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Synthesis, Characterization and Application Studies of Cyanostilbene-based Molecular Materials with Aggregation-Induced Emission (AIE) Characteristics

LAU Wai Sum

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

Principal Supervisor: Prof. WONG Wai Yeung
Hong Kong Baptist University
August 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: _______________________

Date: August 2014
Abstract

The molecular design, synthesis, spectroscopic and photophysical characterization of a series of cyanostilbene-based compounds are studied in this thesis. The thermal, electrochemical and aggregation induced emission (AIE) properties of these cyanostilbene-based compounds, as well as their application in organic lighting-emitting diodes, live cell imaging, chemical vapor sensor were investigated.

Chapter 1 gives a brief introduction on the aggregation-caused quenching (ACQ) behavior of the conventional organic luminogens and the discovery and proposed mechanism of AIE phenomenon. Furthermore, some examples and the applications of these AIE compounds will be discussed.

In Chapter 2, triphenylamine- and carbazole-containing cyanostilbene-based derivatives are presented. From the examination of the emission profile, they are all AIE-active through comparison of the photoluminescence intensity in dissolved and in aggregated states. Additionally, the calculation of the enhancement ratio ($I/I_0 - 1$) of each fluorophore was performed in order to quantify its AIE effect. One of our cyanostilbene-based luminogens has achieved an enhancement ratio with a value of 1128. This cyanostilbene-based luminogens has also shown good performance in OLED investigation. In addition to the OLEDs application, the selected
cyanostilbene-based luminogens with solid-state emission, cell-permeability and reversible switch-on/off capability have illustrated the positive result in live-cell imaging and chemical vapor sensing.

Conjugated polymer with high molecular weight is the superior option by overcoming the weaknesses of low-molecular-weight luminogens with excellent thin-film form ability and comparatively simple and inexpensive fabrication processes. The design and synthesis of the cyanostilbene-based polymeric chromophores are described in Chapter 3. The polymerization of the AIE-active diacetylene ligands by connection of trans-[Pt(PBu$_3$)$_2$] unit at both ends has successfully retained their AIE behavior. In contrast, the ACQ problem has occurred on the polymers with organic spacers and the AIE-active ligands. From the DFT calculation on the Pt polymers and the blue shift of emission spectra in high water content suggested that the AIE phenomenon of Pt polymers is probably originated from the elimination of the non-radiative intramolecular charge transfer (ICT) process.

Owing to the high demand in red-emitting materials in the applications of electroluminescent devices, fluorescent sensing and bio-imaging, effort has been made to design a system with the new chromophores with donor (D) – acceptor (A) system and thus to synthesize phenothiazine (D)-containing cyanostilbene (A)-based derivatives which are depicted in Chapter 4. Consistent with the conventional
AIE-active luminogens with a successively climb of photoluminescence intensities in response to the increase of water proportion, phenothiazine-containing cyanostilbene-based derivatives has exhibited a V-shape fashion of emission intensity. It suggests that the emission of chromophores started to be quenched due to the increase of solvent polarity, overriding that of the molecular aggregation when a “small” volume of water is being introduced. While aggregate formation was dominant from the addition of a “large” amount of poor solvent, less polar local environment was created which suppressed the non-radiative transition to the ICT state and intensified the emission efficiency. Phenothiazine (D) – cyanostilbene (A) system has created a series of red-emitting chromophores with great tunability for the sake of achieving the desired emission color and better emission efficiency.

To functionalize these AIE-active cyanostilbene-based chromophores, pyridine group was attached to the compounds to take the advantage of its metal-chelating capability, which is discussed in Chapter 5. The AIE features of cyanostilbene-based compounds can be preserved after the introduction of the pyridyl unit. Even it possessed a weak photoluminescence in its dilute solution which suggest that the high electron delocalization within the molecule has rigidified the structure to some extent, it is transformed to a highly emissive state with a high proportion of water. The exclusive variation of emission behavior with obvious bathochromic shift and boost
of emission spectrum in the presence of cadmium-(II) ion has demonstrated its potential metal ion sensing ability.

Chapter 6 and 7 present the concluding remarks and the experimental data of the compounds of Chapter 2 to 5, respectively.
Acknowledgements

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List of Abbreviations and Symbols

Abbreviations

Ar     Aryl
n-Bu   n-Butyl
Me     Methyl
Et     Ethyl
OMe    Methoxy
Ph     Phenyl
R      Substituents
AcOH   Acetic acid
CH₂Cl₂ Dichloromethane
CHCl₃  Chloroform
CCl₄   Tetrachloromethane
DMSO   Dimethyl sulfoxide
DMF    Dimethyl formamide
EtOH   Ethanol
Et₂O   Diethyl ether
Fc     Ferricenyl
TMS    Trimethylsilyl
MeCN   Acetonitrile
MeOH   Methanol
NBS    N-Bromosuccinimide
TPA    Triphenylamine
THF    Tetrahydrofuran
$E_g$  Energy gap
HOMO   Highest occupied molecular orbital
LUMO   Lowest unoccupied molecular orbital
TLC    Thin layer chromatography
IR     Infra-red
NMR    Nuclear magnetic resonance
ppm    Part per million
Hz     Hertz
h Hour
min Minute
lm Lumen
cd Candela
A Ampere
W Watt
s Singlet
d Doublet
t Triplet
m Multiplet
CV Cyclic voltammetry
TGA Thermogravimetric analysis
FT-IR Fourier transform infrared
UV-Vis Ultraviolet-visible
PL Photoluminescence
GPC Gel permeation chromatography
XRD X-ray diffraction
AA Atomic absorption
ICP Inductively coupled plasma
MLCT Metal-to-ligand charge transfer
LE Local excited
ICT Intramolecular charge transfer
TICT Twisted intramolecular charge transfer
$S_0$ Singlet ground state
$S_1$ Singlet excited state
$T_1$ Triplet excited state
$T_d$ Decomposition temperature
DP Degree of polymerization
$M_n$ Number-average molecular weight
$M_w$ Weight-average molecular weight
a.u. Arbitrary unit
eV Electron volt
r.t. Room temperature
ACQ  Aggregation caused quenching
AIE  Aggregation induced emission
AEE  Aggregation enhanced emission
RIR  Restriction of intramolecular rotation
PMMA Poly(methyl methacrylate)
HPS  Hexaphenylsilole
TPE  Tetraphenylethylene
D    Donor
A    Acceptor
EL   Electroluminescence
OLEDs Organic light-emitting diodes
PLEDs Polymer light-emitting diodes
ITO  Indium tin oxide
NPB  N,N’-Diphenyl-N,N’-bis(1-naphthyl)-(1,1,’-biphenyl)-4,4’-diamine
BCP  2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline
Alq3  Tris(8-hydroxyquinolinate)aluminum(III)
TPBI 1,3,5-Tris(N-phenylbenzimidizol-2-yl)benzene
TPCz 3,6-bis(diphenylphosphoryl)-9-(4’-(diphenylphosphoryl)phenyl)carbazole
PEDOT Poly(3,4-ethylenedioxythiophene)
PSS  Poly(styrene sulfonated)
CIE  Commission Internationale de l’Eclairage
VOC  Volatile organic vapor
DNT  2,4-dinitrotoluene
TNT  2,4,6-trinitrotoluene
PA   Picric acid
DNA  Deoxyribonucleic acid
RNA  Ribonucleic acid
BSA  Bovine serum albumin
SDS  Sodium dodecyl sulfate
BPO  Benzoyl peroxide
Symbols

°C  Degree Celsius
K   Kelvin
ν   Wavenumber in cm\(^{-1}\)
δ   Chemical shift
Å   Angstrom
Φ\(_F\) Fluorescence quantum yield
τ   Lifetime
\(\lambda_{\text{abs}}\) Absorption wavelength
\(\lambda_{\text{ex}}\) Excitation wavelength
\(\lambda_{\text{em}}\) Emission wavelength
\(\eta_{\text{ext}}\) External quantum efficiency
\(\eta_{L}\) Luminance efficiency
\(\eta_{p}\) Power efficiency
Formula Index

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Ar: \( -H \)

C2  C5  C8

Ar: \( -H \)

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Chapter 1 Introduction

1.1 Background

Organic fluorescent materials with a strong \( \pi \)-conjugation have aroused much attention owing to their potential in high technological applications, such as organic light-emitting diodes (OLEDs), fluorescent chemosensor and bioprobes.\(^1\text{-}^{12}\) In order to improve the luminescence efficiency of the organic luminogens, extending the \( \pi \)-conjugation by connecting more aromatic rings together is an efficient and promising design scheme. Expectedly, the conventional organic luminogens following this design are highly emissive in their dilute solutions. However, the emission is usually quenched or weakened when the compound is in high concentration or being fabricated in the solid state. As mentioned in the book *Photophysics of Aromatic Molecules*\(^13\), this quenching effect is “known to be common to most aromatic hydrocarbon and their derivatives”. In the concentrated state, the molecules are located in immediate vicinity and experience a strong \( \pi-\pi \) stacking interaction between the large framework of aromatic rings, promoting the formation of excimer or exciplexes. These excited states usually decay through a non-radiative decay pathway and the light emission is quenched, which is known as aggregation-caused quenching (ACQ) phenomenon.\(^{14\text{-}18}\)

The ACQ effect has brought a huge obstruction to the practical usage of these
organic luminogens to real-world applications.\textsuperscript{19-21} For instance, the luminogens are required to be fabricated into a thin solid film as the emissive layer inside OLED devices. In the solid state, the absolute absence of solvent has pushed the concentration of the luminogens to the maximum and hence the ACQ effect becomes the worst which induces detriment on the quantum efficiency of the OLEDs. Moreover, the dye molecules are constrained in a very dilute concentration in order to refrain from the quenching of the light emission. The sensitivities of the sensory system are sacrificed and this ACQ problem has harmed the utilization of organic luminogens in the fluorescent sensory system.\textsuperscript{22}

To tackle with the problems induced by ACQ effect, numerous efforts including molecular design, physical aspect and engineering processes have been made to prevent the aggregation of molecules. For example, bulky cyclcics, branched chains and dendritic wedge could be introduced or non-conjugated transporting polymers, such as poly(methyl methacrylate) (PMMA), could be blended with the chromophores in order to avoid the close approach of molecules.\textsuperscript{23-31} However, the use of these non-conjugated entities will break the conjugation of the molecules with twisting of the conformation. The transparent polymer could act as a dilutant of luminogen density and a barrier to the charge transport, resulting in a drop of OLED efficiency. In contrast to hindering the aggregation of molecules, development of a
comprehensive system in which aggregation plays a constructive over destructive role in the luminescence process is an efficient and sustainable passage in the continuous research of organic luminogens and no extra work should be done on artificially interrupting the natural process of the luminogen aggregation.

1.2 Aggregation-Induced Emission (AIE)

1.2.1 Phenomenon

In 2001, Tang’s group reported an intriguing phenomenon, in which light emission of organic luminophore is enhanced by aggregation. This unusual phenomenon was found in a series of silole derivatives, which is non-emissive in its dilute solution, but has turned to strongly emissive in concentrated solution or in solid state. This optical behavior, which is opposite to the ACQ mentioned above, was coined as “aggregation induced emission” as the aggregation of molecules has turned on the light emission.32-34

Hexaphenylsilole (HPS) is the first example among the AIE active silole compounds (Fig. 1-1). From the electronic structure, HPS is extensively conjugated and expected to be strongly emissive. In a routine thin layer chromatography (TLC) test, the spot corresponding to HPS could hardly recognized on the plate once it was taken out from the development chamber; however, a bright-green emitting spot
became visible after evaporation of solvent. In other words, the emission of HPS is turned off and on in wet and dry plate, respectively, suggesting that HPS is non-emissive when it is dissolved and could turn to be luminescent once the solvent is removed or in aggregated state.\textsuperscript{32} The potential AIE behavior of HPS was further confirmed with spectroscopic measurement. The photoluminescence spectrum of HPS dissolved in MeCN solution is nearly parallel to the abscissa and the $\Phi_F$ is 0.22\%. The value of $\Phi_F$ is constant when the solution mixture contains 50\% water. Afterwards, there is a sudden boost of the emission intensity and $\Phi_F$ with an extra addition of water. When the solvent mixture consists of $\sim99\%$ water, the value of $\Phi_F$ is $\sim56\%$, which has increased by $\sim255$-fold as compared to that in pure MeCN solution. In the partial size analyzes, the solvent mixture with 80\% and 90\% water fraction has shown the existence of particles with average size of 190 and 130 nm, respectively. From this result, it is believed that the enhancement in emission of HPS is attributed to the aggregation in its bad solvent.\textsuperscript{32,35}
Figure 1-1 The chemical structure of HPS (Left). Photograph showing the HPS in acetonitrile/water solution with different water fraction under UV illumination. (Right)\textsuperscript{35}

Figure 1-2 (A) The photoluminescence spectra of HPS solution in MeCN/water mixture. (B) The plot of quantum yield (\(\Phi_F\)) against the water fraction in MeCN/water solvent mixture.\textsuperscript{35}
Figure 1-3 (A) The absorption spectra of HPS in MeCN/water solvent mixture with various water fraction. (B) Size distributions of nanoparticles of HPS in MeCN/water mixture with 80% and 90% water.\(^{35}\)

1.2.2 Mechanisms

To sustain the future development of the AIE active fluorophores, the working mechanism behind AIE should be established and understood. A number of possible mechanistic causes can be considered, including J-aggregation, twisted intramolecular charge transfer (TICT) and planarization of conformation. However, none of it could fully support the unusual optical behavior of HPS in different solvent mixture. From the structural view, HPS is a typical non-polar hydrophobic molecule as it does not contain any donor (D) or acceptor (A) functional group and hence does not show any push-pull or D – A interaction. This property discourages HPS in forming J-aggregates and it is further verified by X-ray diffraction (XRD) measurement.\(^{35}\) It
also excludes the possibility of TICT process as the working mechanism of the AIE behavior. By varying the solvent polarity in dissolving HPS, the emission spectra exhibited a small discrepancy in term of emission maximum and intensity. If the conformation of HPS becomes more planar in its aggregation state, there should be a large variation in both absorption and emission spectra in a bathochromic shift fashion. However, they do not change much with the increase of water content. Additionally, a twisted conformation is persisted in the solid state from the crystal structure analysis of HPS.

