a purple solid. Yield: 100 mg, (80%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.97 (s, 1H), 8.98 (s, 1H), 8.55 (d, J = 4.0 Hz, 2H), 8.15 (d, J = 4.0 Hz, 1H), 7.84 (d, J = 4.0 Hz, 1H), 7.13-7.15 (m, 4H), 7.00-7.02 (m, 2H), 6.86-6.88 (m, 4H), 3.95 (t, J = 6.4 Hz, 4H), 1.75-1.81 (m, 4H), 1.45-1.49 (m, 4H), 1.25-1.37 (m, 8H), 0.90 (t, J = 6.4 Hz, 6H). 13C NMR (400 MHz, CDCl₃): δ (ppm) 182.88, 154.45, 150.59, 148.43, 141.22, 140.70, 139.68, 138.87, 134.75, 130.57, 127.74, 127.31, 126.75,
HRMS (MALDI-TOF, m/z): [M+] calcd for (C₄₀H₄₂N₄O₃S₂) 690.2722; found, 690.2787.

(E)-2-cyano-3-(5-(7-(4-(diphenylamino)phenyl)-1,2,5-thiadiazolo[3,4-c]pyridin-4-yl)thiophen-2-yl)acrylic acid (H1): A mixture of precursor 2a (100 mg, 0.20 mmol) with cyanoacetic acid (40 mg, 0.50 mmol) in acetic acid (20 mL) was refluxed in the presence of ammonium acetate (200 mg) overnight under N₂ atmosphere. Then water was added and extracted with CH₂Cl₂. Next solvent was removed under vacuum and the crude compound was purified by column chromatography on silica gel eluted with CH₂Cl₂ and MeOH (20:1, v/v) to give a purple solid. Yield: 81.0 mg (70.0%). ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 9.15 (s, 1H), 8.53 (d, J = 8.8 Hz, 2H), 8.44 (s, 1H), 8.22 (d, J = 4.0 Hz, 1H), 8.02 (d, J = 4.0 Hz, 1H), 7.40 (t, J = 7.8 Hz, 4H), 7.16-7.21 (m, 6H), 7.02 (t, J = 8.8 Hz, 2H). ¹³C NMR (400 MHz, DMSO-d₆): δ (ppm) 163.35, 154.26, 150.81, 149.76, 148.44, 146.16, 144.94, 144.23, 141.84, 138.87, 137.35, 131.02, 129.83, 128.60, 127.36, 125.54, 124.55, 120.04, 118.12, 117.06, 115.01. HRMS (MALDI-TOF, m/z): [M+] calcd for (C₃₁H₁₉N₅O₂S₂) 558.1053; found, 558.1030.

(E)-3-(5-(7-(4-(bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-1,2,5-thiadiazolo[3,4-c]pyridin-4-yl)thiophen-2-yl)-2-cyanoacrylic acid (H2): Using a similar procedure with H1. H2, a dark-purple solid. Yield: 70 mg, (65.2%). δ (ppm) ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 9.10 (s, 1H), 8.56 (d, J = 8.4 Hz, 2H), 8.25 (s, 1H), 8.18 (d, J = 3.6 Hz, 1H), 7.88 (d, J = 3.6 Hz, 1H), 7.72-7.78 (m, 4H), 7.48 (d, J = 7.2 Hz, 2H), 7.36 (d, J = 7.2 Hz, 2H), 7.24-7.32 (m, 4H),
7.11-7.17 (m, 4H), 1.36 (s, 12H). $^{13}$C NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 163.22, 154.94, 154.30, 153.25, 150.44, 149.77, 148.47, 145.73, 144.81, 142.37, 141.46, 139.61, 138.04, 136.84, 134.91, 130.97, 128.94, 128.08, 127.42, 127.10, 126.95, 124.16, 122.70, 121.27, 120.75, 119.75, 119.60, 118.37, 118.19, 46.52, 26.64.

HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{49}$H$_{35}$N$_5$O$_2$S$_2$) 790.2305; found, 790.2274.

**(E)-3-(5-(7-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)thiophen-2-yl)-2-cyanoacrylic acid (H3):** Using a similar procedure with H1. H3, a dark-purple solid. Yield: 82 mg, (69.7%). $\delta$ (ppm) $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 9.07 (s, 1H), 8.51 (d, $J$ = 7.2 Hz, 2H), 8.17 (d, $J$ = 4.0 Hz, 1H), 8.12 (s, 1H), 7.81 (d, $J$ = 8.8 Hz, 1H), 7.13 (d, $J$ = 8.8 Hz, 4H), 6.95 (d, $J$ = 8.8 Hz, 4H), 6.84 (d, $J$ = 8.8 Hz, 2H), 3.96 (t, $J$ = 6.4 Hz, 4H), 1.68-1.75 (m, 4H), 1.39-1.46 (m, 4H), 1.23-1.39 (m, 8H), 0.90 (t, $J$ = 6.4 Hz, 6H).

$^{13}$C NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 156.07, 154.40, 150.68, 150.51, 148.49, 141.29, 140.70, 139.65, 138.71, 138.67, 134.78, 130.87, 127.74, 127.23, 126.76, 119.33, 118.92, 118.19, 116.91, 115.59, 110.87, 67.64, 30.97, 28.66, 25.18, 22.05, 13.88. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{43}$H$_{43}$N$_5$O$_4$S$_2$) 758.2829; found, 758.2814.

### 6.5 References


Chapter 7 Structure-Function Relationships in Thiadiazole[3,4-c]-pyridine-Based Organic Dyes for Dye-Sensitized Solar Cells

7.1 Introduction

Dye-sensitized solar cells (DSSCs) sensitized by organic sensitizers have received remarkably attentions as an alternative to conventional semiconductor silicon-based solar cell since the pioneering work was reported by Grätzel and O’Regan in 1991, owing to their low production costs and potential mass manufacturing application.[1] A typical DSSCs architecture constitutes three functional ingredients: nanocrystalline semiconductor, redox electrolyte, and photosensitizer.[2] In DSSC, photosensitizer exerts a significant influence on the light-harvesting and overall power conversion efficiency as well as the device stability. Recently, considerable attentions have been made in the development of new photosensitizers to improve the photovoltaic performances.[3] Ruthenium(II) polypyridyl complexes based DSSCs have achieved considerable high photovoltaic power conversion efficiencies exceeding 11.5 % under standard AM 1.5 illumination.[4] However, these abovementioned Ru(II) based dyes are complicated in synthetic procedures and the rarity of the metal ruthenium limits the large-scale application in future. Consequently, many efforts have been concentrated on the development of metal-free organic dyes as the most promising candidates in DSSCs due to their low material costs, high molecular absorption extinction coefficients, and structural design flexibility with relative to classical ruthenium complexes. So far, the solar-cell performances of DSSCs based on
metal-free organic dyes have reached impressive efficiencies in the range of 5–9.7%. The major disadvantage limited the efficiency of metal-free organic DSSCs is their relatively poor absorption spectral response in the red and near infrared (NIR) region. Therefore, the judicious organic sensitizer should possess a broadly extended absorption spectrum in both of the entire visible and the near-IR region (panchromatic absorption) in order to achieve good overlap with the solar emission spectrum and to produce large photocurrent responses. One strategy of extending the spectral coverage to enhance the light harvesting efficiency is to reduce the HOMO–LUMO energy gap of the sensitizer. For this purpose, a series of novel D–A–π–A structured sensitizers for DSSCs have been prepared by incorporating electron-deficient or electron-withdrawing fragment into the π-conjugated spacer of organic dyes, such as, benzothiadiazole,[8] thienpyrazine,[9] diketopyrrolopyrrole[10] and benzotriazole.[68] The new sensitizers with D–A–π–A configuration can effectively reduce the band gap to enhance the degree of charge separation and broaden the absorption spectral response. Moreover, the incorporated auxiliary acceptor unit was demonstrated to facilitate the electron transfer from the donor to the acceptor. Recently, thiadiazolo[3,4-c]pyridine (TDAPy), which is a strong electron acceptor unit due to its electron-deficient of the pyridine, have been widely applied to construct copolymers with low band gaps in the field of bulky heterojunction (BHJ) organic photovoltaics[11][12] It has been demonstrated that these compounds containing TDAPy unit display good thermal stability and narrow bandgaps to extend broad optical absorption into the NIR region. However, the utilization of TDAPy unit in molecular sensitizers for
DSSCs has been less explored so far to the best of our knowledge. Herein, we report various organic sensitizers containing the electron-deficient thiadiazolo[3,4-c]pyridine unit in the framework of π-conjugated spacer in combination with dihexyloxy-substituted triphenylamine as the donor, cyanoacetic acid as the acceptor, and benzene, hexylthiophene and thiophene moiety as the conjugation linkage. We investigate the effect of the auxiliary TDAPy acceptor, its relative linkage position and different π-spacer linkers on the molecular absorption, HOMO-LUMO levels and photovoltaic performance. It is essential to understand the structure-property relationships in DSSC applications. The overall conversion efficiencies of liquid-electrolyte DSSCs based on these sensitizers range from 0.46 to 6.30 %, in which Y4-based DSSCs shows the best photovoltaic performance: a short-circuit photocurrent density ($J_{sc}$) of 12.54 mA cm$^{-2}$, an open-circuit photovoltage ($V_{oc}$) of 0.749 V, and a fill factor (FF) of 0.671, under standard global AM 1.5 solar light condition, which correlates well with the efficient electron injection and the effective retardation of charge recombination.
Figure 7.1. Chemical structures of dyes Y1–Y9.