Based on the recognizable structural differences of the conventional disc-like planar organic luminogens, such as pyrene, and HPS, it is possible to figure out the main cause of the emission enhancement by aggregation. Unlike pyrene, HPS adopted a non-planar propeller-shaped conformation owing to the steric effect between benzene rings. In the dilute solution of HPS, the six peripheral phenyl rings serve as the rotors which will perform the intramolecular rotation against the silole moiety (stator) through the single bond axis. As any molecular motion will consume energy, the intramolecular rotation in the free state provides a non-radiative decay pathway for the excited state of HPS, which could explain the low emission in the dilute solution (Fig. 1-1). In aggregate state, the propeller shape renders the elimination of HPS being suffering from the strong \( \pi-\pi \) stacking. Simultaneously, the intramolecular
rotation of HPS is being restricted due to the physical constraint. The restriction of the intramolecular rotation (RIR) could be one of the possible origins in blocking the non-radiative decay channel and activating the radiative decay one, providing the luminescent features of the HPS in aggregation or solid state. In order to verify the hypothesis, a series of control experiments, including increasing viscosity, applying pressure and decreasing temperature, have performed to imitate the RIR process externally. The covalent bond was used to tie up the rotatable moiety to resemble RIR process internally. From both the external and internal control experimental results, the luminogen has turned into more emissive, offering the undeniable evidence to the hypothesis of mechanistic cause of AIE phenomenon.\textsuperscript{37}

1.2.3 AIE Fluorophores

Acquiring a mechanistic understanding on AIE, numerous kinds of luminogens could be developed based on the structural feature of one conjugated stator and several rotatable peripheral aromatic units, such as butadiene, pyran, fulvenes and polyarylated ethene derivatives (Fig. 1-4).\textsuperscript{38-44} In the following sections, more derivatives with AIE feature will be presented separately according to their molecular structures, including hydrocarbon, heterocyclic, supramolecular, polymeric and organometallic compounds.
1.2.3.1 Hydrocarbon Luminogens

A series of 8,8a-dihydrocyclopenta[a]indene derivatives was observed to have the AIE features by Wu and co-workers.\textsuperscript{45-46} Fig. 1-5 displays the structure of an example of 8,8a-dihydrocyclopenta[a]indene derivatives, 1, and its transformation in the emission profile with various water contents in THF/water mixture. 1 behaves as a typical AIE molecule, where the addition of large amount of water has turned on the emission of 1 and has increased the quantum yield of 1 by 73 times through the formation of aggregates. 1 with no heteroatom but only carbon and hydrogen is structurally similar to HPS. Wu has reported that RIR process is the source of the optical properties of 1. Through the inhibition of intramolecular rotation of three aromatic rings against 8,8a-dihydrocyclopenta[a]indene core in aggregation state of 1.
the non-radiative decay channel is blocked thus offering strong light emission for 1.

![Chemical structure of 8,8a-dihydrocyclopenta[a]indene and 1.](image)

**Figure 1-5** Chemical structure of 8,8a-dihydrocyclopenta[a]indene and 1. (Above) The photographs of the solution of 1 in THF/water mixture with different water fraction ($f_w$); fluorescence quantum yield ($\Phi_F$, %) of 1 are measured against quinine sulfate as standard. (Below)$^{46}$

Another group of AIE luminogens comprising of hydrocarbon is polyene, which renders a wider structural diversity and simpler synthetic route than silole derivatives. Taking 1,4-distylbenzene as an example of polyene, it is an conventional luminogen receiving an ACQ effect.$^{47}$ Diau, Hsu and co-worker discovered that replacing two $\alpha$-olefinic hydrogen atoms by methyl group on 1,4-distyrylbenzene could switch on the emission of the diene compound in aggregated state.$^{48}$ This complete reversal of the optical nature in the aggregation state could be explained by the conformation and the packing mode of the compounds. In free state, while all the atoms of 2 are located
in the same symmetry plane with a planar geometry, a non-planar structure is adopted by 3 with one benzene ring twisted out of the molecular plane by 80°. In dilute solution, a planar structure of 2 enjoys the fully extended conjugated system and π-conjugation which gives a strong emission, but the twisted conformation of 3 facilitates the non-radiative intramolecular motion which makes 3 non-emissive in its dilute solution. In the aggregated state, 2 tends to adopt a face-to-face packing, which will generate a strong π–π stacking interaction between the molecules, promote the excimer formation and quench the emission. On the other hand, a herringbone-type aggregate with an edge-to-face feature is preferable for 3 due to the steric hindrance of the methyl groups on the double bonds. Combining the prevention of π–π stacking interaction and effect of restriction of intramolecular rotation, 3 is highly emissive in its aggregation state and exhibits an AIE feature.48,49

![Molecular structure of 2 and 3](image)

**Figure 1-6** Molecular structure of 2 and 3 (Above) and the molecular packing arrangement of 2 and 3 (Below).48
From the above example, it is obvious that the steric hindrance on the ethylene moiety could create an alteration on the molecular geometry, intermolecular interaction, packing structure and optical behavior of the luminogens. According to this guideline, the molecular design of the AIE luminogens could be performed by replacing the olefinic hydrogen on the ethylene moiety with a variety of substituents. Fig. 1-7 displays the molecular structures of compounds by substituting the $\alpha$- and $\beta$-olefinic hydrogen with phenyl rings. From the spectrometric measurement, it is found that the replacement of phenyl ring on the C-C double bond could have an influence as effective as the methyl moiety, regardless of the substitution on the $\alpha$- or $\beta$-position. Moreover, 6, the cis-isomer of 5, is also identified as AIE-active, suggesting the AIE properties can be judged on the non-planar propeller shape of the molecular structure but not the conformation.  

Figure 1-7 Molecular structure of arylenevinylene-based AIE luminogens (4 – 6).

1.2.3.2 Luminogens Containing Heteroatom

The emission color of pure hydrocarbon AIE luminogen is often blue, and red-shifting of emission is necessary in order to cover the whole visible light spectrum
to widen the utilization of AIE luminophores. It is possible to red-shift the emission spectrum of the luminogens by extending the electronic conjugation or planarization of conformation. However, it will promote the intermolecular interaction and the chance of excimer formation. The alternate technique is by incorporation of heteroatoms to induce the polarization of electron cloud and the intramolecular charge transfer (ICT).\textsuperscript{51-53} 7 is one of the examples of AIE luminogens with heteroatom with the emission color beyond blue. From Fig. 1-8, the rise of fluorescence intensity with the increasing proportion of the non-solvent of 7, toluene, in the MeCN/toluene mixture demonstrated that 7 is obviously an AIE active pyridinium salt. In the photograph in the inset of Fig. 1-8, the powdery solid of 7 emits a yellow light, suggesting that the donor-acceptor interaction between amine and pyridinium unit has brought about the red-shift of emission color.\textsuperscript{54,55}

![Molecular structure of 7](image)

**Figure 1-8** Molecular structure of 7 (Left) and the plot of photoluminescence intensity of 7 in acetonitrile/toluene mixture against the toluene fraction (Right). Inset: photograph of 7 in aqueous solution (Soln) and in solid powder form (Solid) taken under illumination of UV lamp.\textsuperscript{54}
Although triphenylamine (TPA) itself is not an AIE active unit, it is usually included in the design strategy of the AIE active luminogens owing to its unique propeller shape and good electron-donating power. In Fig. 1-9, it illustrated the example of the AIE fluorophores built with triphenylamine unit. The propeller shape of TPA unit provides a preference to a twisted molecular conformation and hence the suppression of $\pi-\pi$ stacking. Through the restriction of intramolecular rotation process, the TPA-containing compounds give the strong emissive properties in their aggregation state, similar to the previously mentioned system. On the other hand, the donor-acceptor pairs of TPA-fluorenone (8), TPA-carboxaldehyde (9) and TPA-benzobis(thiadiazole) (10) have created a strong push-pull interaction and polarization of the electron cloud. Due to a strong intramolecular charge transfer effect, the band gap is greatly lowered and the emission color has been shifted to the red or even near-IR region.\textsuperscript{56-58}
AIE luminogens functionalized with cyano group has been intensively investigated in the view of their structural simplicity and high polarizability. Cyano moiety has the influence on both steric and electronic nature of the AIE fluorophores. The steric effect of the cyano group is present in 11, in which the $\alpha$-olefinic hydrogen is replaced by the cyano unit of a diene compound. While the twisted conformation is adopted and intramolecular rotation is active in the dilute solution of 11, this type of non-radiative motion is being restricted in its crystal form. Moreover, the C–H···N hydrogen bond is found between the cyano unit and the hydrogen atom on the adjacent molecule in its crystal structure, providing a further rigidification of the molecules and intensification of light emission. While the steric effect of cyano group plays an important role on the enhancement of emission in the aggregation state, the
electronic effect offers great color tunability of AIE luminogens, in order to widen their emission spectrum. Necker et al. and Chen et al. have reported a series of diphenylfumaronitrile luminogens (12 – 15, shown in Fig. 1-11).\textsuperscript{60-62} By introducing the functional substituent with an increasing electron-donating power on the terminal benzene ring, the color of light can readily vary from purple to red, which covers nearly the entire visible light spectrum. Therefore, the modification on the substituents with different electron-donating/withdrawing properties and push-pull interaction can offer an effective and straightforward platform for the molecular engineering of tuning the color of the AIE luminogens.

\textbf{Figure 1-10} Chemical structure and crystal packing of 11 and the photograph of the crystal of 11 taken under illumination of UV lamp. The C–H···N hydrogen bond is marked by the dotted line.\textsuperscript{59}
Figure 1-11 The molecular structure of 12 – 15 (Top). Photographs of the crystals of 12 – 14 and the nanoaggregates of 15 suspended in THF/water mixture (1:9, v/v) taken under UV illumination (Bottom).  

1.2.3.3 Polymeric Luminogens

In the current research, the AIE system is usually studied and developed with small molecules. For the practical usage, the luminophores have to be fabricated into solid thin film by expensive techniques, for example, vacuum deposition or vacuum sublimation, which are not applicable for the large-area application. One of the possible solutions to remedy the weaknesses of small molecule luminogens is to establish the high-molecular-weight polymers with AIE characteristics. Unlike small molecule luminogens, the AIE polymers could be manufactured into large-area flat-panel device by relative inexpensive and simple process, such as spin-coating and
ink-jet printing at ambient condition. The simplest way to design the polymer with AIE properties is by the incorporation of the well-known AIE small molecules as pendant groups to the rigid polymer strand.\textsuperscript{63} Tang and co-workers have delivered their effort on the synthesis and the optical properties of monosubstituted polyacetylene with silole and tetraphenylethylene (TPE) moiety, where their molecular structures are displayed in Fig. 1-12.\textsuperscript{64-65} The chloroform solution of 16 emits light with red color weakly from the polymer backbone at 652 nm. The addition of poor solvent, such as methanol, into its THF solution could slightly enhance the emission intensity, suggesting that 16 is AIE-inactive. It is believed that the silole pendants cannot pack well in the aggregated state with the direct attachment of silole unit to the rigid polyacetylene chain. On the contrary, the direct connection of TPE derivative to the polymer backbone (17) illustrates an aggregation-enhanced emission (AEE): the THF solution of 17 has a weak emission due to the conjugation between main chain polymer and TPE side group and the emission could be enhanced with the aggregation of polymer in the presence of water. Although the direct linkage of the AIE luminogens to the polymer backbone could favor the electronic conjugation, the exciton trap by structural defect in the skeleton of the polymer is also procured, which will diminish the emission efficiency. Through the insertion of the flexible alkyl spacer between polymer backbone and the AIE pendant group, the analogous
polymers, 18 and 19 are synthesized and discovered to be AIE active. In contrast to direct attachment, the alkyl spacer can provide a room for the molecules to undergo intramolecular rotation in its dissolved solution, which has prescribed the important criteria in the design of polymer with AIE nature.

1.3 Applications

Aggregation-induced emission effect has brought an innovative concept on the utilization of the fluorescence materials. The device performance of OLEDs of the
conventional planar luminogens has a room for improvement because of ACQ phenomenon.\textsuperscript{66,67} Owing to the highly emissive behavior of the AIE fluorophores in solid state, they should be the potential candidates for emissive layer in the OLED device.\textsuperscript{68-70} Besides, the fluorescence sensory systems based on the conventional organic dyes are usually operated in a “turn-off” mode as the emission will drop largely in their high concentration.\textsuperscript{71} The uncommon AIE effect offers a promising avenue to the development of sensory system functioning with a “turn-on” mode.\textsuperscript{72-74} The lighting-up sensors is superior to the fading-up counterpart as the “turn-on” fashion has a high sensitivity and is less likely to pronounce the false positive signal.\textsuperscript{75-77} In the following part, several operations with the employment of the AIE luminogens is reported and discussed.

1.3.1 Electroluminescence Devices

In the area of organic light-emitting diodes, numerous sets of AIE luminogens with TPE as the building block have been reported. They could be classified according to their structure, allowing the study of the structure-property relationship. Although TPE could emit deep blue light strongly in solid film, its OLED devices with a configuration of ITO/NPB (50 nm)/20 (30 nm)/BCP (20 nm)/Alq\textsubscript{3} (20 nm)/LiF (1nm)/ Al (120 nm) exhibited an inferior result with maximum luminance ($L_{\text{max}}$).
current efficiency ($\eta_{c,\text{max}}$) and external quantum efficiency ($\eta_{\text{ext,\text{max}}}$) of 1800 cd/m$^2$, 0.45 cd/A$^{-1}$ and 0.4%, respectively, in which NPB, DCP and Alq$_3$ are the hole-transport, hole-blocking and electron-transport layers, respectively. By attaching two more phenyl rings to 20, the electroluminescence performance has been improved. The OLED device of 21 with a configuration of ITO/NPB (50 nm)/21 (30 nm)/BCP (20 nm)/Alq$_3$ (10 nm)/LiF (1nm)/Al (160 nm) turned on at ~5 V, accompanying with $L_{\text{max}}$ of 10680 cd/m$^2$ at 16 V and $\eta_{c,\text{max}}$ of 5.15 cd/A and $\eta_{\text{ext,\text{max}}}$ of 2.56% at an applied voltage at ~5.5 V. By inserting one more ethylene unit on 20, the OLED performance of 22 is slightly better than 20 and 21. The OLED based on 22 emits a bright sky-blue EL at 488 nm with $L_{\text{max}}$, $\eta_{c,\text{max}}$ and $\eta_{\text{ext,\text{max}}}$ up to 10800 cd/m$^2$, 5.8 cd/A and 2.7%, respectively. However, the additional ethylene unit does not always improve the device performance if a severe steric congestion is created. A low molecular conjugation should be the main element for the inferior EL efficiency (3530 cd/m$^2$, 2.8 cd/A and 1.6%) for the starburst TPE derivatives, 23. Instead of the insertion of extra triphenylvinyl unit, connecting two TPE units in 24 gives the best OLED performance among these five TPE-containing luminogens. The multilayer device with configuration of ITO/NPB (60 nm)/24 (20 nm)/TPBi (10 nm)/Alq$_3$ (30 nm)/LiF (1nm)/Al (100 nm) turned on at low bias (down to ~4 V) and emitted light brilliantly with $L_{\text{max}}$ up to 11180 cd/m$^2$ at 15 V, $\eta_{c,\text{max}}$ of 7.26 cd/A and $\eta_{\text{ext,\text{max}}}$ of
3.17%.  

Figure 1-13 Examples of TPE-containing AIE fluorophores (20 – 24).

1.3.2 Chemosensors

With the reversible emission turn-on/off properties, a TPE-containing derivative, 25, could be employed as a volatile organic vapor (VOC) detector. From Fig. 1-14, it is clear that the emission from the spot of 25 on a TLC plate (B) has been switched off when the plate is put into a Petri-dish set saturated with CHCl₃ vapor (C). Afterwards, the emission has been recovered when CHCl₃ is evaporated. As the organic vapor condensed to form a thin liquid layer of VOC on the surface of TLC plate, it will dissolve the AIE luminogens adsorbed on the plate and diminish the emission from the spot. Once the volatile organic compound is evaporated, the aggregation of
molecules is resumed to switch on the emission. As this luminescence turn-on/off is a non-destructive aggregation/deaggregation physical process, it provides a reversible and repeatable chemosensor.\textsuperscript{80,81}

Figure 1-14 Spot of (A) 1,4-diphenyl-1,2-bis(4-phenylphenyl)ethene (25) on TLC plate in Petri-dish set (B) without CHCl$_3$ and (C) saturated with CHCl$_3$ vapor. Photograph of (D) was taken after the organic vapor in (C) had been evacuated.\textsuperscript{80}

The chemosensor for detection of explosives has been developed from the utilization of an efficient AIE luminogen, 26. Nitroaromatics, such as 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) are commonly used as explosives for industrial and military applications. Picric acid (PA) is used as the representative explosive as DNT and TNT are commercially unavailable. A strong emission is observed from the nanoaggregate of 26 prepared by the mixture of 1% of its THF solution to 99% water and is weakened with the addition of PA. A photoluminescence quenching constant ($K_{sv}$) of $1.67 \times 10^{-5}$ M$^{-1}$ is given from the
Stern-Volmer plot of 26, suggesting nanoaggregates of 26 could act as a sensitive explosive detector. In addition, the amino groups on this HPS allow 26 to become a potential pH sensor. When a sufficient amount of acid is added into the water, the amino group will be transformed to the ammonium salt and it will lead to the dissolution of the protonated form of 26 in water. Owing to the AIE feature, the emission of the nanoaggregate of 26 has dramatically been quenched in the acidic medium. As displayed in Fig. 1-15, the photoluminescence intensity in the range of low pH value (2 – 5.4) remained unchanged at a low level. When pH value of the solution mixture exceeded 5.4, the ammonium salt has been transformed back to the amino form, in which the decrease of solubility facilitated the aggregation of 26 and turned on its emission. This reversible transformation between amino group and ammonium salt by varying the pH value of the solution offers a chance for 26 to be an efficient fluorescent pH sensor and provides an avenue in the future development of this area through the use of aminated AIE luminogens.
**Figure 1-15** (A) Aminated HPS derivative (26) and its protonated form (26^{2+}). (B) PL spectra of 26 in THF/water mixture with different amount of picric acid (PA). Inset: Plot of $I_0/I - 1$ against the concentration of PA; $I_0 = $ PL intensity at [PA] = 0 µM. (C) Change of PL intensity of nanoaggregates of 26/26^{2+} against pH value; $I_0 = $ PL intensity at pH = 2. Inset: Photographs of the suspension of 26 and the solution of 26^{2+} at pH 12 and 2, respectively, taken under UV illumination.\(^3\)

### 1.3.3 Fluorescent Biosensors

Apart from the various investigation of applying different AIE luminogens as chemosensors, the development of high-tech applications, such as biopores, is
examined and discussed in the following part. To improve the solubility of the compounds in water, the insertion of hydrophilic functional group, such as hydroxyl, amino, ammonium and sulfonate group can be performed to the structure of AIE luminogens. From this design, the water-soluble AIE fluorophores is non-emissive in aqueous buffer but becomes emissive once they are bounded to the biological target molecules. As mentioned before, a turn-on biosensor is superior to the fade-off counterpart, as it is easier to spot the formation of emissive species in dark background by naked eye and is less likely to create a false positive signal.\(^{75-77}\)

1.3.3.1 DNA Sensing

The emission of cationic AIE luminogens is turned-on when it meets anionic biomacromolecules, such as DNA and RNA from the RIR process induced by the electrostatic interaction-aided complexation.\(^ {84-85}\) A single-stranded (ss) DNA with a guanine (G)-rich repeat sequence will fold into the secondary structure, G-quardruplex, which is stabilized by the monovalent cations, such as K\(^+\), located at the center of G-quardruplex plates. The formation of quadruplex will inhibit the telomerase activity in cancer cell and affect the gene expression. The development of quadruplex-targeting drug will have an impact on the artificial regulation of gene express and the control on the cancer cell proliferation. Therefore, the detection of
G-quadruplex has great importance on the design of medicine and anticancer therapeutics. A specific recognition of DNA conformation or folding structure by a cationic AIE fluorophore, 27, was observed and developed. Owing to its hydrophilicity, the aqueous solution of 27 is non-emissive. Upon the binding of 27 to a DNA strand of HG21, the intramolecular rotation is being restricted and thus the emission is turned on. Addition of potassium ion to the solution will induce HG21 folding into the G-quadruplex structure, which could be detected with a red-shifted emission peak from 470 to 492 nm. The presence of complementary DNA, C21, will unfold the quardruplex and give a duplex (ds) structure. As the binding of 27 to dsDNA is largely suppressed by the competition with potassium ions, the molecules of 27 will release back to the water medium with a turn-off of light emission. The distinct bathochromic shift of fluorescence in the presence of quadruplex structure offers a label-free visual detection of quadruplex from other DNA conformation with a low detection limit of 0.5 µM.86
**Figure 1-16** Chemical structure of 27 and the schematic illustration of differentiation of DNA conformation by 27.

1.3.3.2 Protein Sensing

In contrast to the traditional sensory systems for protein detection and quantification showing small Stokes shifts and non-linear curves, the use of 28 in the detection presents a large Stoke shift (> 100 nm) and linear calibration curve over a wide range of concentration (up to 100 mg/L). Additionally, the AIE nature of 28, in which the emission is amplified with the increase of concentration, could remedy the deficiencies of the conventional fluorophores with the ACQ problem in high
concentration. A turn-on sensor for detection of bovine serum albumin (BSA) making use of a sulfonated TPE derivative (28) has been developed.\textsuperscript{87}

The performance of 28 as a turn-on sensor for protein assay is demonstrated in Fig. 1-17. The water-soluble fluorophore, 28 is non-luminescent in a neutral phosphate buffer. When BSA is introduced to the buffer, the fluorescence is switched on with an increment of 240-fold at [BSA] = 500 mg/L as compared to the case in the absence of BSA. A linear calibration curve obtained from the plot of fluorescence intensity against the concentration of BSA, together with a high sensitivity in the detection of BSA at a concentration as low as 50 ppb, indicate that 28 can be employed in the quantification of BSA in a wider concentration range. Unlike the working mechanism behind VOC sensor, the aggregation of the AIE luminogens in the detection of BSA is not induced by the decrease in the solubility in the surrounding media, but is influenced by the protein conformation. From the PL spectrum of 28 in the presence of BSA, it is identical to that in its nanoaggregate form, proving that the introduction of BSA could induce the aggregation of 28. The hydrophobic pocket present in the native folding structure of BSA chain provides a binding site for 28. When the molecules of 28 enter and dock in the interdomain hydrophobic cavities of BSA with native folding structure, the rotational motion of aryl rotor is restricted and hence induces the fluorescence behavior of 28. To verify
that aggregation of molecules is being induced by the presence of hydrophobic region of BSA in native folding structure, sodium dodecyl sulfate (SDS) is added to unfold protein structure and destroy the hydrophobic cavities. As expected, the addition of SDS to the BSA solution of 28 has effectively dropped the emission, suggesting that molecules of 28 has been deaggregated and released to the buffer solution. Apart from being a bioprobe in the quantitation of protein, the sensitivity of the AIE luminogens to the native-conformation can give a hand in the visualization of the folding structure, the hydrophobic pocket and the active site of protein.³⁸
Figure 1-17 (A) Photoluminescence intensity of sulfonated TPE salt 28 in phosphate buffer (pH = 7.0) with different concentration of bovine serum albumin (BSA) (B) The plot of $I/I_0 - 1$ against [BSA]; $I_0$ = the PL intensity at [BSA] = 0 mg/mL. (C) Linear region of [BSA] versus $I/I_0 - 1$ plot in panel B.$^{87}$

1.4 Scope of Thesis

Through discovering the intriguing AIE phenomenon, development of a new system of AIE luminogens is under our consideration. Most of the researches have been focused on the study and discussion of the well-known AIE frameworks, silole and TPE; it is indispensable to explore another zone and investigate its prospective development. In the previous description of numerous categories of AIE luminogens,
the fluorophores containing cyano moiety, especially cyanostilbene derivatives, have caught our greatest attention and curiosity, owing to their structural simplicity and great color tunability. The fascinating properties of cyanostilbene derivatives encouraged us to devote our effort to the comprehensive research on the synthetic scheme, photophysical behavior, as well as exploration of their potential high-tech applications to enrich the whole story of aggregation-induced emission.

A series of AIE luminogens comprising of triphenylamine and carbazole unit was designed and synthesized. To enhance the OLED performance, multilayers are generally adopted to balance the injection and transportation of charge carriers. In reality, it is better if the emissive layer is capable of hole- and/or electron-transporting in order to simplify the device construction and to reduce the cost of fabrication. The electron-rich units, such as triphenylamine and carbazole, can be introduced into the AIE-active moiety to turn themselves from ACQ chromophores in AIE counterpart and to improve the hole-transporting capability of AIE luminogens. Here, the design, synthesis and characterization of the triphenylamine and carbazole containing AIE luminogens are explored and the detailed results are illustrated in Chapter 2.

The AIE system is usually reported as low-molecular-weight molecules and that with high-molecular-weight polymer is seldom discussed. In the practical usage, the
fabrication of high-molecular-weight polymer is relatively simple and inexpensive, which aroused our enthusiasm in exploring this area of the AIE system. From recent research work, the rigid polymer backbone has effectively brought the molecules of AIE fluorophores in close vicinity and suppressed the intramolecular rotation, even in dissolved state, making these AIE compounds tied in polymer chain AIE-inactive. Insertion of flexible alkyl chain or lengthening the distance of luminophores is the feasible solution to the failure in retaining the AIE feature in the polymerization of AIE-active molecules. In Chapter 3, the connection of the triphenylamine-containing cyanostilbene derivatives with AIE characteristics by the organic and trans-Pt(PBu₃)₂ spacers is performed to investigate the discrepancies in their optical behavior and to verify the efficiency of the above method.

Apart from the restriction of intramolecular rotation process, a new mechanism called “restriction of twisted intramolecular charge transfer” was suggested from the study on a series of boron dipyrromethene (BODIPY) derivatives. Unlike the representative AIE chromophore, the photoluminescence intensity with the variation of water fraction is going down at the beginning and rises up after a U-turn. It is suggested that the drop of emission is a consequence of increasing solvent polarity of the solvent and the rise comes from the growth of hydrophilicity. The dual photoresponse to the solvent polarity and luminogen aggregation provide a fresh
concept on the AIE mechanism and encourage us to develop a family of compounds to examine this interesting phenomenon. In the research period, phenothiazine-containing cyanostilbene derivatives were discovered in which they possess the similar optical responses to the variation of solvent polarity and water content of the solution to the BODIPY one, which will be further elaborated in Chapter 4.