7.2.1 Photophysical Properties

The UV-vis absorption spectra of these dyes Y1–Y9 measured in dichloromethane solutions are shown in Figure 7.2 and the corresponding spectroscopic data are summarized in Table 7.1. These dyes exhibit similar broad and strong absorption spectrum covering a wide range of 300~800nm. The short wavelength region corresponds to the π-π* transitions of the conjugated system and the longest wavelength region can reasonably be assigned to the efficient intramolecular charge transfer (ICT) between the donor and the acceptor. The broadened absorption responses of these dyes Y1–Y9 are obvious due to the
incorporation of the strong electron withdrawing thiadiazolo[3,4-c]pyridine moiety as an auxiliary acceptor into the π-conjugated spacer, which decrease the energy band-gaps, resulting in a broad responsive wavelength region. As listed in Table 7.1, the absorption spectra of dyes Y1–Y3 display the maximal absorption peak at 543 nm with (ε) of 1.63 × 10^4 M\(^{-1}\) cm\(^{-1}\), 547 nm with (ε) of 1.50 × 10^4 M\(^{-1}\) cm\(^{-1}\) and 562 nm with (ε) of 3.25 × 10^4 M\(^{-1}\) cm\(^{-1}\), respectively. However, the absorption spectra of dyes Y4–Y6 display the maximal absorption peak at 549 nm with (ε) of 6.14 × 10^4 M\(^{-1}\) cm\(^{-1}\), 555 nm with (ε) of 2.27 × 10^4 M\(^{-1}\) cm\(^{-1}\) and 571 nm with (ε) of 4.90 × 10^4 M\(^{-1}\) cm\(^{-1}\), respectively. The dyes Y4–Y6 show obviously red-shifted absorption peaks as well as higher molar extinction coefficients in comparison with that of Y1–Y3, respectively, due to an increase in conjugation length of these dyes by the incorporation of the additional hexylthiophene. It indicates that the dyes Y4–Y6 are beneficial for light-harvesting. Compared with Y4–Y6, the dyes Y7–Y9 without the hexyl chains on the thiophene units exhibit large bathochromic shifts of the maximum absorption peaks, which can be attributed to the coplanar structures of Y7–Y9 formed between the less steric thiophene unit and the thiadiazolo[3,4-c]pyridine. When adsorbed on a transparent thin TiO\(_2\) film, these three dyes show broad absorption spectra in agreement with that in above solutions (Figure 7.3), while the ICT absorption peaks of Y1, Y3 and Y7–Y9 display slightly hypsochromic shift due to the formation of dye H-aggregation and the deprotonation of the carboxylate acid when adsorbed on TiO\(_2\) film.\(^{[13]}\) Notably, the maximum absorption bands of Y2 and Y4–Y6 are red-shifted to a different extent with relative to that of dyes in solutions, which
can be attributed to the formation of J-aggregation on TiO$_2$ film. The phenomenon demonstrates that the intermolecular $\pi-\pi$ aggregation can be suppressed in a large degree by possessing long alkyl chains into the $\pi$-conjugated spacer.

**Figure 7.2.** Absorption spectra of dyes Y1–Y9 in CH$_2$Cl$_2$ solutions.

**Figure 7.3.** Absorption spectra of dyes Y1–Y9 on TiO$_2$ films.
Table 7.1. Photophysical and electrochemical properties of dyes Y1–Y9.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}^{[a]}$ [nm] ($\varepsilon$/$10^4$ M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}^{[b]}$ [nm]</th>
<th>$E_{\text{ox}}^{[c]}$ [V]</th>
<th>$E_{0,0}^{[d]}$ [eV]</th>
<th>$E_{\text{red}}^{[e]}$ [V]</th>
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<tbody>
<tr>
<td>Y1</td>
<td>543 (1.63)</td>
<td>525</td>
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<tr>
<td>Y2</td>
<td>547 (1.50)</td>
<td>556</td>
<td>0.60</td>
<td>1.89</td>
<td>-1.29</td>
</tr>
<tr>
<td>Y3</td>
<td>562 (3.25)</td>
<td>548</td>
<td>0.50</td>
<td>1.82</td>
<td>-1.32</td>
</tr>
<tr>
<td>Y4</td>
<td>549 (6.14)</td>
<td>561</td>
<td>0.49</td>
<td>2.07</td>
<td>-1.58</td>
</tr>
<tr>
<td>Y5</td>
<td>555 (2.27)</td>
<td>563</td>
<td>0.48</td>
<td>1.98</td>
<td>-1.50</td>
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<tr>
<td>Y6</td>
<td>571 (4.90)</td>
<td>574</td>
<td>0.50</td>
<td>1.81</td>
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<tr>
<td>Y7</td>
<td>570 (2.91)</td>
<td>536</td>
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<td>Y8</td>
<td>576 (2.62)</td>
<td>555</td>
<td>0.47</td>
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<tr>
<td>Y9</td>
<td>592 (6.10)</td>
<td>569</td>
<td>0.49</td>
<td>1.68</td>
<td>-1.19</td>
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</table>

7.2.2 Electrochemical Properties

To evaluate the thermodynamical possibility of electron injection and sensitizer regeneration, the cyclic voltammograms were performed in CH$_2$Cl$_2$ solutions (Figure 7.4) to determine the oxidation potentials ($E_{\text{ox}}$). The oxidation potentials corresponded to HOMOs. The LUMOs can be calculated by the values of $E_{\text{ox}}$ and the zero-zero band gaps at the onset of the UV-visible absorption spectra. The voltammograms of the dyes show well symmetrical and reversible behaviors, indicative of high redox stability. The HOMO and LUMO levels of these dyes were summarized in Table 7.1. The HOMO values of these dyes are more positive than iodide/tri-iodide redox potential value (0.4 V), indicating that the oxidized dyes can be efficiently regenerated by the electrolyte. As estimated from the band gap derived from the zero-zero band gaps at the onset of the
UV-visible absorption spectra, the resulting $E_{0-0}$ are in the range of 1.68 eV to 2.07 eV, which are relatively low, indicating the incorporation of thiadiazolo[3,4-c]pyridine can effectively decrease the energy bandgap and redshift the absorption band. Also, the LUMO values of the dyes, calculated from $E_{HOMO} - E_{0-0}$, are more negative than the conduction band edge (CB) of TiO$_2$ (-0.5 V vs. NHE), energetically allowing an efficient electron injection into the TiO$_2$ conduction band from the excited dyes. Therefore, the processes of electron injection and dye regeneration in DSSCs based on these dyes are feasible.

![Figure 7.4](image_url)

**Figure 7.4.** Oxidation potential of dyes Y1–Y9 in CH$_2$Cl$_2$ solutions.
7.2.3 Molecular Calculations

To understand the electronic distribution in the frontier molecular orbitals and electronic processes upon photoexcitation, DFT calculations were performed using Gaussian 03 program package at the B3LYP/6-31G(d)* hybrid functional for full geometrical optimization (Figure 7.6). The electron density distributions of the LUMO orbitals of all dyes are delocalized mainly on the thiaadiazolo[3,4-c]pyridine and the cyanoacrylic acid segment. The electron density distribution of the HOMO orbitals of Y1–Y3 are delocalized over the whole systems from the triphenylamine donor to the cyanoacrylic acid acceptor, while the electron density of HOMOs of Y4–Y9 are primarily located over the triphenylamine, thiophene, TDAPy and thiophene segments. And the sufficient overlap between the HOMO and LUMO orbitals guarantees a fast charge transfer transition. Thus, excitation from the HOMO to the LUMO should lead to an
efficient photoinduced electron transfer from the electron donating triphenylamine moiety to the terminal cyanoacrylic acid, and finally into the conduction band of TiO$_2$. Notably, the HOMOs in Y1–Y3 are more delocalized than those in Y4–Y9, due to the better coplanarity in the whole molecule.[14] In the optimized structures of Y4–Y6, the dihedral angles formed between the $\pi$-conjugated moiety (hexylthiophene, TDAPy and hexylthiophene) and the different $\pi$-linked spacers (benzene, hexylthiophene and thiophene) near anchoring group are computed to 47.8°, 9.3°, and 5.6°, respectively. Accordingly, the twist conformation leads to a blue shift of Y4 relative to Y5 and Y6 observed in absorption spectra. Similar phenomena can be observed in Y1–Y3 dyes and Y7–Y9 dyes.

<table>
<thead>
<tr>
<th>Dye</th>
<th>HOMO</th>
<th>LUMO</th>
<th>Optimized structure</th>
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</tr>
<tr>
<td>Y6</td>
<td><img src="image7.png" alt="HOMO" /></td>
<td><img src="image8.png" alt="LUMO" /></td>
<td><img src="image9.png" alt="Structure" /></td>
</tr>
</tbody>
</table>

**Figure 7.6.** Calculated frontier molecular orbitals of HOMO and LUMO and optimized structure diagram of Y4, Y5 and Y6.
7.2.4 Photovoltaic Properties of DSSCs

Figure 7.7 shows the incident photon-to-current conversion efficiency (IPCE) action spectra of cells based on the dyes Y1–Y9. The DSSCs based on these dyes exhibit remarkably broad IPCE action spectra covering the whole visible region and partial NIR region. It means that these constructed organic dyes with thiaiazolo[3,4-c]pyridine unit can produce good delocalization between the donor and the acceptor, leading to a broad IPCE. It is worth noting that the IPCEs for DSSCs based on these dyes Y1–Y6 containing hexylthiophene units are higher than that of dyes Y7–Y9. Generally, the IPCE is a product of the electron injection yield and charge collection efficiency.[18] The higher IPCE values of the DSSCs sensitized by dyes Y1–Y6 indicate that the alkyl chains can reduce intermolecular aggregation and improve electron injection efficiency. The solar cell based on Y4 exhibits the highest IPCE value in the range of 300~780 nm. The result also indicates that Y4 possesses the best light harvesting ability and would generate the highest photocurrent among these dyes.
Figure 7.7. IPCE curves of organic dyes Y1–Y9.

The photocurrent-voltage characteristics of all devices are shown in Figure 7.8. The photovoltaic parameters of DSSCs fabricated with these dyes, i.e., short-circuit current ($J_{sc}$), open-circuit photovoltage ($V_{oc}$), fill factor (FF), and total power conversion efficiency ($\eta$), are collected in Table 7.2. Under standard global AM 1.5 solar irradiation, DSSC based on Y4 exhibited the best overall sunlight to electricity conversion efficiency of 6.30% with a $J_{sc}$ of 12.54 mA cm$^{-2}$, an $V_{oc}$ of 0.749 V, and a FF of 0.671. With a relatively lower $J_{sc}$ and $V_{oc}$, solar cells based on Y5 and Y6 show inferior efficiencies of 3.60% ($J_{sc}=7.54$ mA cm$^{-2}$, $V_{oc}=0.699$ V and FF=0.683) and 3.47% ($J_{sc}=7.90$ mA cm$^{-2}$, $V_{oc}=0.634$ V and FF=0.693), respectively. The lower photocurrent of the device sensitized with dyes Y5 and Y6 is mainly attributed to the disadvantaged electron injection efficiency with respect to Y4, which can be confirmed by IPCE spectra. The three dyes Y4–Y6 display a
wide spectral coverage of 300–780 nm, but the maximum IPCE at 550 nm for dye Y4 is 45% as compared to 30% for dye Y6 and 20% for dye Y5. Obviously, Y4 is the most effective in the process of the electron injection from the excited sensitizer to the conductive band of TiO2. The main reason is that the introduction of a twisted benzene spacer can interrupt the co-planarity of π-conjugation between the donor and acceptor and inhibit the back electron transfer,\(^{[15]}\) as a result, the charge recombination rate can be slowed down to a great extent and the dye Y4 gives the highest \(V_{oc}\) value among the three dyes. Similar with Y4–Y6, Y1 and Y7 perform the highest \(J_{sc}\) and \(V_{oc}\) values for Y1–Y3 and Y7–Y9, respectively. Finally, the Y1–Y3 sensitized solar cells give a \(J_{sc}\) of 9.05, 8.42 and 6.47 mA/cm\(^2\), a \(V_{oc}\) of 0.717, 0.657 and 0.655 V, and a FF of 0.687, 0.694 and 0.672, corresponding to an overall conversion efficiency of 4.46%, 3.84% and 2.89%, respectively. Under the same condition, the photovoltaic parameters (\(J_{sc}, V_{oc}, FF\) and \(\eta\)) of cell sensitized by Y7–Y9 are 3.24 mA cm\(^{-2}\), 0.650 V, 0.627, and 1.32 %; 3.19 mA cm\(^{-2}\), 0.585 V, 0.590, and 1.10 %; 1.56 mA cm\(^{-2}\), 0.547 V, 0.539, and 0.46 %, respectively. Remarkably, the cells sensitized with the dyes Y7–Y9 without hexyl chains on the thiophene units show greatly inferior \(J_{sc}\) and \(V_{oc}\), leading to a significantly lower PCEs, even though they have much higher molar extinction coefficient and broader absorption spectral response. The dramatic reduction of photocurrent is attributed to the good planarity of thiophene-bridged Y7–Y9, which is liable to form intermolecular π-π stacked aggregation on the TiO\(_2\) surface, leading to a decrease in the yield of electron injection owing to intermolecular energy transfer. Also, hexylthiophene-bridged dyes are more effective than the
thiophene-bridged dyes for blocking I$_3^-$ ions approaching the TiO$_2$ surface for charge recombination, thus show a decrease in $V_{oc}$ due to the relative larger dihedral angle. It can be concluded that these dyes containing benzene unit as the π-linker would exhibit better device performances.

Figure 7.8. $J – V$ curves of Y1–Y9 sensitized solar cells.

7.2.5 Electrochemical Impedance Spectroscopy Analysis

Electrochemical Impedance Spectroscopies (EIS) analysis can be used to elucidate the interfacial charge recombination process in DSSCs based on these dyes under a forward bias of −0.73 V in the dark. In the Nyquist plots (Figure 7.9), a major semicircle is observed for each dye, which is related to the transport process at the interfaces between TiO$_2$ and electrolyte/dye.$^{[16]}$ The charge recombination resistance at the TiO$_2$ surface ($R_{rec}$) can be deduced by fitting the curves using Z-view software. This value is related to the charge recombination
rate, \textit{e.g.}, a smaller $R_{\text{rec}}$ indicates a faster charge recombination with I$_3^-$ ions in the electrolyte, thus a smaller $V_{\text{oc}}$. The radius of the major semicircles in Nyquist plots for DSSCs based on the two dyes increases in the order $Y_9 < Y_8 < Y_6 < Y_7 < Y_2 < Y_3 < Y_5 < Y_1 < Y_4$. The trend observed is consistent with the results yielded here for the $V_{\text{oc}}$ value. Among $Y_1$–$Y_9$, $Y_6$ sensitized DSSCs shows the highest $V_{\text{oc}}$ up to 0.749 V, indicating that the electron recombination rate between the TiO$_2$ film and the electrolyte is effectively retarded by the introduction of hexylthiophene and twisted benzene.

\textbf{Figure 7.9.} EIS Nyquist plots for DSSCs based on $Y_1$–$Y_9$ under dark.
Table 7.2. Photovoltaic parameters in DSSCs based on Y1–Y9 at full sunlight (AM 1.5G, 100 mW cm\(^{-2}\)).\(^{[a]}\)

<table>
<thead>
<tr>
<th>Dye</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>(V_{oc}) (V)</th>
<th>FF</th>
<th>(\eta) (%)</th>
<th>(R_{rec}) (Ω cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y1</td>
<td>9.05</td>
<td>0.717</td>
<td>0.687</td>
<td>4.46</td>
<td>132.1</td>
</tr>
<tr>
<td>Y2</td>
<td>8.42</td>
<td>0.657</td>
<td>0.694</td>
<td>3.84</td>
<td>54.1</td>
</tr>
<tr>
<td>Y3</td>
<td>6.47</td>
<td>0.665</td>
<td>0.672</td>
<td>2.89</td>
<td>70.2</td>
</tr>
<tr>
<td>Y4</td>
<td>12.54</td>
<td>0.749</td>
<td>0.671</td>
<td>6.30</td>
<td>322.8</td>
</tr>
<tr>
<td>Y5</td>
<td>7.54</td>
<td>0.699</td>
<td>0.683</td>
<td>3.60</td>
<td>77.9</td>
</tr>
<tr>
<td>Y6</td>
<td>7.90</td>
<td>0.634</td>
<td>0.693</td>
<td>3.47</td>
<td>49.3</td>
</tr>
<tr>
<td>Y7</td>
<td>3.24</td>
<td>0.650</td>
<td>0.627</td>
<td>1.32</td>
<td>50.1</td>
</tr>
<tr>
<td>Y8</td>
<td>3.19</td>
<td>0.585</td>
<td>0.590</td>
<td>1.10</td>
<td>43.6</td>
</tr>
<tr>
<td>Y9</td>
<td>1.56</td>
<td>0.547</td>
<td>0.539</td>
<td>0.46</td>
<td>41.3</td>
</tr>
</tbody>
</table>

7.3 Conclusions

In summary, a series of strong electron-withdrawing unit thiadiazolo[3,4-c]-pyridine-based sensitizers (Y1–Y9) comprising a dihexyloxy-substituted triphenylamine as the donor, cyanoacetic acid as the acceptor, and benzene, hexylthiophene and thiophene moiety as the conjugation linker were synthesized and applied in DSSCs applications. The incorporation of thiadiazolo[3,4-c]pyridine unit in the \(\pi\)-conjugation frameworks can effectively lower the energy bandgaps of these organic sensitizers and redshift the absorption spectral coverage into the NIR region. The overall conversion efficiencies of liquid-electrolyte DSSCs based on these sensitizers range from 0.46 to 6.30%, in
which $Y_4$-based DSSCs shows the best photovoltaic performance: a short-circuit photocurrent density ($J_{sc}$) of 12.54 mA cm$^{-2}$, an open-circuit photovoltage ($V_{oc}$) of 0.749 V, and a fill factor (FF) of 0.671, under standard global AM 1.5 solar light condition. These dyes ($Y_1$–$Y_6$) containing hexylthiophene as the $\pi$-conjugated spacer exhibit higher photocurrent and photovoltage than that of thiophene-functioned dyes ($Y_7$–$Y_9$), owing to the attached hexyl chains can effectively suppress dye-dye stacked aggregation on TiO$_2$ film, thus enhancing electron injection from the excited sensitizers, and also retarding charge recombination by shielding the surface of TiO$_2$ from the I$_3^-$ ions. In comparison with hexylthiophene and thiophene units as the $\pi$-conjugated linkers beside the cyanoacetic acid, the three sensitizers ($Y_1$, $Y_4$, and $Y_7$) featuring benzene unit based DSSCs produce higher photocurrent and photovoltage, which are attributed to the out-of-plane twist of the additional phenyl ring interrupt the $\pi$-conjugation between the donor and acceptor, suppressing intermolecular $\pi$-$\pi$ stacked aggregation on the TiO$_2$ surface as well as back electron transfer, which lead to the enhanced electron injection efficiency and the reduced charge recombination rate. The primary findings will facilitate our understanding of the crucial importance of structure-function relationships on optimizing metal-free organic dyes for highly efficient DSSCs.