Finally, throughout the examination and studies of numerous AIE compounds and mechanism, a realistic application in the utilization of the AIE luminogens is established through the pyridyl-functionalization of the cyanostilbene derivatives. Pyridine, a heteroatom-containing aromatic ring, has a strong affinity to metal ion and is known to be capable of enhancing the metal chelating process. Owing to the metal-to-ligand charge transfer induced in the chelation of metal ion, there is an obvious transformation in the emission of the resultant complexes, which furnish the potentiality of the pyridyl-functionalized luminogens in the qualitative and quantitative measurement of metal ion. In Chapter 5, a pyridyl-functionalized cyanostilbene compounds are designed and synthesized. From the introduction of various metal ions, only cadmium ion (Cd$^{2+}$) has an outstanding response which offers a qualitative investigation of metal ion. In addition, a linear calibration curve over a range of concentration could be obtained from the ratio of enhancement intensity to
the concentration of Cd\textsuperscript{2+} which enables the pyridyl-functionalized cyanostilbene compound to be employed in the quantitation of Cd\textsuperscript{2+} in unknown sample.
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Chapter 2 Synthesis and Characterization of Cyanostilbene-Based Arylacetylide Small Molecules with AIE Characteristics

2.1 Introduction

Organic compounds with an enhanced emission in their solid state have been utilized recently in organic light-emitting diodes (OLEDs). 1-5 Most conventional luminogens, such as pyrene, are strongly emissive in dilute solution. However, the photoluminescence intensity has been diminished dramatically once they are poured in their poor solvent or fabricated into thin film in devices, causing aggregation of the molecules due to the strong $\pi$-$\pi$ interaction together with the formation of excimers. 6 Instead of suppressing the natural process in molecular aggregation, developing a new class of materials with stronger emission in the solid state is an alternative solution to this problem such that the molecular aggregation acts as the constructive player in the photoluminescence process. 7

To increase the performance of device, OLEDs in multilayer configurations are adopted to balance the charge injection and transport. Generally, a hole-transporting layer was used to facilitate the transportation of hole from anode to emissive layer, while an electron-transporting layer transports electron from cathode. In practice, an ideal material should have a good quantum efficiency in solid-state emission and good charge-transporting properties as it would simplify the charge transport process and
the device structure and lower the cost of device construction. Triphenylamine (TPA) and carbazole unit are the electron-rich chromophores and also the promising hole-transporting layer for OLEDs. However, their emissions were quenched at high concentration. By introducing TPA or carbazole moiety to the cyanostilbene unit, the effective solid-state emitter with good hole-transporting properties can be achieved.

Thanks to extraordinary behavior of AIE luminogens, there is great interest in the potential applications of this class of materials in bioimaging and functional materials, particularly solid-state emitters and chemosensors. In biological application, the emission of common organic dyes has been quenched after the binding of analytes to the cell as the hydrophobic properties has compelled the molecules to aggregate inside cytoplasm with high water content (70% - 90%). The ACQ problem has limited the analysis of the label-to-analyte ratio and forced the studies of bioimaging in a dilute solution of the fluorophores, which hampers their sensing and imaging sensitivity. On the contrary, the opposite behavior of AIE luminogens to conventional organic dyes is an emphasis for this class of materials serving as a prospective candidate in turn-on fluorescence imaging system which offers a direct visualization of analytes in aqueous media with high sensitivity and accuracy.

In this chapter, we describe the design and synthesis of a series of novel cyanostilbene-based arylacetylide molecules with different terminal substituents and
central connecting group. By virtue of the AIE properties and high thermal stability of the compounds, they become a potential candidate for electroluminescence and bio-imaging. In addition, the intense emissions of materials in solid state promote their use as a chemical vapor sensor to take advantage of the reversible fluorescence switch on/off properties of cyanostilbene acetylide compounds.

2.2 Synthesis of Cyanostilbene-Based Arylacetylide Small Molecules

The methods for the synthesis of TPA- and carbazole-containing arylacetylide derivatives are outlined in Schemes 2-1 to 2-6. The procedures and experimental data of the synthesis of intermediates and final products are described in the experimental section in Chapter 7. First, the Sonogashira coupling sequence of trimethylsilylacetylene with 4-bromophenylacetonitrile in the presence of palladium catalyst readily provided the key reactant, CNTMS in good yield.

![Scheme 2-1 Synthetic route of CNTMS](image)
For CHO1, the aldehyde group is introduced to the commercially available TPA by Vilsmeier-Haack reaction with phosphorus oxychloride (POCl₃) and dry dimethylformamide (DMF). The synthesis of CHO2 begins with the bromination of TPA by a stoichiometric amount of N-bromosuccimide (NBS), which can give TPA boronic acid by reaction with n-butyllithium and trimethylborate under liquid N₂-acetone bath. Then, the resultant boronic acid was reacted with the commercially available 5-bromothiophene-2-carbaldehyde to obtain CHO2. Similarly, CHO3 and CHO4 are acquired by the introduction of aldehyde functional group to the products from the alkylation reaction and copper-catalyzed Ullmann coupling reactions of 9H-carbazole, respectively.
Scheme 2-2 Synthetic route of CHO1 to CHO4

To increase the π-conjugation of the TPA-based cyanostilbene compounds, different substituent is connected to the terminal group on the TPA moiety through the palladium-catalyzed Suzuki coupling reaction between the product of halogenation of CHO1 and the appropriate aryl boronic acid. Then, the four TPA-based cyanostilbene derivatives with extended conjugation were synthesized as outlined in Scheme 2-3.
After the synthesis of all eight aldehyde precursors, the Knoevenagel condensation reaction between the appropriate aldehyde precursor (CHO1 to CHO8) and CNTMS in a basic condition gave the desired TPA- and carbazole-containing cyanostilbene derivatives. The synthetic routes for L1 to L8 are outlined in Scheme 2-4.
Scheme 2-4 Synthetic route of L1 to L8
Afterwards, D1 to D4 are further made from the reaction of L1 to L4 with 9,9-dibutyl-2,7-diiodo-9H-fluorene via palladium-catalyzed Sonogashira coupling reaction to connect two cyanostilbene moiety through the terminal acetylide group at the two ends of fluorene unit in a 2,7-position (Scheme 2-5). This connection could ensure a higher conjugation as the delocalization of electron over the molecules works better in a linear form than in a bend conformation (3,6-position).

Scheme 2-5 Synthetic route of D1 to D4
On the other hand, L1 to L4 underwent a dehydrohalogenation reaction with \(\text{trans-}[\text{Pt}(\text{PBU}_3)_2\text{Cl}_2]\) to yield Pt1 to Pt4, replacing the central group of fluorene unit by a \(\text{trans-}\text{Pt}(\text{PBU}_3)_2\) moiety. In this aspect, the platinum in Pt1 to Pt4 acts as a building block other than the aromatic ring to downsize the risk for the compounds in experiencing the strong \(\pi - \pi\) stacking interaction.

\[\text{L1 - L4} \rightarrow \text{trans-}\text{PtCl}_2(\text{PBU}_3)_2\text{Cl}\]

**Scheme 2-6 Synthetic route of Pt1 to Pt4**
2.3 Spectroscopic Characterization of Cyanostilbene-Based Arylacetylide Small Molecules

All newly synthesized cyanostilbene derivatives were fully characterized with common analytical and spectroscopic method, including Fourier transform infrared (FTIR), $^1$H, $^{13}$C and $^{31}$P-$^1$H NMR spectroscopy, in which the experimental data are summarized in the experimental section in Chapter 7. All the signals are consistent with the structure of the compounds. In $^1$H NMR, the signals from the protons on the aromatic ring are downfield-shifted (above ppm). Meanwhile, the protons on the alkyl group give the peaks in the upfield region (below ppm). A characteristic signal around 3.1 ppm from the terminal acetylenic hydrogen (C≡C-H) could be observed in the $^1$H NMR spectra of L1 to L8. It gives the evidence that the basic medium required for the Knoevenagel condensation reaction not only provides an appropriate condition for the reaction to be carried out, but also triggers the desilylation and affords the terminal alkyne compounds. Taking L1 as an example, a sharp peak at $\delta = 3.2$ ppm can be observed (Fig. 2-1). In the $^1$H NMR spectra of D1 to D4 and Pt1 to Pt4, the absence of the sharp signal corresponding to the terminal acetylenic hydrogen indicates that the completion of reaction between L1 – L4 with 9,9-dibutyl-2,7-diiodo-9H-fluorene and trans-Pt(PBu$_3$)$_2$Cl$_2$. The selected $^1$H NMR spectra for the cyanostilbene compounds are shown in Figs. 2-1 to 2-4. For $^{13}$C NMR, the chemical shifts
representing the terminal alkynyl and cyano carbon are located at around 90 and 107 ppm, respectively, where the two distinct $^{13}$C signals for two alkynyl carbons have been observed due to their unsymmetrical structure (Fig. 2-5 and Fig. 2-6). For the platinum-containing cyanostilbene derivatives (Pt1 – Pt4), the $^{31}$P-$^1$H NMR spectra have displayed a sharp signal at 3.2 ppm with two satellite peaks consistent with the structure of $trans$ geometry of Pt(PBu$_3$)$_2$(C≡C)$_2$ unit. The value of $^1J_{P-Pt}$ is around 2890 Hz, which is a typical value for related $trans$-PtP$_2$ system. Owing to the symmetrical structure around Pt(PBu$_3$)$_2$(C≡C)$_2$ unit, there is only one sharp peak in the $^{31}$P-$^1$H NMR spectra (Fig. 2-7).

Figure 2-1 $^1$H NMR spectrum of L1 in CDCl$_3$. 
Figure 2-2 $^1$H NMR spectrum of L3 in CDCl$_3$.

Figure 2-3 $^1$H NMR spectrum of D4 in CDCl$_3$. 
Figure 2-4 $^1$H NMR spectrum of Pt1 in CDCl$_3$.

Figure 2-5 $^{13}$C NMR spectrum of L3 in CDCl$_3$. 
Figure 2-6 $^{13}$C NMR spectrum of L7 in CDCl$_3$.

Figure 2-7 $^{13}$C NMR spectrum of Pt4 in CDCl$_3$. 
The FTIR spectrometry is employed to further verify the presence of certain functional groups through the investigation of the peaks from the FTIR spectra and comparison to the particular vibrational frequencies of functional groups. All cyanostilbene derivatives possess the characteristic IR peak located at 2200 cm\(^{-1}\) which matches the vibrational frequency for the cyano group, suggesting the presence of the cyano group on the product from the Knoevenagel condensation reaction. Additionally, a peak with weak to medium intensity at 2090 cm\(^{-1}\) can be addressed to the existence of the alkynyl group. With the terminal acetylenic hydrogen in \textbf{L1 – L8}, the IR spectra demonstrate the distinctive signal at a region of 3330 - 3270 cm\(^{-1}\), which is the typical region for the stretching vibrational frequencies from the functional group with small molecules, such as hydrogen. Similarly, the absence of the peak over 3200 cm\(^{-1}\) for \textbf{D1 – D4} and \textbf{Pt1 – Pt4} implies the complete reaction for the \textbf{L1 – L4} with 9,9-dibutyl-2,7-diiodo-9H-fluorene and \textit{trans}-Pt(PBu\(_3\))\(_2\)Cl\(_2\), respectively.
Figure 2-8 FTIR spectrum of L2 as KBr disc.

Figure 2-9 FTIR spectrum of D2 as KBr disc.
Figure 2-10 FTIR spectrum of Pt2 as KBr disc.
2.4 Electrochemical Properties of Cyanostilbene-Based Arylacetylide Small Molecules

The electrochemical properties of cyanostilbene-based compounds were investigated by cyclic voltammetry (CV). The experiments are performed in thin film of samples on glassy carbon working electrode in 0.1 M tetrabutylammonium hexafluorophosphate ([Bu$_4$N]PF$_6$) in acetonitrile solution at a scan rate of 100 mV s$^{-1}$. On the basis of the potentials of oxidation and reduction couples, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of all compounds are calculated from the following equations: $E_{\text{HOMO}} = -(E_{\text{onset, ox}} + 4.73)$ eV and $E_{\text{LUMO}} = -(E_{\text{onset, red}} + 4.73)$ eV, where the unit of potential is V versus Ag/AgCl.$^{17}$ The results are summarized in Table 2-1.

The energy gaps of the cyanostilbene-based compounds determined from the difference between HOMO and LUMO energy levels are in the range of 1.7 – 2.1 eV. From the literature, the cooperation of the thiophene ring to the structure will elevate the HOMO energy level,$^{18}$ leading to a drop of oxidation potential and energy band gap. This behavior can be observed from the comparison of L1-series (L1, D1 and Pt1) and L2-series (L2, D2, and Pt2), in which the energy gap of L2-series is lower than that of L1-series. On the other hand, the lower energy gap resulted from the Pt-bridged complexes (Pt1 – Pt4) than the fluorene-bridged compounds (D1 – D4).
suggested that Pt(PBu$_3$)$_2$(C≡C)$_2$ unit can afford a more extended electron delocalization and $\pi$-conjugation. A similar argument could be applied in the comparison of L$_3$-derivatives to L$_4$-derivatives, where the former series show a smaller energy gap by 0.14 eV. It was suggested that the phenyl ring at 9-position of L$_3$-derivatives has contributed to the $\pi$-conjugated system and electron delocalization of the molecule in certain extent, which is in contrast to an alkyl chain with less or no influence on it.