7.4 Experimental Section

Materials. All solvents and reagents were purchased from Sigma-Aldrich Company and used as received without further purification. TiO$_2$ paste and
iodide-based liquid electrolyte (HL-HPE) were purchased from Dyesol company.

The important intermediates of 4,7-Dibromo-2,1,3-azabenzothiadiazole,[11a] 4,7-bis(5-bromothiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine,[11b] 4,7-bis(5-bromo-3-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine,[11b] 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde, 3-hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carbaldehyde,[7d,17] 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carbaldehyde,[7d,17] and 4-(hexyloxy)-N-(4-(hexyloxy)phenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline[17] were synthesized according to the corresponding literature methods. The synthetic routs of these dyes Yn are outlined in Scheme 7.1 and the details are depicted as follows.
4-(7-bromo-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)-N,N-bis(4-(hexyloxy)phenyl)anilie (1)

The mixture of 4,7-dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine (0.5 g, 1.7 mmol), 4-(hexyloxy)-N-(4-(hexyloxy)phenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (1.0 g, 1.8 mmol), Pd(PPh₃)₄ (100 mg, 0.016 mmol) and 2N aqueous solution of K₂CO₃ (2 mL) in THF (50 mL) under N₂ atmosphere was heated to reflux for about 12 h. Then the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 1:4 mixture of hexane and CH₂Cl₂ as eluent to afford the red compound. Yield: 0.81 g, (72%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.69 (s, 1H), 8.42 (d, J = 6.4 Hz, 2H), 7.14 (t, J = 6.4 Hz, 2H), 6.99-7.06 (m, 4H), 6.80-6.88 (m, 4H). HRMS (MALDI-TOF, m/z): [M+] calcd for (C₃₅H₃₉BrN₄O₂S) 658.2034; found, 658.1907.

4-(hexyloxy)-N-(4-(hexyloxy)phenyl)-N-(4-(7-(3-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)phenyl)aniline (2)

A mixture of 1 (0.8 g, 1.14 mmol), tributyl(3-hexylthiophen-2-yl)stannane (1.5 mmol), Pd(PPh₃)₄ (100 mg, 0.016 mmol) in toluene (50 mL) was heated to reflux under a N₂ atmosphere for about 12 hrs. Then, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 1:4 mixture of hexane and CH₂Cl₂ as eluent to afford the dark red compound. Yield: 0.8 g, (90%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.61 (s, 1H), 8.49 (d, J = 2.0 Hz, 1H), 7.83 (t, J = 2.0 Hz, 1H), 7.81 (t, J = 2.0 Hz, 1H), 7.15 (d, J = 2.0 Hz, 1H), 7.13 (t, J = 2.0 Hz, 2H), 7.10 (t, J = 2.0 Hz, 2H), 7.05 (t,
J = 2.0 Hz, 1H), 7.03 (t, J = 2.0 Hz, 1H), 6.86 (t, J = 2.0 Hz, 2H), 6.83 (t, J = 2.0 Hz, 2H), 3.93 (t, J = 6.0 Hz, 4H), 2.72 (t, J = 7.2 Hz, 2H), 1.50-1.72 (m, 6H), 1.46-1.50 (m, 4H), 1.31-1.39 (m, 14H), 0.89-0.96 (m, 9H). 13C NMR (400 MHz, CDCl3): δ (ppm) 156.31, 155.94, 149.40, 148.30, 146.05, 145.15, 141.60, 141.50, 140.09, 132.77, 129.56, 127.21, 126.07, 125.64, 125.18, 119.53, 115.37, 68.27, 31.74, 31.66, 30.74, 30.51, 29.36, 29.07, 25.81, 22.91, 22.68, 14.18, 14.12. HRMS (MALDI-TOF, m/z): [M+] calcd for (C48H44N4O2S2) 746.3746; found, 746.3749.

4-(7-(5-bromo-3-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)-N, N-bis(4-(hexyloxy)phenyl)aniline (3)

NBS (200 mg, 1.15 mmol) was added in one portion to the solution of 2 (0.8 g, 1.07 mmol) in THF (50 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirring was continued for 1.5 h. Then, the reaction was quenched by addition of water (50 mL), and extracted with dichloromethane. The collected organic layer was evaporated under vacuum and the residue was purified by column chromatography on silica gel with a 1:4 mixture of hexane and CH2Cl2 as eluent to afford the dark red compound. Yield: 0.88 g, (87%). 1H NMR (400 MHz, CDCl3): δ (ppm) 8.62 (s, 1H), 8.48 (d, J = 2.0 Hz, 1H), 7.84 (t, J = 2.0 Hz, 1H), 7.80 (t, J = 2.0 Hz, 1H), 7.16 (d, J = 2.0 Hz, 1H), 7.13 (t, J = 2.0 Hz, 2H), 7.10 (t, J = 2.0 Hz, 2H), 7.06 (t, J = 2.0 Hz, 1H), 7.02 (t, J = 2.0 Hz, 1H), 6.86 (t, J = 2.0 Hz, 2H), 6.83 (t, J = 2.0 Hz, 1H), 3.94 (t, J = 6.0 Hz, 4H), 2.73 (t, J = 7.2 Hz, 2H), 1.50-1.72 (m, 6H), 1.46-1.50 (m, 4H), 1.31-1.39 (m, 14H), 0.89-0.96 (m, 9H). 13C NMR (400 MHz, CDCl3): δ (ppm) 156.32, 155.92, 149.40, 148.30, 146.05,
145.15, 141.60, 141.50, 140.09, 132.77, 129.56, 127.21, 126.07, 125.64, 125.17, 119.52, 115.97, 68.27, 31.74, 31.66, 30.74, 30.51, 29.36, 29.07, 25.81, 22.91, 22.68, 14.18, 14.13.

HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{45}H_{53}N_{4}O_{2}S_{2}) 824.2845; found, 824.2877.

General synthetic procedures for 4-14 are similar with 1.

4-(5-(4-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4-hexylthiophen-2-yl)benzaldehyde (4)

A purple compound. Yield: 0.21 g, (73%). 1H NMR (400 MHz, CDCl3): δ (ppm) 10.06 (s, 1H), 8.64 (s, 1H), 8.55 (s, 1H), 7.94-7.97 (m, 2H), 7.82-7.85 (m, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.10-7.14 (m, 4H), 7.03-7.07 (m, 2H), 6.85-6.89 (m, 4H), 3.94 (t, J = 6.0 Hz, 4H), 2.93 (t, J = 7.2 Hz, 2H), 1.61-1.78 (m, 6H), 1.36-1.49 (m, 4H), 1.27-1.35 (m, 14H), 0.85-0.93 (m, 9H). 13C NMR (400 MHz, CDCl3): δ (ppm) 191.64, 156.31, 156.01, 149.54, 148.36, 145.42, 142.06, 141.58, 141.05, 140.95, 140.72, 140.01, 135.29, 134.08, 130.06, 129.60, 129.54, 127.26, 126.47, 125.46, 119.43, 115.40, 68.29, 31.63, 31.61, 30.85, 29.73, 29.34, 29.27, 25.79, 22.65, 22.63, 14.09, 14.08. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{52}H_{58}N_{4}O_{3}S_{2}) 850.4013; found, 850.4022.

5’-(4-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4,4’-dihexyl-[2,2’-bithiophene]-5-carbaldehyde (5)

A purple compound. Yield: 0.17 g, (70%). 1H NMR (400 MHz, CDCl3): δ (ppm) 9.91 (s, 1H), 8.64 (s, 1H), 8.52 (s, 1H), 7.83 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.38 (d, J = 4.0 Hz, 1H), 7.12-7.14 (m 4H), 7.03 (d, J = 8.0 Hz, 2H), 6.85-6.88 (m, 3H), 3.94 (t, J = 6.0 Hz, 4H), 2.90-2.94 (m, 4H), 1.75-1.82 (m, 4H),
1.43-1.47 (m, 4H), 1.29-1.36 (m, 14H), 0.87-0.92 (m, 12H). $^1$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 182.71, 156.31, 156.01, 149.54, 148.36, 145.42, 142.06, 141.58, 141.13, 141.05, 140.72, 140.01, 135.05, 134.51, 130.06, 129.76, 129.61, 127.29, 126.75, 125.46, 119.34, 115.38, 68.28, 31.71, 31.65, 31.61, 30.85, 30.27, 30.15, 29.73, 29.34, 27.88, 26.89, 25.80, 22.67, 22.63, 17.56, 14.16, 14.11, 13.67. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{58}$H$_{66}$N$_4$O$_3$S$_3$) 940.4517; found, 940.4523.