Moreover, from the lowered band gap for L$_5$ – L$_8$ with respect to L$_1$, the extension of $\pi$-conjugation of L$_1$ through the attachment of the aromatic substituents on the TPA unit terminally (L$_5$ – L$_8$) is supported by the experimental data. It is also clear that the order of the $E_{\text{HOMO}}$ of L$_5$ – L$_8$ is in parallel to their electron-donating ability of the substituents on TPA moiety: TPA (L$_8$) > benzene (L$_5$) ≈ fluorene (L$_7$) > difluorobenzene (L$_6$). The slightly fluctuation in the magnitude of LUMO energy level, regardless of the variation in substituents on TPA group, suggests that the electron clouds of HOMO levels are dominated by electron-rich TPA portion; however, those of the LUMO levels are mainly located on electron-deficient cyano group, which is consistent with the calculation results.
Table 2-1 Electrochemical properties of cyanostilbene-based compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{ox}$ (V)$^a$</th>
<th>$E_{HOMO}$ (eV)$^b$</th>
<th>$E_{red}$ (V)$^a$</th>
<th>$E_{LUMO}$ (eV)$^c$</th>
<th>$E_g$ (eV)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>0.61</td>
<td>-5.34</td>
<td>-1.24</td>
<td>-3.49</td>
<td>1.85</td>
</tr>
<tr>
<td>L2</td>
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<td>-1.23</td>
<td>-3.50</td>
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</tr>
<tr>
<td>L3</td>
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<td>-1.23</td>
<td>-3.50</td>
<td>2.05</td>
</tr>
<tr>
<td>L4</td>
<td>0.97</td>
<td>-5.70</td>
<td>-1.22</td>
<td>-3.51</td>
<td>2.19</td>
</tr>
<tr>
<td>L5</td>
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<td>-5.22</td>
<td>-1.25</td>
<td>-3.48</td>
<td>1.74</td>
</tr>
<tr>
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<td>-1.24</td>
<td>-3.49</td>
<td>1.76</td>
</tr>
<tr>
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<tr>
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<td>-1.18</td>
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</tr>
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</table>

$^a$ Obtained from the onset oxidation and reduction potentials

$^b$ $E_{HOMO} = -(E_{ox} + 4.73)$ (eV)

$^c$ $E_{LUMO} = -(E_{red} + 4.73)$ (eV)

$^d$ $E_g = E_{LUMO} - E_{HOMO}$
2.5 Thermal Properties of Cyanostilbene-Based Arylacetylide Small Molecules

The thermal properties of TPA- and carbazole-based cyanostilbene compounds were examined by thermogravimetric analysis (TGA) under a nitrogen stream at a heating rate of 20 °C min⁻¹ and the experimental results are summarized in Table 2-2. The TGA results have illustrated the good thermal stability of these luminogens, in which the decomposition temperatures \( T_d \), temperature at which a sample loses its 5% weight) of all cyanostilbene compounds exceed 300 °C. The end-capped platinum- and fluorene-bridged compounds exhibited better thermal properties than their corresponding terminal alkyne ligands as the ligand with terminal acetylenic hydrogen is less stable and readily decomposes than the end-capped one. In addition to their efficient solid-state emission, a high value of \( T_d \) of the compound reveals they are the promising candidates for electroluminescent applications as a solid emitter.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T_d/°C )</th>
<th>Compound</th>
<th>( T_d/°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>346</td>
<td>D1</td>
<td>348</td>
</tr>
<tr>
<td>L2</td>
<td>343</td>
<td>D2</td>
<td>345</td>
</tr>
<tr>
<td>L3</td>
<td>355</td>
<td>D3</td>
<td>414</td>
</tr>
<tr>
<td>L4</td>
<td>317</td>
<td>D4</td>
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<tr>
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<td>430</td>
<td>Pt4</td>
<td>349</td>
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2.6 Photophysical Properties of Cyanostilbene-Based Arylacetylide Small Molecules

2.6.1 Absorption Properties

All TPA- and carbazole-containing cyanostilbene compounds have good solubility in common organic solvents, such as tetrahydrofuran (THF) and dichloromethane (CH\(_2\)Cl\(_2\)), but are insoluble in water. The absorption properties have been recorded in THF and in dispersion of aggregated form from the solvent mixture of water and THF in 9:1 ratio. The UV-Vis absorption spectra of all luminogens are set out in Figs. 2-11 to 2-18.

The UV-Vis absorption spectra of most cyanostilbene derivatives are dominated by the absorption of aromatic segment and \(\pi - \pi^*\) transition in TPA or carbazole core, locating in higher energy (near UV) region. Additionally, some of the derivatives exhibit an extra absorption band beyond 400 nm, which is assigned to the intramolecular charge transfer (ICT) between the electron-rich TPA or carbazole unit and the electron-deficient cyano segment.

In the comparison of the absorption maximum of the TPA-containing cyanostilbene ligand, it is clear that the \(\lambda_{\text{abs, max}}\) of L2 is greater than that of L1, proposing that the introduction of thiophene ring into the structure of L1 has extended the \(\pi\)-conjugated system. The same information can be applied to the
carbazole-containing cyanostilbene luminogens. In the 9-position of carbazole unit, 

\textbf{L3} with the phenyl rings owns a more expanded electron delocalization than \textbf{L4} with an alkyl chain counterpart, resulting in a higher $\lambda_{\text{abs,max}}$ for \textbf{L3}. Not only does this phenomenon observe in the terminal acetylide ligand series (\textbf{L1 – L4}), but also in their corresponding end-capped platinum- (\textbf{Pt1 – Pt4}) and fluorene-bridged derivatives (\textbf{D1 – D4}). Moreover, it is more obvious for the change of $\lambda_{\text{abs,max}}$ in the extended conjugation system of \textbf{L1} in \textbf{L5 – L8} by the insertion of extra aromatic ring on the TPA unit terminally. The blue-shifted absorption spectrum in \textbf{L6} relative to \textbf{L5} is rationalized by the substitution of two fluorine atoms on the phenyl rings that strengthens the electron-withdrawing power, leading to a shorter absorption wavelength of \textbf{L6}.

Besides, the absorption properties of all cyanostilbene derivatives in their aggregated form have also been investigated. From the absorption spectra of \textbf{L1} in THF (0% water) and in aggregated form (90% water), there is a noticeable bathochromic shift in absorption band, illustrating that the planarization of distorted structure from diluted solution owing to the intermolecular steric hindrance in aggregated state has largely extended the $\pi$-conjugated system. The red-shifted fashion in aggregated state could clearly be observed for all TPA-containing cyanostilbene derivatives (\textbf{L1}, \textbf{L2} and \textbf{L5 – L8}), but is less likely to be established in
carbazole-part (L3 and L4). From the structural analysis, the carbazole can be expressed as a “locked” figure of TPA unit as the intramolecular rotation of rings is blocked in certain extent from the covalent C-C single bond in between two rotatable benzene rings in TPA. Therefore, the degree of conformation twisting of carbazole-containing cyanostilbene compounds is not as significant as TPA-containing one in the isolated form, leading to an unrecognizable planarization of distorted structure and thus indistinguishable variation in the absorption band for L3- and L4-series in dissolved and aggregated state.
**Figure 2-11** Absorption spectra of L1 – L4 in THF (0% water) and in dispersion of aggregated form (90% water) at a concentration of 1 x 10^{-5} M.

**Figure 2-12** Absorption spectra of L1 – L4 in THF at a concentration of 1 x 10^{-5} M.
Figure 2-13 Absorption spectra of L5 – L8 in THF (0% water) and in dispersion of aggregated form (90% water) at a concentration of 1 x 10^{-5} M.

Figure 2-14 Absorption spectra of L5 – L8 in THF at a concentration of 1 x 10^{-5} M.
Figure 2-15 Absorption spectra of D1 – D4 in THF (0% water) and in dispersion of aggregated form (90% water) at a concentration of $1 \times 10^{-5}$ M.

Figure 2-16 Absorption spectra of D1 – D4 in THF at a concentration of $1 \times 10^{-5}$ M.
**Figure 2-17** Absorption spectra of Pt1 – Pt4 in THF (0% water) and in dispersion of aggregated form (90% water) at a concentration of $1 \times 10^{-5}$ M.

**Figure 2-18** Absorption spectra of Pt1–Pt4 in THF at a concentration of $1 \times 10^{-5}$ M.
2.6.2 AIE Properties

To investigate the AIE features of the TPA- and carbazole-containing cyanostilbene-based compounds, the photoluminescence spectra of all dyes in various THF/water fraction ($f_w = 0 – 90\%$) at a concentration of $1 \times 10^{-5}$ M and the plot of enhancement ratio ($I/I_0 – 1$) at each water fraction have been obtained and portrayed in Fig. 2-19 to 2-22.

All cyanostilbene derivatives enjoy an obvious AIE feature with different emission behavior in dissolved and aggregated state. From the first row in Fig. 2-19, it demonstrates the emission spectra in different water content ($f_w$) and the AIE phenomenon of $\textbf{L1}$. With a low water proportion in the solvent mixture, $\textbf{L1}$ could emit weakly and its photoluminescence intensity remains constant before $f_w$ reached 70%. Beyond the watershed, the fluorescence intensity has increased significantly and achieved its maximum value at the highest water content. To obtain the quantification of the AIE feature of this category of dyes, the calculation on the enhancement ratio ($I/I_0 – 1$) was performed, while $I$ and $I_0$ is the photoluminescence intensity at every water content and in THF, respectively. Furthermore, the plot of the enhancement ratio against water fraction could illustrate the variation and the influence of water addition and aggregation clearly. From the plot, it reveals the emission intensity of $\textbf{L1}$ in aggregated state is almost double with respect to that in the dissolved medium.
From the previous studies, the presence of bulky cyano group on ethylene unit encourages the molecules twisting and adopting a non-planar conformation to minimize the steric obstruction. The twisted conformation of the molecules tolerates the radiationless intramolecular rotation, thus rendering the luminogens weakly emissive or even non-emissive in the isolated form. With the introduction of a bad solvent, the solubility of dye molecules drop dramatically which forces them to be constrained in the small volume of good solvent and begins the aggregation process of the molecules. Unlike the conventional planar luminogens, such as pyrene, the twisted conformation of the cyanostilbene has suppressed the $\pi-\pi$ stacking interaction between molecules and the formation of excimer and this hypothesis could be supported by the observation from absorption spectra of the cyanostilbene-based derivatives. A bathochromic shift in the absorption band could provide the evidence that the molecules are arranged in a J-type aggregation, where the molecules are packed in a head-to-tail style. This aggregation morphology could reduce the parallel face-to-face interaction, which is commonly found in the conventional planar dyes, and thus the excimer formation.\textsuperscript{19} Additionally, the bathochromic shift could be accounted for the enhancement of emission through the planarization of distorted conformation of molecules in isolated state. When the two aromatic rings are twisted out of the central plane, the $\pi$-conjugation and the electron delocalization has been
broken and destroyed in certain extent and thus the emission efficiency is lowered significantly. With the elimination of conformation twisting by restriction of intramolecular rotation due to the physical constraint of bulky group, the electron delocalization throughout the whole molecules could be recovered by prolonging the conjugation and hence the emission of the luminogen is retrieved and strengthened.

The end-capped cyanostilbene derivatives showed a larger enhancement ratio than their corresponding terminal acetylene ligands, suggesting that the connection of two AIE-active ligands with either fluorene or Pt(PBu$_3$)$_2$(C≡C)$_2$ unit reinforce the influence of aggregation in the emission enhancement. The enhancement ratio is a relative value of the photoluminescence intensity in dissolved and aggregated state. Therefore, the enhancement ratio is amplified by either increasing the value of numerator ($I$) or decreasing the magnitude of denominator ($I_0$) or both. For the cyanostilbene compounds, the intramolecular rotations within the twisted conformation are active in giving rise to the weak emission for the luminogens in isolated state. Comparing to the terminal acetylene ligands, the end-capped complexes possess “double” rotatable joints and a weaker emission is observed in dissolved medium. In these cases, the justification of the larger enhancement ratio for the end-capped compounds could be assigned to the smaller value of the denominator, which is the photoluminescence intensity in dissolved state. A similar phenomenon
could be observed in the comparison of \textbf{L1} and \textbf{L5} – \textbf{L8}. The extended conjugation of \textbf{L1} is performed by attaching the aromatic ring, such as benzene or extra TPA unit, on the TPA unit terminally. The insertion of these aromatic rings not only has an effect in prolonging conjugation of molecule, but also brings the accessional rotatable joint to the structure. For example, the enhancement ratio of \textbf{L8} in $f_w = 90\%$ is the highest one with a value of 1128 among eight terminal acetylene ligands. It indicates the meaning that the fluorescence intensity of \textbf{L8} in the aggregated state is 1128-higher than in dissolved medium, which could be justified by the same argument in the previously mentioned case that it owns the most rotatable connections.