5'-{(4-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4'-hexyl-[2,2'-bithiophene]-5-carbaldehyde (6)

A purple compound. Yield: 0.18 g, (74%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.89 (s, 1H), 8.64 (s, 1H), 8.56 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.69 (s, 1H), 7.12 (d, J = 8.8 Hz, 5H), 7.04 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 4H), 3.94 (t, J = 6.8 Hz, 4H), 2.94 (t, J = 6.8 Hz, 2H), 1.75-1.82 (m, 4H), 1.45-1.48 (m, 6H), 1.25-1.36 (m, 14H), 0.87-0.92 (m, 9H). $^1$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 182.88, 156.32, 156.02, 149.58, 148.35, 145.26, 144.91, 143.95, 142.74, 142.27, 141.55, 139.99, 139.45, 137.70, 133.01, 132.05, 129.63, 127.26, 126.61, 125.40, 119.42, 115.40, 68.29, 31.63, 31.59, 30.72, 29.33, 27.87, 25.79, 22.65, 22.61, 17.55, 14.08, 14.11. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{50}$H$_{56}$N$_4$O$_3$S$_3$) 856.3547; found, 856.3543.

4-(5-(7-(5-bromo-3-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)-4-hexylthiophen-2-yl)-N,N-bis(4-(hexyloxy)phenyl)aniline (7)

A dark red compound. Yield: 0.67 g, (76%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.63 (s, 1H), 8.54 (t, J = 4.0 Hz, 2H), 7.76 (d, J = 4.0 Hz, 1H), 7.43-7.48 (m, 2H), 7.05-7.16 (m, 4H), 6.97 (s, 1H), 6.90 (s, 1H), 6.86-6.89 (m,
4H), 3.94 (t, J = 7.2 Hz, 4H), 1.76-1.80 (m, 4H), 1.47-1.56 (m, 4H), 1.33-1.38 (m, 8H), 0.91 (t, J = 7.6 Hz, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 155.90, 154.52, 150.33, 149.21, 147.83, 146.49, 140.47, 140.01, 138.98, 138.29, 133.74, 130.80, 127.23, 127.06, 126.65, 125.24, 123.44, 119.63, 118.78, 115.34, 114.45, 68.26, 31.74, 31.65, 31.66, 30.99, 30.83, 29.45, 29.34, 29.25, 29.16, 25.86, 25.03, 22.65, 22.66, 22.46, 14.15, 14.12, 14.10 HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{55}$H$_{67}$BrN$_4$O$_2$S$_3$) 990.3648; found, 990.3643.

4-(5-(7-(5-bromothiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)thiophen-2-yl)-N,N-bis(4-(hexyloxy)phenyl)aniline (8)

A dark red compound. Yield: 0.89 g, (78%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.65 (s, 1H), 8.53 (t, J = 4.0 Hz, 2H), 7.72 (d, J = 4.0 Hz, 1H), 7.47-7.49 (m, 2H), 7.06-7.11 (m, 4H), 6.92 (s, 1H), 6.90 (s, 1H), 6.86-6.89 (m, 4H), 3.94 (t, J = 7.2 Hz, 4H), 1.75-1.80 (m, 4H), 1.43-1.49 (m, 4H), 1.33-1.37 (m, 8H), 0.90 (t, J = 7.6 Hz, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 155.90, 154.51, 150.13, 149.22, 147.89, 146.49, 140.47, 140.00, 138.95, 138.29, 133.74, 130.80, 127.20, 127.06, 126.65, 125.20, 123.44, 119.63, 118.77, 115.34, 114.43, 68.27, 31.66, 29.36, 25.82, 22.68, 14.12. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{43}$H$_{43}$BrN$_4$O$_2$S$_3$) 822.1747; found, 822.1741.

4-(5-(7-(5-(4-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-3-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4-hexylthiophen-2-yl)benzaldehyde (9)

A purple red compound. Yield: 0.24 g, (81%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 10.05 (s, 1H), 8.77 (s, 1H), 8.51 (s, 1H), 7.93-7.97 (m, 3H), 7.67 (d, J = 8.4 Hz, 2H), 7.32-7.34 (m, 2H), 7.09-7.13 (m, 4H), 6.94 (t, J = 8.8 Hz, 2H), 6.85-6.89
(m, 4H), 3.94 (t, J = 6.8 Hz, 4H), 2.72-2.78 (m, 4H), 1.62-1.78 (m, 6H), 1.40-1.48 (m, 4H), 1.27-1.38 (m, 22H), 0.89-0.93 (m, 12H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 191.68, 155.86, 154.82, 148.71, 148.11, 146.55, 144.72, 141.44, 140.90, 140.63, 140.17, 140.08, 138.05, 137.85, 136.30, 135.08, 131.78, 131.09, 130.52, 130.06, 129.57, 129.49, 127.13, 125.46, 119.28, 115.35, 68.26, 31.72, 31.63, 31.62, 30.99, 30.89, 29.35, 29.32, 29.24, 29.14, 25.80, 25.07, 22.69, 22.66, 22.45, 14.17, 14.12, 14.10. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{62}$H$_{72}$N$_{4}$O$_3$S$_3$) 1016.4845; found, 1016.4841.

5'-(4-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-3-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4,4'-dihexyl-[2,2'-bithiophene]-5-carbaldehyde (10)

A purple compound. Yield: 0.20 g, (84%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.88 (s, 1H), 8.75 (d, J = 4.0 Hz, 1H), 8.52 (d, J = 4.0 Hz, 1H), 7.99 (d, J = 4.0 Hz, 1H), 7.67 (s, 1H), 7.32-7.35 (m, 3H), 7.07-7.12 (m, 2H), 6.94 (d, J = 8.8 Hz, 3H), 6.84-6.96 (m, 4H), 3.94 (t, J = 7.2 Hz, 4H), 2.70-2.79 (m, 6H), 1.60-1.78 (m, 6H), 1.41-1.49 (m, 8H), 1.30-1.38 (m, 13H), 0.83-0.94 (m, 15H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 182.87, 155.87, 154.78, 148.73, 148.09, 146.67, 144.83, 143.91, 142.65, 141.02, 140.17, 140.10, 139.39, 138.04, 137.72, 137.53, 135.14, 129.57, 129.44, 128.78, 127.13, 125.46, 119.28, 119.07, 115.35, 100.41, 68.26, 31.72, 31.65, 31.61, 31.00, 30.77, 30.61, 29.35, 29.32, 29.21, 29.17, 29.05, 28.99, 27.99, 27.88, 27.76, 26.89, 25.81, 22.69, 22.63, 22.59, 17.55, 14.18, 14.13. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{66}$H$_{82}$N$_4$O$_3$S$_4$) 1106.5349; found, 1106.4847.
5’-(4-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-3-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4’-hexyl-[2,2’-bithiophene]-5-carbaldehyde (11)

A purple compound. Yield: 0.18 g, (77%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.84 (s, 1H), 8.75 (d, $J = 4.0$ Hz, 1H), 8.60 (d, $J = 4.0$ Hz, 1H), 8.37 (d, $J = 4.0$ Hz, 1H), 7.32-7.39 (m, 3H), 7.09-7.12 (m, 2H), 6.92 (d, $J = 8.8$ Hz, 3H), 6.84-6.94 (m, 4H), 3.94 (t, $J = 7.2$ Hz, 4H), 2.67-2.78 (m, 4H), 1.69-1.79 (m, 4H), 1.62-1.68 (m, 8H), 1.41-1.49 (m, 8H), 1.30-1.37 (m, 12H), 0.83-0.93 (m, 12H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 182.50, 155.88, 154.39, 148.68, 147.84, 146.39, 145.93, 144.90, 142.92, 142.23, 140.89, 140.15, 139.98, 137.90, 136.78, 136.54, 130.93, 130.57, 129.49, 127.13, 126.99, 126.08, 125.43, 119.23, 118.50, 115.36, 68.27, 31.73, 31.66, 30.96, 30.19, 30.02, 29.37, 29.27, 27.88, 26.89, 25.82, 22.72, 22.67, 17.56, 14.19, 14.17, 14.11, 13.66. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{60}$H$_{70}$N$_4$O$_3$S$_4$) 1022.4351; found, 1022.4447.