From Fig. 2-23, the emission maxima of TPA-containing cyanostilbene compounds (\textbf{L1}, \textbf{L2} and \textbf{L5} – \textbf{L8}) are examined. Similar to the behavior in absorption spectra, a notable red-shifted in emission band of \textbf{L2} is observed as compared to that of \textbf{L1}, proposing that the thiophene ring does have an influence on the band gap by extending the length of $\pi$-conjugation system. From other approach, the increase in fluorescence maxima of substituted TPA cyanostilbene derivatives (\textbf{L5} – \textbf{L8}) could also be encountered in the comparison to the bare TPA cyanostilbene compound (\textbf{L1}). It further verifies that the explanation in UV spectra that the rings have extended the conjugation of the molecules. In the comparison of the emission spectra of \textbf{L5} – \textbf{L8} in aggregated state (Fig. 4), \textbf{L8} exhibits the most red-shifted emission maximum while
**L1** is the most blue-shifted one, which is in an agreement with their order of electron-donating ability of the substituents: triphenylamine $>$ benzene $\approx$ fluorene $>$ difluorobenzene.
Figure 2-19 The fluorescence spectra (left) and the plot of $I/I_0 - 1$ (right) of L1 – L4 in THF/water mixture with different water fraction.
Figure 2-20 The fluorescence spectra (left) and the plot of $I/I_0 - 1$ (right) of L5 – L8 in THF/water mixture with different water fraction.
Figure 2-21 The fluorescence spectra (left) and the plot of $I/I_0 - 1$ (right) of D1 – D4 in THF/water mixture with different water fraction.
Figure 2-22 The fluorescence spectra (left) and the plot of $I/I_0 - 1$ (right) of Pt1 – Pt4 in THF/water mixture with different water fraction.
Figure 2-23 Normalized fluorescence spectra of \textbf{L1, L2, L5 – L8} in THF/water mixture with $f_w = 90\%$. 
2.7 Molecular Orbital Calculations

To study and understand the electronic structures of the new cyanostilbene compounds, density functional theory (DFT) based on B3LYP/6-31G(d) level using Gaussian 09 were conducted for selected molecules. The optimized geometries and HOMO/LUMO plots of selected cyanostilbene-based compounds are displayed in Fig. 2-24. Obviously, the electron cloud of HOMO level of the cyanostilbene molecules is spread within the entire $\pi$-conjugated framework, while the LUMO level is dominated by the orbital of electron-accepting cyano side of the molecule. In addition, the HOMO and LUMO levels are highly delocalized for both molecules, indicating efficient $\pi$-conjugation within the molecular framework.
2.8 Application Studies of Cyanostilbene-Based Arylacetylide Small Molecules

2.8.1 Live Cell Imaging

The luminescent images of the HeLa cell after incubating with 20 μM of cyanostilbene-based luminogens for 1 hour at 25 °C are shown in Fig. 2-25. The cells internalized are excited by laser with 760 nm excitation and emitted bright-red fluorescence. Fig. 2-25 shows that the fluorescence areas are overlaid with the location of the cell, demonstrating that the AIE luminogens are uptake by the cell and accumulated with the cell. From the dark area in the cell (location of the nucleus), it illustrated that the intracellular distributions of the fluorophore are mainly located within cytoplasm, instead of nucleus and membrane. According to the fluorescence
image of the cell, the AIE luminogens demonstrate strong fluorescence intensity, good cell-permeability and biocompatibility, which promote these fluorescent nanomaterials as the promising candidates for bioprobe in bioimaging studies and application.
2.8.2 Chemical Vapor Sensor

In the previous studies, as the fluorescence properties of the cyanostilbene acetylide compounds were presumed to be switchable in common organic solvent vapor, it is suggested this behavior could be applied in one of the potential applications as a chemical vapor sensor. As shown in Fig. 2-26a, a thin layer of D1 is developed on a TLC silica plate which emits strongly with bright yellow color under illumination with a 365 nm UV lamp at room temperature, due to the restriction of intramolecular rotations of the cyanostilbene molecules in absolute absence of solvent. Afterwards, the emission of the TLC plate with the adsorption of D1 is turned off in
the presence of dichloromethane vapor, as the solvation of vapor of good solvent sparks on the re-organization and free rotation of the molecules. This fluorescence turn on/off properties are also applied for D2 and D3 which are illustrated in Fig. 2-26b and Fig 2-26c, respectively. Owing to the reversible turn-on/off capability in an atmosphere of dichloromethane vapor, they are suitable candidate for on/off fluorescence switching application.

![Figure 2-26](image)

**Figure 2-26** On/off fluorescence switching of (a) D1, (b) D3, and (c) D4 on TLC plates in dichloromethane vapor (left) and without vapor (right) under 365 nm UV lamp at room temperature.

### 2.8.3 Electroluminescence Devices

The performance of electroluminescent properties of selected cyanostilbene acetylide compounds has been investigated with OLED structure: ITO/PEDOT:PSS (Al4083, 35 nm)/AIE material (15 mg/ml, 700 rpm, 70 °C, 30 min)/TPBI (50 nm)/LiF (1 nm)/Al (100 nm). All the devices were fabricated by inexpensive solution processing technique for the emissive layer preparation.
Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is employed as the hole injection layer and to smooth the anode indium tin oxide (ITO) surface. 1,3,5-Tris(N-phenylbenzimidazol-2-yl)benzene (TPBI) acts as electron transporting layer, while LiF acts as the electron injection layer and Al as the cathode. Each of the devices exhibits a strong orange to orange-red EL peak in the wavelength range of 564-620 nm. The relatively high driving voltages may be due to the lack of host material in the emissive layer which results in large charge transfer barrier at the device layer interface. We noted that the EL peaks are slightly dependent of the driving voltage but all their $\lambda_{\text{EL}}$ are close to the maxima of their aggregation induced emission peaks in $f_w = 90\%$. The best EL performance was observed in L1 based device with maximum: luminous efficiency of 0.90 cd/A, power efficiency of 0.47 lm/W and external quantum efficiency of 0.54 %. All the devices do not suffer from significant efficiencies roll off as the current density increases. Further optimization is needed to enhance the performance of the OLED device based on our compounds.
Figure 2-27 Luminous and power efficiencies of selected compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{EL} (nm)</th>
<th>V_{on} (V)</th>
<th>L_{max} (cd/m^2) (^a)</th>
<th>(\eta_L) (cd/A) (^a)</th>
<th>(\eta_p) (lm/W) (^a)</th>
<th>(\eta_{ext}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>612</td>
<td>5.14</td>
<td>372 (10.2)</td>
<td>0.90</td>
<td>0.473</td>
<td>0.54</td>
</tr>
<tr>
<td>L3</td>
<td>600</td>
<td>6.60</td>
<td>162 (12)</td>
<td>0.455</td>
<td>0.21</td>
<td>0.24</td>
</tr>
<tr>
<td>L4</td>
<td>596</td>
<td>7.60</td>
<td>28.1 (16.8)</td>
<td>0.136</td>
<td>0.0526</td>
<td>0.086</td>
</tr>
<tr>
<td>D1</td>
<td>620</td>
<td>4.39</td>
<td>72.3 (10.8)</td>
<td>0.11</td>
<td>0.0875</td>
<td>0.057</td>
</tr>
<tr>
<td>D2</td>
<td>564</td>
<td>12.01</td>
<td>69.7 (17.8)</td>
<td>0.033</td>
<td>0.0086</td>
<td>0.0266</td>
</tr>
</tbody>
</table>

\(^a\) Maximum values of the devices. Values in parentheses correspond to the voltage where they are collected.

For the sake of improving the performance of L1, the electroluminescent properties of the cyanostilbene-based luminogens with extended conjugation of L1 have also been examined with the OLED structure: ITO/PEDOT:PSS (AI4083, 35 nm)/AIE material (15 mg/ml, 700 rpm, 70 °C, 30 min)/TPCz (8nm)/TPBI (42 nm)/LiF (1 nm)/Al (100 nm). L5 – L8 exhibited an orange-red EL emission at 588 – 620 nm, which match the emission pattern to the PL spectra in aggregation state constituted by water fraction of 90%. In Table 2-4, it summarized the EL data for L5...
– **L8.** The best OLED performance was obtained in L8 based device, with the maximum brightness ($L_{\text{max}}$) of 1446.9 cd/m$^2$ at 10.8 V, a luminance efficiency ($\eta_L$) of 3.38 cd/A, a power efficiency ($\eta_p$) of 3.08 lm/W and a peak external quantum efficiency ($\eta_{\text{ext}}$) of 2.84%. Similarly, all L5 – L8 based devices do not suffer from a significant efficiency roll off with the increase of current density. The OLED performance for L8 based device has been improved with respect to that for L1 based device, suggesting the extended conjugation system of the molecules facilitates and ameliorates the charge recombination and charge transporting processes. From the performance tendency, it has furnished a prospective strategy in the evolution of OLED performance through the molecular design engineering in extending conjugation of AIE-active cyanostilbene-based compounds.
Figure 2-28 Luminous and power efficiencies of L5 – L8.

Table 2-4 Electroluminescent properties of L5 – L8

<table>
<thead>
<tr>
<th>λ&lt;sub&gt;EL&lt;/sub&gt; (nm)</th>
<th>( L_{\text{max}} ) (cd/m&lt;sup&gt;2&lt;/sup&gt;)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>( \eta_\text{L} ) (cd/A)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>( \eta_\text{P} ) (lm/W)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>( \eta_\text{ext} ) (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>L5</td>
<td>620</td>
<td>629.8 (12.4)</td>
<td>2.25</td>
<td>1.21</td>
</tr>
<tr>
<td>L6</td>
<td>600</td>
<td>769.2 (10)</td>
<td>0.879</td>
<td>0.80</td>
</tr>
<tr>
<td>L7</td>
<td>588</td>
<td>1332.7 (14)</td>
<td>2.47</td>
<td>1.07</td>
</tr>
<tr>
<td>L8</td>
<td>612</td>
<td>1446.9 (10.8)</td>
<td>3.38</td>
<td>3.08</td>
</tr>
</tbody>
</table>

<sup>a</sup> Maximum values of the devices. Values in parentheses correspond to the voltage where they are collected.
2.9 Concluding Remarks

A series of TPA- and carbazole-containing cyanostilbene-based compounds were designed, synthesized and well characterized by common spectroscopic techniques. We have discussed the electrochemical, thermal and photophysical properties of all cyanostilbene derivatives. The decomposition temperatures ($T_d$) of all cyanostilbene compounds exceed 300 °C, revealing they can be used in the application of electroluminescent device as a solid emitter. From the investigation of the emission profile of cyanostilbene-based luminogens, they are all AIE-active by comparing the photoluminescence intensity in dissolved ($f_w = 0\%$) and in aggregated ($f_w = 90\%$) state. In the quantification of the AIE effect, the calculation of the enhancement ratio ($III_0 – 1$) of each fluorophore was performed. Among all AIE-active dyes, L8 possesses the highest enhancement ratio with a value of 1128, which means the photoluminescence intensity of L8 has been increased by 1128-times in aggregated form as compared to that in isolated state. With the understanding of the emissive behavior in solid state, the application in live cell imaging, chemical vapor sensor and electroluminescence devices by applying the selected chromophores were studied. In the examination of the fluorescent image of HeLa cell incubated with the selected cyanostilbene-based luminogens, they are believed to have a strong fluorescence intensity, good cell-permeability and biocompatibility. This renders these fluorescent nanomaterials
to be a potential bioprobe in bioimaging studies and selected application. With the reversible switch-on/off capability in the atmosphere of common organic solvents, the cyanostilbene-based dyes are qualified in the employment as a fluorescent detector in an organic vapor sensor. Being an efficient solid-state emission with high decomposition temperature, utilization of these cyanostilbene derivatives in electroluminescence devices has been considered. Among all selected compounds, \textbf{L8} based device has the best device performance with maximum: luminous efficiency of 3.38 cd/A, power efficiency of 3.08 lm/W and external quantum efficiency of 2.84\%. Further optimization on the device configuration has to be carried out to obtain an enhancement in device performance.
References


Chapter 3 Synthesis and Characterization Cyanostilbene-Based Platinum-Arylacetylide Polymers with AIE Characteristics

3.1 Introduction

The advanced organic polymeric luminescent materials have drawn the attention of scientists owing to the potential utilization of these class of materials in the fabrication of optoelectronic device,\(^1\)-\(^4\) as fluorescent sensor\(^5\)-\(^8\) and bioprobes.\(^10\)-\(^11\) Holding a typical highly \(\pi\)-conjugated, disc-like and highly planar molecular structure of most conventional luminogens, the highly emissive properties at diluted solutions have vanished once the fluorophores aggregated in the solid state. By virtue of the strong \(\pi\)-\(\pi\) stacking interaction between the aromatic rings, the excimer formation has facilitated the non-radiative relaxation process for the excited species and led to a decline in fluorescent intensity in condensed condition, so-called aggregation-caused quenching (ACQ) effect.\(^12\)-\(^15\)

Recently, an aggregation-induced emission (AIE) phenomenon expressed by silole,\(^16\)-\(^18\) tetraphenylethylene (TPE)\(^19\)-\(^21\) and cyanostilbene\(^22\)-\(^25\) derivatives illustrate an anti-ACQ behavior, where the non-luminescent compounds in dilute solution has been converted to highly emissive one with the introduction of non-solvent for the generation of nanoaggregates of the compounds. Although most of the up-to-date AIE-active materials are low-molecular-weight molecules, the fabrication method of
these luminogens into thin solid film for practical applications, such as vacuum deposition and vapor deposition, are relatively expensive and not applicable in large-area devices. On the other hand, organic conjugated polymers with high molecular weight and excellent thin-film form ability could be an alternative candidate to remedy the weaknesses of low-molecular-weight luminogens, since the comparatively simple and inexpensive fabrication processes, such as spin-coating and ink-jet printing, could be employed in the formation of large-area thin film solid at ambient condition.

In this chapter, we will work on the construction of a new class of polymers, along with organic and platinum-containing one, based on the AIE-active cyanostilbene-based ligand. We also study the photophysical properties, including absorption and emission, of these polymers in response to the surrounding environment (viz. the spacers and the corresponding linkage distance).

3.2 Synthesis of Platinum-containing Polymers Containing Cyanostilbene-Based Arylacetylide

3.2.1 Synthesis of Cyanostilbene-based Arylacetylide Ligands

The synthetic pathways of polymers containing cyanostilbene-based arylacetylide, P1 – P7, are outlined in Schemes 3-1 to 3-5. The key ligand precursor,
CHO9, was synthesized from the Sonogashira coupling reaction of trimethylsilylacetylene and 4-(bis(4-iodophenyl)amino)benzaldehyde in the presence of a palladium catalyst, which is the product from the idodination reaction of CHO1 in Chapter 2 (Scheme 3-1). Being the other key ligand precursors, the benzyl cyanide derivatives (CN1 – CN3) were obtained from the Pd-catalyzed Suzuki coupling reaction of the boronic acid with different substituents and 2-(4-bromophenyl)acetonitrile (Scheme 3-2).

Scheme 3-1 Synthetic route of CHO9

Scheme 3-2 Synthetic scheme of benzyl cyanide derivatives (CN1 – CN3)
As depicted in Scheme 3-3, the key ligands, \textbf{L9} – \textbf{L11}, were readily synthesized from the Knoevenagel condensation reaction in basic ethanol from the previously prepared \textbf{CHO9} and \textbf{CN1} – \textbf{CN3} in good yields. At the beginning, the ethoxide ion in the solution deprotonates the acidic hydrogen on the CH$_2$-unit of benzyl cyanide molecule. Then, the deprotonated benzyl cyanide would react with aldehyde and the resulting adduct can undergo subsequent base-induced elimination of water to yield the desired ligand. Apart from the condensation reaction of aldehyde and benzyl cyanide, the desilylation reaction could also be achieved in one-pot reaction in a basic medium.

\textbf{Scheme 3-3} Synthetic route of cyanostilbene-based arylacetylide ligands (\textbf{L9} – \textbf{L11})
3.2.2 Synthesis of Cyanostilbene-Based Platinum-Arylacetylide Polymers

After the preparation of diacetylene ligands, the two connecting ports are ready to be linked with different spacer terminally. In Scheme 3-4, two distinct aromatic-ring linkers with two terminal connecting sites, 1,4-diiodobenzene and 9,9-dibutyl-2,7-diodo-9H-fluorene are employed in the polymerization. For dialkyl substituted fluorene moiety, it was obtained from the dialkylation of 2,7-diodo-9H-fluorene with alkylating reagent, 1-bromobutane, in a strong base (50% KOH aqueous solution) for deprotonation on the 9-position carbon. In the polymerization reaction, the halogen-containing linkers were reacted with one equivalent of diacetylene ligand via Sonogashira coupling reaction to get the corresponding organic polymers, P1 – P4. On the other hand, the diacetylene ligands were reacted with trans-[Pt(PBu₃)₂Cl₂] in 1:1 molar ratio by CuI-catalyzed dehydrohalogenation reaction to give P5 – P7. The time duration for the polymerization reaction is important in order to optimize the solubility and the number of repeating unit of the polymers. While the resultant polymers with very high molecular weight will have a poor solubility in any organic solvent, low molecular weight polymer could not illustrate the influence of polymerization of AIE-active ligands on their optical properties. It is necessary to control the reaction time precisely by virtue of formation of a relatively high molecular weight polymer with sufficient
solubility for the following measurement.

Scheme 3-4 Synthetic chart of P1 – P7
3.3 Characterization of Cyanostilbene-Based Platinum-Arylacetylide Polymers

All the newly synthesized polymers are air-stable and could be stored without any precautions. They are all generally soluble in THF or common chlorocarbons, such as CH$_2$Cl$_2$ and CHCl$_3$, but exhibit a poor solubility in aliphatic hydrocarbon and alcohol. The chemical structure of all ligands and polymers are characterized by $^1$H, $^{13}$C, $^{31}$P-$^1$H NMR and FTIR spectroscopy. Since the proton resonance of polymers is broadened, the integral and the coupling constant cannot be determined accurately.

In proton NMR spectroscopy, the signals located at the downfield region correspond to the aromatic protons, while the protons of the alkyl chain give the peaks at the upfield region. For the key ligand precursor of benzyl cyanide derivatives, it exhibits the characteristic signal with an integral of 2 at around 3.8 ppm from the methylene hydrogen. After the condensation reaction between active methylene compounds with aldehyde, the absence of the signal at around 3.8 ppm verifies the complete nucleophilic addition reaction and dehydration. On the other hand, the terminal acetylenic hydrogen (–C≡CH) of the cyanostilbene-based ligand gives the unique sharp signal at 3.1 ppm which indicates that the desilylation and condensation reaction could be carried out in an one-pot synthesis. For the reaction between diacetylene ligand and organic or Pt-linker, the disappearance of the sharp signal at around 3.1 ppm gives information for the completion of polymerization between the
linkers and ligands. In addition, the characteristic peaks at 0.90 – 2.90 ppm belong to the PBu\textsubscript{3} units on the platinum-linked polymers. The selected NMR spectra of the compounds are shown in Fig. 3-1 to Fig. 3-4. The $^{31}\text{P}-\{^{1}\text{H}\}$ NMR spectrum of platinum-linked polymers exhibits a single resonance with a pair of $^{195}\text{Pt}$ satellites, which confirm a trans-arrangement of the PBu\textsubscript{3} ligand around platinum in a square planar geometry. The $J_{P-Pt}$ value of 2906 Hz for PBu\textsubscript{3} unit is typical of those for related trans-PtP\textsubscript{2} system.\textsuperscript{31} All IR spectra of the cyanostilbene compounds have illustrated the peculiar peak at around 2210 cm\textsuperscript{-1}, corresponding to the cyano group (C≡N) and the absence of the C≡C-H stretching mode at around 3300 cm\textsuperscript{-1} of the polymer suggests the formation of the Ar-C≡C (for organic polymers) and Pt-C≡C (for platinum-containing polymers) bonds.
Figure 3-1 $^1$H NMR spectrum of CN2 in CDCl$_3$.

Figure 3-2 $^1$H NMR spectrum of L10 in CDCl$_3$. 
Figure 3-3 $^1$H NMR spectrum of P2 in CDCl$_3$.

Figure 3-4 $^1$H NMR spectrum of P6 in CDCl$_3$. 
The molecular weight data of all polymers were measured by gel permeation chromatography (GPC) in THF using polystyrene as the standard and tabulated in Table 3-1. The degree of polymerization (DP) calculated from $M_n$ for the cyanostilbene-based polymer is in the range of 6 – 18, where the platinum-containing polymers enjoy a higher value of DP owing to the presence of flexible alkyl chain enhancing the solubility of the polymers during the reaction of polymerization. Indexes of polydispersity ($M_w/M_n$) of around 2 are determined, which is a common value of polycondensates. However, it should be noted that the data obtained from GPC are not the absolute value of molecular weight but a measure of hydrodynamic volume, as the calibration by polystyrene standard has created certain systematic error.

Figure 3-5 FTIR spectra of L1, P1, P2 and P5 as KBr disc.
to the measurement of molecular weight of the rigid rodlike polymers, such as polyynes, which holds a different hydrodynamic behavior to the flexible polymers.

The thermal properties of the cyanostilbene-based polymers are examined by thermal gravimetric analysis (TGA) in a nitrogen atmosphere with a heating rate of 20 °C min⁻¹. All polymers have high onset decomposition temperatures ($T_d$, temperature with 5% loss of sample) over 300 °C, suggestive of the good thermal stability of the polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$ a</th>
<th>$M_n$ a</th>
<th>$M_w/M_n$ a</th>
<th>$T_d$ (°C) b</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>9422</td>
<td>3269</td>
<td>2.88</td>
<td>310</td>
</tr>
<tr>
<td>P2</td>
<td>11297</td>
<td>6750</td>
<td>1.68</td>
<td>342</td>
</tr>
<tr>
<td>P3</td>
<td>11421</td>
<td>9042</td>
<td>1.26</td>
<td>340</td>
</tr>
<tr>
<td>P4</td>
<td>11218</td>
<td>9173</td>
<td>1.22</td>
<td>342</td>
</tr>
<tr>
<td>P5</td>
<td>27039</td>
<td>19294</td>
<td>1.40</td>
<td>311</td>
</tr>
<tr>
<td>P6</td>
<td>21012</td>
<td>13724</td>
<td>1.53</td>
<td>377</td>
</tr>
<tr>
<td>P7</td>
<td>21442</td>
<td>17023</td>
<td>1.26</td>
<td>308</td>
</tr>
</tbody>
</table>

a Estimated by GPC in THF on the basis of a polystyrene calibration

b Decomposition temperature at which a sample loses its 5% weight
3.4 Electrochemical properties of Cyanostilbene-Based Platinum-Arylacetylide Polymers

The electrochemical behavior of the cyanostilbene-based ligands and polymers were investigated by cyclic voltammetry (CV) in 0.1 M [Bu₄N]PF₆ in acetonitrile solution with glassy carbon as working electrode at a scan rate of 100 mV s⁻¹. All the experiments were performed with a conventional three-electrode configuration, consisting with a thin film of sample on glassy carbon working electrode, one Ag/Ag⁺ reference electrode and one Pt-wire auxiliary electrode. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy level of all cyanostilbene-based ligands and polymers were calculated using the equations $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.73) \text{ eV}$ and $E_{\text{LUMO}} = -(E_{\text{red}} + 4.73) \text{ eV}$, respectively, where $E_{\text{ox}}$ and $E_{\text{red}}$ are the onset oxidation and reduction potentials relative to ferrocence/ferrocenium (Fc/Fc⁺) couple. The experimental data are summarized in Table 3-2.

With the electron-rich diphenylamino group attached to the phenyl ring, L10 is more difficult to be reduced and has a more negative reduction potential. On the other hand, the replacement of hydrogen on phenyl ring by the electron-withdrawing trifluoromethyl group makes the compound electron deficient and result in a less negative reduction potential. Additionally, the HOMO energy level of polymer (P1 –
P7) is elevated in comparison to that of ligand (3), suggesting that polymerization has an effect on the extensive delocalization of electrons structure. Comparing to the degree of variation by different substituent, the $E_{\text{onset-red}}$ of the entire cyanostilbene derivatives are approximately constant (~ -1.2 eV), regardless of the electron delocalization, which corroborated with the calculation result in which the electrons in LUMO energy level mainly located on electron deficient cyano group.

**Table 3-2** Electrochemical properties of cyanostilbene-based compounds (L9 – L11 and P1 – P7)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox}}$ (V)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$E_{\text{HOMO}}$ (eV)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$E_{\text{red}}$ (V)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$E_{\text{LUMO}}$ (eV)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>$E_g$ (eV)&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>L9</td>
<td>1.03</td>
<td>-5.76</td>
<td>-1.25</td>
<td>-3.48</td>
<td>2.28</td>
</tr>
<tr>
<td>L10</td>
<td>1.00</td>
<td>-5.73</td>
<td>-1.27</td>
<td>-3.46</td>
<td>2.27</td>
</tr>
<tr>
<td>L11</td>
<td>1.02</td>
<td>-5.75</td>
<td>-1.25</td>
<td>-3.48</td>
<td>2.27</td>
</tr>
<tr>
<td>P1</td>
<td>0.90</td>
<td>-5.63</td>
<td>-1.22</td>
<td>-3.51</td>
<td>2.12</td>
</tr>
<tr>
<td>P2</td>
<td>0.94</td>
<td>-5.67</td>
<td>-1.22</td>
<td>-3.51</td>
<td>2.16</td>
</tr>
<tr>
<td>P3</td>
<td>0.83</td>
<td>-5.56</td>
<td>-1.23</td>
<td>-3.50</td>
<td>2.06</td>
</tr>
<tr>
<td>P4</td>
<td>0.98</td>
<td>-5.71</td>
<td>-1.22</td>
<td>-3.51</td>
<td>2.20</td>
</tr>
<tr>
<td>P5</td>
<td>0.81</td>
<td>-5.54</td>
<td>-1.25</td>
<td>-3.48</td>
<td>2.06</td>
</tr>
<tr>
<td>P6</td>
<td>0.68</td>
<td>-5.41</td>
<td>-1.25</td>
<td>-3.48</td>
<td>1.93</td>
</tr>
<tr>
<td>P7</td>
<td>0.69</td>
<td>-5.42</td>
<td>-1.25</td>
<td>-3.49</td>
<td>1.94</td>
</tr>
</tbody>
</table>

<sup>a</sup> Obtained from the onset oxidation and reduction potentials  
<sup>b</sup> HOMO = -(E<sub>ox</sub> + 4.73) (eV)  
<sup>c</sup> LUMO = -(E<sub>red</sub> + 4.73) (eV)  
<sup>d</sup> $E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$
3.5 Photophysical Properties of Cyanostilbene-Based Platinum-Arylacetylide Polymers

3.5.1 Absorption Properties

The photophysical properties of all cyanostilbene-based ligands and polymers have been recorded in THF and THF/water mixture with various water fractions at 298 K. From Fig. 3-6, it is clear that two distinguishable absorption bands could be observed from the spectra of the cyanostilbene-based diacetylene ligands (L9 – L11). While the higher-energy absorption band is assigned to the $\pi - \pi^*$ transition in the near UV region, the absorption band at the lower energy is the result from the intramolecular charge transfer (ICT) between donor and acceptor moiety.\textsuperscript{32}

A lower band gap and red-shift of the absorption spectrum is expected to be the consequence of the polymerization reaction through the extension of the $\pi$-conjugation. In this aspect, the absorption spectrum of P1 displayed a single band with absorption maximum nearly equal to the lower-energy band of L9. It is believed that electronic communication between L9 and benzene spacer has lowered the band gap, leading to an increase in the wavelength of $^1\pi-\pi^*$ absorption band and a merge of $^1\pi-\pi^*$ and ICT absorption band. A similar observation can be detected in other pairs of ligands and polymers with fluorene as the linker (L9/P2, L10/P3 and L11/P4). A little increase in the wavelength of absorption maximum for P2 with respect to P1
is observed, indicating that a higher electron delocalization within the polymer backbone is achieved by the more electron-rich fluorene moiety. Surprisingly, the platinum-containing polymers, \( \text{P7 – P9} \), did not exhibit the same phenomenon as in the organic polymer. The absorption spectrum of \( \text{P7} \) shares the same pattern with that of \( \text{L9} \), which displays two distinct groups of absorption bands. As compared to the ligand \( \text{L9} \), the absorption maximum of the higher-energy absorption bands has illustrated a red shift of 30 nm approximately in wavelength, indicating alkynylplatinum moiety in polymer backbone lengthens the conjugation length, similar to that of aromatic unit. However, the longer-wavelength absorption band has simultaneously presented a red-shifted manner resulting from the metal-to-ligand charge transfer (MLCT) excitation caused by the \( \text{trans-}[\text{Pt(PBu_3)_2}] \) unit and cyanostilbene-based ligand.\(^{33} \)

![Absorption spectra of L9 – L11 and P1 – P7 in THF (0% water) at a concentration of 1 x 10^{-5} M.](image)

**Figure 3-6** Absorption spectra of \( \text{L9 – L11} \) and \( \text{P1 – P7} \) in THF (0% water) at a concentration of 1 x 10^{-5} M.
3.5.2 AIE Properties

The aggregates of the cyanostilbene-based ligands and polymers are prepared by simple precipitation method by introduction of poor solvent without surfactants. In this case, water is chosen as the poor solvent for theses cyanostilbene compounds. In Fig. 3-7, it has demonstrated the photoluminescence spectra of $L_9$ in a variety of water proportion (0 – 90%) in THF/water mixture. In THF solution, the emission spectrum of $L_9$ exhibits only noisy photoluminescence signal with no discernible peak maximum. To examine the AIE properties, a poor solvent of $L_9$ is added to THF solution and the change in PL signal is monitored. The PL intensities of $L_9$ remain at low value in the aqueous solution with water fraction less than 60%, but increase rapidly beyond 60%. From THF to aqueous solution with 90% water, the PL intensity of $L_9$ has been increased by almost 17 fold. This AIE phenomenon is not an isolated case for $L_9$, but could be observed in other cyanostilbene-based ligands, $L_{10}$ and $L_{11}$.