4-(5-(4-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)benzaldehyde (12)

A purple compound. Yield: 0.16 g, (74%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.95 (s, 1H), 8.72 (s, 1H), 8.50 (d, $J = 7.2$ Hz, 1H), 7.96-8.00 (m, 6H), 7.85 (d, $J = 7.2$ Hz, 2H), 7.73-7.79 (m, 2H), 7.43-7.48 (m, 4H), 7.23 (d, $J = 8.8$ Hz, 1H), 7.07-7.09 (m, 2H), 6.84-6.87 (m, 2H), 3.94 (t, $J = 7.2$ Hz, 4H), 2.67-2.78 (m, 4H), 1.75-1.80 (m, 4H), 1.45-1.49 (m, 4H), 1.33-1.37 (m, 8H), 0.93 (d, $J = 8.8$ Hz, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 182.53, 155.89, 154.34, 148.65, 147.83, 146.33, 145.93, 144.90, 142.91, 142.23, 140.33, 140.14, 139.97, 137.88, 136.78,
5'-(4-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4-hexyl-[2,2'-bithiophene]-5-carbaldehyde (13)

A purple compound. Yield: 0.19 g, (71%). 1H NMR (400 MHz, CDCl3): δ (ppm) 9.83 (s, 1H), 8.79 (s, 1H), 8.61 (d, J = 4.0 Hz, 1H), 8.04 (d, J = 4.0 Hz, 1H), 7.60 (s, 1H), 7.50 (d, J = 4.0 Hz, 2H), 7.35 (d, J = 4.0 Hz, 1H), 7.31 (d, J = 4.0 Hz, 1H), 7.09 (t, J = 4.0 Hz, 2H), 7.06 (t, J = 4.0 Hz, 2H), 6.91-6.94 (m, 2H), 6.84-6.87 (m, 4H), 3.94 (t, J = 6.8 Hz, 4H), 2.87 (t, J = 7.6 Hz, 2H), 1.75-1.87 (m, 4H), 1.42-1.49 (m, 8H), 1.34-1.41 (m, 12H), 0.87-0.93 (m, 9H). 13C NMR (400 MHz, CDCl3): δ (ppm) 182.53, 155.93, 154.70, 150.37, 149.30, 148.03, 146.71, 141.01, 140.89, 140.85, 140.51, 139.98, 139.04, 138.66, 136.23, 133.88, 128.34, 127.96, 127.06, 126.70, 125.21, 123.53, 125.41, 119.63, 118.95, 115.37, 68.29, 31.64, 30.96, 30.32, 29.63, 29.35, 29.23, 25.80, 22.72, 22.65, 14.16, 14.09. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{50}H_{48}N_{4}O_{3}S_{3}) 848.2901; found, 848.2917.

5'-(4-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4-hexyl-[2,2'-bithiophene]-5-carbaldehyde (14)

A purple compound. Yield: 0.23 g, (76%). 1H NMR (400 MHz, CDCl3): δ (ppm) 9.65 (s, 1H), 8.40 (d, J = 4.0 Hz, 1H), 8.21 (d, J = 4.0 Hz, 1H), 7.57-7.62 (m, 2H), 7.42 (d, J = 4.0 Hz, 1H), 7.28-7.32 (m, 2H), 6.96-7.04 (m, 6H), 6.74-6.77 (m, 8H), 3.85 (t, J = 6.8 Hz, 4H), 1.66-1.73 (m, 2H), 1.35-1.40 (m, 4H), 1.16-1.28 (m, 7H), 0.85 (t, J = 7.6 Hz, 6H). 13C NMR (400 MHz, CDCl3): δ (ppm) 182.55, 155.96,
ATPase, [M+] calcd for (C<sub>48</sub>H<sub>46</sub>N<sub>4</sub>O<sub>3</sub>S<sub>4</sub>) 854.2532; found, 854.2468.

**General synthetic procedures for the preparation of dyes Y1-Y9.**

A mixture of the precursor carbaldehyde (0.20 mmol) and cyanoacetic acid (100 mg, 1.30 mmol) in acetic acid (20 mL) was refluxed in the presence of ammonium acetate (200 mg) overnight under a N<sub>2</sub> atmosphere. Then, water was added and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Next, the solvent was removed under vacuum and the crude compound was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (20:1, v/v) to give targeted dyes.

**(E)-3-(4-(5-(4-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4-hexylthiophen-2-yl)phenyl)-2-cyanoacrylic acid (Y1)**

A dark purple compound. Yield: 0.12 g, (69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ (ppm) 8.51 (s, 1H), 8.39 (s, 1H), 8.12 (s, 1H), 7.84 (d, J = 1.6 Hz, 2H), 7.77 (t, J = 6.8 Hz, 2H), 7.61 (s, 1H), 7.26 (d, J = 3.6 Hz, 1H), 7.02 (d, J = 9.2 Hz, 4H), 6.86 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 4H), 3.86 (t, J = 6.4 Hz, 4H), 2.81 (t, J = 7.6 Hz, 2H), 1.64-1.71 (m, 6H), 1.35-1.41 (m, 6H), 1.16-1.27 (m, 12H), 0.79-0.84 (m, 9H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ (ppm) 167.65, 157.60, 155.55, 148.87, 147.48, 143.33, 142.08, 141.14, 140.84, 140.15, 139.25, 137.95, 137.07, 136.17, 135.94, 133.86, 133.72, 133.27, 129.45, 127.00, 126.51, 125.64, 124.79, 118.33, 115.28, 67.59, 31.07, 31.04, 29.82, 29.52, 29.43.
(E)-3-((5'-((4-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-[1,2,5]thiadiazolo[3,4-c]
pyridin-7-yl))-4,4'-dihexyl-[2,2'-bithiophen]-5-yl)-2-cyanoacrylic acid (Y2)

A dark purple compound. Yield: 0.11 g, (71%). \(^1\)H NMR (400 MHz, CDCl\(_3\) + DMSO-\(d_6\)): \(\delta\) (ppm) 8.59 (s, 1H), 8.49 (s, 1H), 8.17 (s, 1H), 7.83 (d, \(J = 8.4\) Hz, 2H), 7.68 (s, 1H), 7.02 (d, \(J = 8.4\) Hz, 4H), 6.82-6.87 (m, 6H), 3.88 (t, \(J = 6.4\) Hz, 4H), 2.55-2.63 (m, 4H), 1.60-1.70 (m, 4H), 1.52-1.58 (m, 6H), 1.36-1.41 (m, 4H), 1.24-1.31 (m, 18H), 0.79-0.86 (m, 12H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\) + DMSO-\(d_6\)): \(\delta\) (ppm) 155.53, 154.33, 148.92, 147.54, 144.18, 144.01, 142.86, 141.82, 141.27, 140.81, 139.26, 136.00, 135.69, 132.50, 131.46, 129.42, 128.70, 126.93, 125.78, 124.82, 122.21, 118.42, 117.25, 115.21, 112.15, 67.59, 31.03, 30.98, 30.97, 30.13, 29.86, 28.73, 28.43, 28.36, 27.65, 26.44, 25.22, 22.09, 21.98, 13.80, 13.77, 13.57. HRMS (MALDI-TOF, m/z): [M+] calcd for (C\(_{59}\)H\(_{69}\)N\(_5\)O\(_4\)S\(_3\)) 1009.4812; found, 1009.4832.

(E)-3-((5'-((4-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-[1,2,5]thiadiazolo[3,4-c]
pyridin-7-yl))-4'-hexyl-[2,2'-bithiophen]-5-yl)-2-cyanoacrylic acid (Y3)

A dark purple compound. Yield: 0.10 g, (70%). \(^1\)H NMR (400 MHz, CDCl\(_3\) + DMSO-\(d_6\)): \(\delta\) (ppm) 8.55 (s, 1H), 8.29 (s, 1H), 8.17 (s, 1H), 7.83 (d, \(J = 8.4\) Hz, 2H), 7.68 (s, 1H), 7.02 (d, \(J = 8.4\) Hz, 4H), 6.82-6.87 (m, 6H), 3.88 (t, \(J = 6.4\) Hz, 4H), 2.55-2.63 (m, 4H), 1.60-1.70 (m, 4H), 1.52-1.58 (m, 6H), 1.36-1.41 (m, 4H), 1.24-1.31 (m, 18H), 0.79-0.86 (m, 12H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\) + DMSO-\(d_6\)): \(\delta\) (ppm) 155.43, 155.36, 148.75,
(E)-3-(4-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-3-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4,4'-dihexyl-[2,2'-bithiophen]-5-yl)-2-cyanoacrylic acid (Y5)

A dark purple compound. Yield: 0.14 g, (77%). $^1$H NMR (400 MHz, CDCl$_3$ + DMSO-$d_6$): $\delta$ (ppm) 8.59 (s, 1H), 8.17-8.22 (m, 2H), 8.02 (d, $J = 8.0$ Hz, 2H), 7.83 (s, 1H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 6.94 (d, $J = 8.4$ Hz, 4H), 6.79 (d, $J = 8.4$ Hz, 4H), 6.71 (d, $J = 8.4$ Hz, 2H), 3.86 (t, $J = 2.0$ Hz, 4H), 2.60 (t, $J = 6.0$ Hz, 4H), 1.63-1.70 (m, 5H), 1.36-1.39 (m, 5H), 1.21-1.28 (m, 22H), 0.79-0.86 (m, 12H). $^{13}$C NMR (400 MHz, CDCl$_3$ + DMSO-$d_6$): $\delta$ (ppm) 163.76, 155.96, 154.10, 152.70, 148.63, 147.43, 145.35, 143.77, 141.18, 140.43, 139.78, 139.42, 138.37, 138.15, 137.84, 135.83, 134.45, 131.37, 130.95, 130.48, 129.45, 129.05, 127.43, 124.97, 118.93, 118.68, 116.80, 115.73, 68.06, 31.53, 31.27, 31.03, 30.73, 30.56, 30.24, 29.23, 29.12, 29.03, 26.24, 25.73, 24.71, 24.03, 22.59, 14.37, 14.34. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{65}$H$_{73}$N$_5$O$_4$S$_3$) 1084.4903; found, 1084.4940.

(E)-3-(5'-(4-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)amino)phenyl)-3-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4,4'-dihexyl-[2,2'-bithiophen]-5-yl)-2-cyanoacrylic acid (Y5)
A dark purple compound. Yield: 0.13 g, (67%). $^1$H NMR (400 MHz, CDCl$_3$ + DMSO-$d_6$): $\delta$ (ppm) 8.70 (s, 1H), 8.32 (s, 1H), 8.28 (s, 1H), 7.95 (s, 1H), 7.76 (s, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 6.97 (d, $J = 8.0$ Hz, 4H), 6.75-6.80 (m, 6H), 3.86 (t, $J = 6.0$ Hz, 4H), 2.48-2.59 (m, 6H), 1.62-1.70 (m, 5H), 1.54-1.58 (m, 8H), 1.32-1.39 (m, 5H), 1.19-1.28 (m, 22H), 0.84-1.09 (m, 15H). $^{13}$C NMR (400 MHz, CDCl$_3$ + DMSO-$d_6$): $\delta$ (ppm) 163.63, 155.47, 153.83, 150.69, 149.70, 148.24, 147.08, 145.33, 144.94, 144.65, 143.58, 143.41, 142.84, 140.41, 139.29, 139.15, 137.67, 136.64, 135.50, 134.31, 132.15, 129.01, 128.51, 126.90, 124.46, 118.42, 118.25, 116.53, 115.18, 67.57, 31.06, 31.04, 31.00, 30.90, 30.36, 30.31, 30.11, 29.85, 29.05, 28.74, 28.66, 28.53, 28.39, 28.19, 27.63, 26.42, 25.23, 22.09, 22.04, 22.00, 13.85, 13.81, 13.56. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{60}$H$_{83}$N$_3$O$_4$S$_4$) 1174.5406; found, 1174.5401.

(E)-3-(5'-(4-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-3-hexylthiophen-2-yl)-1-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4'-hexyl-[2,2'-bithiophen]-5-yl)-2-cyanoacrylic acid (Y6)

A dark purple compound. Yield: 0.16 g, (67%). $^1$H NMR (400 MHz, CDCl$_3$ + DMSO-$d_6$): $\delta$ (ppm) 8.34 (s, 1H), 8.10 (s, 1H), 8.02 (s, 1H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.05 (t, $J = 8.0$ Hz, 3H), 6.93 (d, $J = 6.8$ Hz, 4H), 6.73 (t, $J = 7.2$ Hz, 7H), 3.84 (t, $J = 5.6$ Hz, 4H), 2.58 (t, $J = 5.6$ Hz, 2H), 2.45 (t, $J = 5.6$ Hz, 2H), 1.56-1.69 (m, 4H), 1.36-1.38 (m, 7H), 1.16-1.27 (m, 21H), 0.78-0.83 (m, 12H). $^{13}$C NMR (400 MHz, CDCl$_3$ + DMSO-$d_6$): $\delta$ (ppm) 163.85, 155.34, 153.36, 147.97, 146.81, 145.02, 144.74, 144.46, 143.64, 142.12, 139.89, 139.35, 138.90, 138.12, 137.35, 135.79, 134.45, 134.10, 130.55, 129.71, 128.73, 126.67, 126.50,
(E)-3-(4-(5-(4-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid (Y7)

A dark purple compound. Yield: 0.17 g, (71%). \(^1\)H NMR (400 MHz, CDCl\(_3\) + DMSO-\(d_6\)): \(\delta\) (ppm) 8.81 (s, 1H), 8.44 (d, J = 4.0 Hz, 1H), 8.06 (d, J = 4.0 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 4.0 Hz, 1H), 7.47 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 4.0 Hz, 1H), 7.01 (d, J = 4.8 Hz, 4H), 6.85 (d, J = 4.8 Hz, 4H), 6.73 (d, J = 8.0 Hz, 2H), 3.89 (t, J = 6.4 Hz, 4H), 1.65-1.72 (m, 4H), 1.36-1.42 (m, 4H), 1.19-1.30 (m, 8H), 0.86 (t, J = 7.0 Hz, 6H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\) + DMSO-\(d_6\)): \(\delta\) (ppm) 163.41, 155.52, 153.70, 152.97, 149.54, 148.85, 148.65, 147.05, 145.10, 143.49, 143.09, 142.69, 140.20, 139.18, 138.64, 136.85, 136.24, 133.22, 131.67, 130.71, 126.96, 126.30, 125.89, 125.31, 124.28, 123.47, 118.66, 118.43, 115.28, 67.59, 31.03, 30.58, 25.22, 22.09, 13.85. HRMS (MALDI-TOF, m/z): [M+\(^{+}\)] calcd for (C\(_{63}\)H\(_{71}\)N\(_5\)O\(_4\)S\(_4\)) 1090.4467; found, 1090.4507.

(E)-3-(5'-(4-(4-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-4-hexyl-[2,2'-bithiophen]-5-yl)-2-cyanoacrylic acid (Y8)

A dark purple compound. Yield: 0.11 g, (69%). \(^1\)H NMR (400 MHz, CDCl\(_3\) + DMSO-\(d_6\)): \(\delta\) (ppm) 8.49 (s, 1H), 8.03-8.13 (m, 2H), 7.75 (s, 1H), 7.46 (s, 1H), 6.83 (d, J = 4.8 Hz, 4H), 6.59 (d, J = 8.0 Hz, 2H), 4.39 (t, J = 6.4 Hz, 4H), 2.02 (d, J = 4.8 Hz, 4H), 1.58-1.65 (m, 4H), 1.34-1.39 (m, 4H), 1.15-1.24 (m, 8H), 0.85 (t, J = 7.0 Hz, 6H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\) + DMSO-\(d_6\)): \(\delta\) (ppm) 163.34, 155.50, 153.97, 152.47, 149.53, 148.91, 148.51, 146.90, 143.04, 143.02, 142.68, 140.20, 139.18, 138.64, 136.81, 136.23, 133.21, 131.67, 130.71, 126.96, 126.30, 125.89, 125.31, 124.30, 123.47, 118.65, 118.35, 115.28, 67.59, 31.03, 30.50, 25.22, 22.09, 15.85. HRMS (MALDI-TOF, m/z): [M+\(^{+}\)] calcd for (C\(_{63}\)H\(_{71}\)N\(_5\)O\(_4\)S\(_3\)) 916.3025; found, 916.3059.
7.24 (d, J = 7.2 Hz, 2H), 7.08 (d, J = 7.2 Hz, 2H), 6.90 (d, J = 7.2 Hz, 4H), 6.77 (d, J = 4.0 Hz, 4H), 6.65 (d, J = 4.8 Hz, 2H), 3.85 (t, J = 6.4 Hz, 4H), 2.63 (t, J = 6.0 Hz, 2H), 1.35-1.39 (m, 4H), 1.21-1.27 (m, 6H), 1.18-1.24 (m, 14H), 0.81-0.87 (m, 9H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\) + DMSO-\(d_6\)): \(\delta\) (ppm) 162.37, 154.23, 152.65, 147.80, 147.32, 146.21, 145.70, 143.94, 143.38, 143.18, 138.84, 138.62, 137.93, 137.27, 136.49, 136.25, 134.54, 131.78, 126.00, 125.56, 124.85, 123.05, 121.82, 119.18, 117.22, 116.80, 115.80, 115.35, 113.84, 68.76, 29.82, 29.23, 28.11, 27.74, 27.52, 27.46, 23.99, 20.89, 20.85, 12.60, 12.52. HRMS (MALDI-TOF, m/z): [M+] calcd for (C\(_{57}\)H\(_{59}\)N\(_5\)O\(_4\)S\(_4\)) 1006.3528; found, 1006.3547.

(E)-3-(5\(^{\prime}\)-(4-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)-[2,2\(^{\prime}\]-bithiophen]-5-yl)-2-cyanoacrylic acid (Y9)

A dark purple compound. Yield: 0.14 g, (68%). \(^1\)H NMR (400 MHz, CDCl\(_3\) + DMSO-\(d_6\)): \(\delta\) (ppm) 8.75 (s, 1H), 8.47 (s, 1H), 8.18 (s, 1H), 7.97 (s, 1H), 7.63 (d, J = 3.6 Hz, 1H), 7.26-7.42 (m, 5H), 6.99 (d, J = 8.8 Hz, 4H), 6.77 (t, J = 8.4 Hz, 6H), 6.65 (d, J = 4.8 Hz, 2H), 3.87 (t, J = 6.4 Hz, 4H), 1.66-1.70 (m, 4H), 1.37-1.45 (m, 4H), 1.26-1.29 (m, 8H), 0.84 (t, J = 6.8 Hz, 6H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\) + DMSO-\(d_6\)): \(\delta\) (ppm) 164.35, 155.39, 153.65, 149.32, 148.53, 147.06, 145.42, 144.12, 143.55, 139.93, 139.21, 138.32, 137.67, 137.33, 136.48, 134.68, 131.11, 128.48, 127.71, 126.61, 125.93, 124.78, 124.27, 124.03, 122.80, 118.59, 118.00, 116.98, 114.89, 67.68, 31.02, 28.73, 25.18, 22.05, 13.57. HRMS (MALDI-TOF, m/z): [M+] calcd for (C\(_{51}\)H\(_{47}\)N\(_5\)O\(_4\)S\(_4\)) 922.2589; found, 922.2514.
**Measurement and Characterizations.** $^1$H and $^{13}$C NMR spectra were recorded with a Bruker Ultrashield 400 Plus NMR spectrometer. The UV-visible absorption spectra of these dyes were measured in CH$_2$Cl$_2$ solution with a Varian Cary 100 UV-Vis spectrophotometer. Emission spectra were performed using a Photon Technology International (PTI) Alphascan spectrofluorimeter. High-resolution matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer. The cyclic voltammograms (CV) were measured with Versastat II electrochemical work station using a normal three-electrode cell with a Pt working electrode, a Pt wire counter electrode and a Ag/Ag$^+$ reference electrode. The supporting electrolyte was 0.1 M tetra-n-butylammonium hexafluorophosphate in DCM solution. The potential of the reference electrode was calibrated by ferrocene after each set of measurements, and all potentials mentioned in the work were against normal hydrogen electrode.

**Fabrication and characterization of cells.** To make a reasonable comparison, all the anode films for the DSSCs were made under the same standard manner, which are composed of 12 μm thick of transparent layer (TiO$_2$ with diameter of 20 nm) and 6 μm thick of scattering layer (TiO$_2$ nanoparticles with diameter of 200 nm). In specific, a doctor-blade technique was utilized to prepare photoanode (TiO$_2$) films. Firstly, a layer of ca. 6 μm TiO$_2$ paste (20 nm) was doctor-bladed onto the FTO conducting glass and then relaxed at room temperature for 3 min before heating at 150 °C for 6 min, this procedure was repeated once to achieve a film thickness of ca. 12 μm and the resulting surface was finally coated by a scattering
layer (ca. 6 μm) of TiO₂ paste (200 nm). The electrodes were gradually heated under an air flow at 275 °C for 5 min, 325 °C for 5 min, 375 °C for 5 min, 470 °C for 30 min to remove polymers and generate three-dimensional TiO₂ nanoparticle network. After that, the sintered films were soaked with 0.02 M TiF₄ aqueous solution for 45 min at 70°C, washed with deionized water, and further annealed at 450 °C for 30 min. After cooling down to ca. 80°C, the electrodes were immersed into a 5 × 10⁻⁴ M dye bath in CH₂Cl₂ solution for Yn dye series maintained in the dark for 16 hrs. Afterwards, the electrodes were rinsed with ethanol to remove the non-adsorbed dyes and dried in air. Pt counter electrodes were prepared by sputtering method at 15 mA for 90 s at a power of 150 W. Two holes (0.75 mm in diameter) were pre-drilled in the FTO glass for introducing electrolyte. The dye-adsorbed TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt parafilm at about 100 °C. The liquid electrolyte consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I₂ in a mixture of acetonitrile and tert-butyl alcohol (volume ratio, 1:1) was introduced into the cell through the drilled holes at the back of the counter electrode. At last, the holes were sealed by parafilm and covering glass (0.1 mm thickness) at elevated temperature. The effective areas of all the TiO₂ electrodes were 0.24 cm². The current-voltage (J-V) characteristics of the assembled DSSCs were measured by a semiconductor characterization system (Keithley 236) at room temperature in air under the spectral output from solar simulator (Newport) using an AM 1.5G filter with a light power of 100 mW/cm². IPCEs of DSSCs were recorded in Solar Cell QE/IPCE Measurement System.
(Zolix Solar Cell Scan 100) using DC mode. CHI 660D electrochemical workstation was used to characterize the electrochemical properties of the DSSCs. Electrochemical impedance spectroscopy (EIS) was recorded under dark condition over a frequency range of 0.1-105 Hz with an AC amplitude of 10 mV and the parameters were calculated from Z-View software (v2.1b, Scribner Associates, Inc.).

7.5 References


Chapter 8 General Conclusions and Outlook.

The dye-sensitized solar cells (DSSCs) has been considered the “new” generation of solar cell for the 21st century and is a fast growing multi-disciplinary subject. In the near future, this system will promote the acceptance of clean and renewable energy technology, at least by setting new standard of convenience and economy. As one of the crucial parts in DSSCs, it is still challenging to search for optimum sensitizers which are capable of absorbing the whole region of visible light to get the high power conversion efficiency. Promising strategies to gain higher molecular absorptivity of sensitizers, metal-free organic dyes-based ones in this case. The objective of this work is to improve the photovoltaic performance of DSSCs using different types of sensitizers. It is worth noting that a phenothiazine-based dye containing electron-rich nitrogen and sulfur heteroatoms in a heterocyclic structure with high electron-donating ability, and its non-planar butterfly conformation can sufficiently inhibit molecular aggregation and the formation of intermolecular excimers. Meanwhile, the N(10)-substituent on can further enhance the charge separation at the oxide solution interface. Furthermore, the two phenyl groups are arranged in a small torsion angle related to N(10) and S(9) atoms, so that \( \pi \)-delocalization can be extended over the entire chromophore. The structural features of phenothiazine-based dye make it a promising type of sensitizers for DSSCs. Thus, a series of new organic dyes (PT-Cn) based on the phenothiazine unit were synthesized, in which a cyanoacrylate moiety was appended at the C(3) position of the phenothiazine ring as an electron acceptor, a 4-(1-hexyloxy)phenyl
group at the C(7) atom as an electron donor on the opposite side, and an alkyl chain with different length at the N(10) atom of phenothiazine as a block against electrolyte. The molecular design strategy was demonstrated to effectively improve the photovoltaic performance with the best efficiency up to 8.18%, which exceeds the reference Ru(II)-based N719 dye (7.76%) in parallel investigations. Co-sensitization is an effective approach to enhance the device performance through a combination of two or more dyes sensitized on semiconductor films together, extending the light-harvesting ability so as to increase the photocurrents of the devices. To further improve the PCE of PT-C₆, we designed a stepwise approach for co-adsorption of the organic dye PT-C₆ with a porphyrin dye (ZnP) for the fabrication of co-sensitized DSSCs. The co-sensitized PT-C₆ + ZnP device showed significantly enhanced $J_{sc}$ relative to its single-dye sensitized devices. Upon optimization, the device made of the PT-C₆ + ZnP system yielded $J_{sc} = 19.36$ mA cm$^{-2}$, $V_{oc} = 0.735$ V, FF = 0.71 and $\eta = 10.10\%$. This performance is superior to that of single-dye device made from PT-C₆ (8.18%) or ZnP (7.44%) under the same conditions of fabrication.

In DSSCs, dye aggregation and charge recombination limit the light conversion efficiency, incorporating steric hindered groups in the organic sensitizer molecular structure is an effective way to slow down the charge recombination rate and prevent dye aggregation. Thus, we try to extend our works by using phenothiazine as a building group to construct 3D bulky organic dyes, in which the cyanoacrylate acceptor directly attached to the C(3) position of phenothiazine, and the triphenylamine donor group at C(7) on the opposite side of
the acceptor, and different side of bulky substituents, i.e., hexyl, hexyloxybenzene, hexylcarbazole, and dihexylfluorene at N(10) of the phenothiazine periphery as the \( \pi \)-conjugated linker. We have systematically investigated the influence of 3D bulky substituents on the suppression of dye aggregation and charge recombination as well as photovoltaic performance of DSSCs. The molecular design strategy demonstrated that high \( V_{oc} \) can be realized by employing 3D-phenothiazine dyes featuring with a bulky substituents. Impressively, the coadsorbent-free DSSCs based on dye \textbf{TP3} exhibits the photovoltaic performance with the best efficiency up to 8.00 \% in combination with liquid electrolyte under standard global AM 1.5 solar light illumination. However, there is still a need to further improve the energy conversion efficiency of DSSCs to enable successful commercialization in the near future. To achieve this goal, the photosensitizer needs to capture broad absorption covering most of the visible to near-infrared (NIR) region of solar spectrum. Co-sensitized DSSCs using two and more dyes have been proved to be successful strategy to extend the absorption into the red to NIR region. To further improve the PCE of \textbf{TP3}, we designed a stepwise approach for co-adsorption of the organic dye \textbf{TP3} with a NIR dye \textbf{YR6} for the fabrication of co-sensitized solar cells. The co-sensitized \textbf{TP3} and \textbf{YR6} device shows significantly enhanced \( J_{sc} \) relative to its single-dye sensitized devices. Upon optimization, the device made of the \textbf{TP3 + YR6} system yielded \( J_{sc} = 19.18 \text{ mA cm}^{-2}, \ V_{oc} = 0.721 \text{ V}, \ FF = 0.712 \text{ and } \eta = 9.84 \% \); This performance is superior to that of single-dye device made from either \textbf{TP3} (8.00\%) or \textbf{YR6} (2.16\%) under the same conditions of fabrication. The power-conversion efficiency of 9.84\% is
the highest reported efficiency for a squaraine dye-based co-sensitized DSSCs.

To further improve the energy conversion efficiency of metal-free organic DSSCs, a broad and intense light harvesting spectrum in both of the visible and the near-IR region and a low interfacial charge recombination at the TiO$_2$ surface are desirable. Thus, a series of new NIR organic sensitizers incorporation strong electron-withdrawing thia diazolo[3,4-c]pyridine moiety as the conjugated spacer have been designed for DSSCs. The sensitizers exhibit good photovoltaic performance as well as broader incident photon-to-current conversion efficiency spectrum expanding into the long-wavelength visible and NIR region above 850 nm.

Future work of this project may be focused on the design of new NIR photosensitizers and systematic analysis to understand efficiency loss mechanism in the cells.
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List of Publications