The enhanced fluorescence emission of $L_9$ could be explained in terms of the intramolecular effect. Due to the conformational change of chromophores with respect to the outside environment, it is supposed that the non-radiative relaxation process arising from conformation twisting will suppress the radiative process, leading to a quenching of emission.$^{34-35}$ In aggregated environment, there is a conformational
change of the cyanostilbene compounds from twisted to more planar framework as the 
physical constraint between the molecules is strong enough to overcome the steric 
repulsion between aromatic rings and bulky cyano group.\textsuperscript{36-37} Owing to the 
planarization of the compounds and inhibition of non-radiative relaxation process, 
fluorescent property of cyanostilbene derivatives is modified to induce emission in 
aggregate state, even though it is non-luminescent in free condition.

In order to verify the proposed mechanism of the induced emission, the 
experimental UV-vis absorption measurement of \textbf{L9} with various compositions were 
performed. Fig. 3-8 shows the absorption spectra of \textbf{L9} at $f_w = 0\%$ and 90\%, and the 
maximum peaks of absorption band are red-shifted. The bathochromic shift of 
higher-energy band associated with $\pi-\pi^*$ transition and lower-energy band along with 
ICT transition reveals extension of the effective conjugation length and development 
of a more effective channel for the donor-acceptor charge transfer by the planarization 
of the twisted molecular conformation in aggregated state, respectively.
Figure 3-7 The fluorescence spectra (left) and the plot of $I/I_0 - 1$ (right) of L9 – L11 in THF/water mixture with different water fractions.
Figure 3-8 Absorption spectra of L9 – L11 in THF (0% water) and in dispersion of aggregated form (90% water) at a concentration of 1 x 10^{-5} M.

From previous research works, attachment of an AIE-active pendant, such as silole and tetraphenylethylene (TPE) to polymer backbone will result in an AIE or AEE (aggregation-enhanced emission) effect depending on the structure and ways of linkage. Following this approach, the AIE-active units L9 – L11 underwent polymerization through the Sonogashira coupling with aromatic moiety containing two iodo group in a para position to compose a polymer backbone with an alternate alkynyl unit (polyyne). According to the scheme, two polymers, P1 and P2 – P5, are created with different aromatic spacer, benzene and fluorene, respectively.

Unexpectedly, the aggregation of P1 caused the quenching of fluorescence instead (Figure 3-9). In pure THF solution of P1, it shows a strong PL signal at 530
nm, which behaves oppositely with reference to \( \mathbf{L9} \), since the polymerization process has connected the AIE-active ligand tightly and given rise to the planarization of the molecular conformation to certain extent, even in its isolated form. However, the addition of non-solvent, water, to the THF solution of \( \mathbf{P1} \) generally decreases its emission and its PL spectra are shifted by 60 nm bathochromically. In aggregation state, the shrinkage of its molecular volume in the aqueous condition has brought the aromatic rings together in a much closer distance. This physical motion arouses the orientation of the molecules into a better order of packing accompanying with a further planarization of the molecules, accounting for the bathochromic shift in the emission spectra in high water fraction. However, the \( \pi - \pi \) stacking interaction between aromatic rings has also been enhanced and hence the excimer formation is induced, leading to a non-radiative transition and quenching of emission. To deal with the problem, \( \mathbf{P2} \) was created through the replacement of benzene with a comparatively larger spacer, fluorene, in the position between AIE-active ligands on the backbone. However, it does not make the difference that \( \mathbf{P2} - \mathbf{P5} \) exhibit an ACQ effect similarly with a large drop in PL intensity in the aggregated state. Meanwhile, the absence of bathochromic shift in the absorption band of the organic polymers has suggested conformation planarization along with emission enhancement has not occurred, which is noticeable in the corresponding AIE-active ligands (Fig. 3-10).
Figure 3-9 The fluorescence spectra (left) and the plot of $I/I_0 - 1$ (right) of P1 – P4 in THF/water mixture with different water fractions.
Figure 3-10 Absorption spectra of P1 – P4 in THF (0% water) and in dispersion of aggregated form (90% water) at a concentration of $1 \times 10^{-5}$ M.

Although a flexible alkyl spacer insertion between ligand and polymer backbone or an even larger spacer could be the potential solution, it will disrupt the extensive $\pi$-conjugation system, harm the solubility of the polymer dramatically and favor the exciton trap with the structural defect on the polymer.\textsuperscript{40} Thus, platinum-containing polymers, P5 – P7, with a $\text{trans-}[\text{−Pt(PBu}_3\text{)}_2\text{C≡CRC≡C−}]_n$ system have been developed. Unlike polymer with organic spacer, P5 is nearly non-luminescent when it is dissolved in its good solvent, in which the PL spectrum of its dilute THF solution is almost parallel to the abscissa. (Fig. 3-10) Nonetheless, the emission signal is gradually intensified with the increment of water proportion in the solvent mixture and achieves an approximately 11-times amplification of the magnitude at $f_w = 90\%$
as compared to that in THF solution, illustrating $P_5$ is AIE-active. From the large red shift of the emission maximum of $P_5$ (593 nm) relative to $L_9$ (524 nm), it is suggested that the $\pi$-conjugation system originated with triphenylamine-based cyanostilbene unit of $L_9$ is remarkably prolonged by the extensive delocalization of polymer backbone with the electron-rich Pt ion. Not only does electron-rich Pt ion offer an avenue for extending conjugation, but also provides an obstruction in the $\pi-\pi$ stacking interaction among the highly planarized molecules as demonstrated by the unobservable shift in the emission maximum, in which it is the primary constraint in provoking the corresponding organic polymer possessing an aggregation-caused quenching feature. A similar behavior can be clearly observed for the other two ligand/polymer pairs.
Figure 3-11 The fluorescence spectra (left) and the plot of $I/I_0 - 1$ (right) of P5 – P7 in THF/water mixture with different water fractions.
Figure 3-12 The normalized photoluminescence spectra of the cyanostilbene-based ligands and the corresponding platinum-containing polymers (L9/P5, L10/P6 and L11/P7) in THF/water mixture with $f_w = 90\%$. 
To further understand the mechanism of the AIE behavior of the cyanostilbene-based platinum-containing polymers, P5 and P7 were selected as model for the calculation in computational quantum mechanical modeling by density functional theory (DFT). DFT/BP86 method was employed to optimize the ground-state structures of P5 and P7 with one to three repeat units (monomer, dimer and trimer) and electronic transition energies and corresponding oscillator strengths of these compounds was calculated using TDDFT/Cam-B3LYP according to the above optimized geometries. While the first 12 absorbing transition will be predicted in the theoretical calculation for the polymers with one repeating unit (monomer), first 36
absorbing transitions for the polymer with two (dimer) and three (trimer) repeating units. Then, the absorption profiles were calculated using the Gaussian model (Fig. 3-14). It can be noted that the calculated absorption spectra are red-shifted and much closer to experimental results with the increase of repeat unit from 1 to 3 (Fig. 3-13), indicating that this calculations method is reliable.

The calculated electronic transition energies and the corresponding oscillator strengths (f) of the low-lying excited states for P5 and P7 are listed in Table 3-3. The first excited state (S1) transition of the monomers of P5 and P7 corresponds to the orbital transition from the HOMO to LUMO. For the dimers, the first excited state (S1) and the second excited state (S2) are degenerated states and these excited-state transitions are contributed to the frontier molecular orbitals comprising of the HOMO-1 to the LUMO+1. Meanwhile, the S1, S2 and S3 are degenerated state for the trimer, and frontier molecular orbitals spanning the HOMO-2 to the LUMO+2 are involved in these transitions. Fig. 3-15 shows the calculated frontier molecular orbitals for these low-lying excited-state transitions of P5 and P7. The low-lying states of these compounds could be regarded as π→π* transitions due to the π-type symmetry of electron density of the orbitals. For the monomers, the low-lying transition corresponds to HOMO→LUMO, while the low-lying transitions occur from two degenerate states with mixed HOMO→LUMO+1 and HOMO-1→LUMO for
dimers and the low-lying transitions occur from three degenerate states with mixed HOMO-2→LUMO, HOMO-1→LUMO+1, HOMO-1→LUMO+2, HOMO→LUMO+1 and HOMO→LUMO+2 for trimers. All of these transitions are characterized as intramolecular charger transfer (ICT) for monomers, dimers and trimers. As the ICT process induced by a polar solvent, such as THF, provides a non-radiative transition pathway for the excited state to decay to the ground state, the low-lying excited state with evident ICT character for P5 and P7 is the origin for the fluorescence quenching in their THF solution. With the introduction of a poor solvent, the aggregation has blocked the ICT process as the inner environment of the aggregates of polymer becomes less polar than outside. The ICT excited state is no longer stabilized by the molecules of the polar solvent, and the non-radiative decay process is suppressed and thus switch on the radiative one to result in emission. The elimination of the ICT process through aggregation could be supported by the blue-shift of emission spectrum. From Fig. 3-11, it is recognized that the emission maximum in THF/water mixture with $f_w = 90\%$ was blue-shifted with a magnitude of 9, 13 and 16 for P5 – P7, respectively, in accordance with to the previous claim. In addition, the emission lifetimes of the selected cyanostilbene-based polymers, P5 and P7 in THF and THF/water mixture with 90% water at 298 K are given in Table 3-4. The excited states of P5 and P7 decay in a single exponential fashion, implying that

all excited species decay through the same pathway. The lifetime for the excited state of P5 is 0.97 ns in THF solution and 1.34 ns in a mixture with $f_w$ of 90%. On the other hand, P7 exhibits the same movement at various lifetimes of the excited state, in which the lifetime has been increased to 1.26 ns from 0.62 ns. The longer lifetime for the excited state of the aggregates of P5 and P7 could account for the enhanced emission in the aqueous solution.

**Figure 3-14** Calculated absorption spectra of a) P5 and b) P7. Monomer: black line; dimer: red line; and trimer: blue line, obtained at the TD-DFT/Cam-B3LYP/SVP
Table 3-3 Calculated electronic transition energies and major contribution for the low-lying singlet excited states of P5 – P7

<table>
<thead>
<tr>
<th>Cpd</th>
<th>Repeating unit</th>
<th>Electronic transition</th>
<th>Energy $f^b$</th>
<th>Contribution$^c$</th>
<th>CI$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5</td>
<td>1 monomer</td>
<td>$S_0 \rightarrow S_1$</td>
<td>414 (2.99)</td>
<td>1.7238</td>
<td>HOMO→LUMO</td>
</tr>
<tr>
<td></td>
<td>2 dimer</td>
<td>$S_0 \rightarrow S_1$</td>
<td>428 (2.90)</td>
<td>1.8997</td>
<td>HOMO→LUMO+1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S_0 \rightarrow S_2$</td>
<td>415 (2.99)</td>
<td>1.7055</td>
<td>HOMO-1→LUMO</td>
</tr>
<tr>
<td></td>
<td>3 trimer</td>
<td>$S_0 \rightarrow S_1$</td>
<td>429 (2.89)</td>
<td>2.4620</td>
<td>HOMO-1→LUMO+1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S_0 \rightarrow S_2$</td>
<td>425 (2.91)</td>
<td>1.2588</td>
<td>HOMO-1→LUMO+2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S_0 \rightarrow S_3$</td>
<td>414 (3.00)</td>
<td>1.7263</td>
<td>HOMO-2→LUMO</td>
</tr>
<tr>
<td>P7</td>
<td>1 monomer</td>
<td>$S_0 \rightarrow S_1$</td>
<td>419 (2.96)</td>
<td>1.7688</td>
<td>HOMO→LUMO</td>
</tr>
<tr>
<td></td>
<td>2 dimer</td>
<td>$S_0 \rightarrow S_1$</td>
<td>431 (2.88)</td>
<td>1.9910</td>
<td>HOMO→LUMO+1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S_0 \rightarrow S_2$</td>
<td>417 (2.97)</td>
<td>1.6927</td>
<td>HOMO-1→LUMO</td>
</tr>
<tr>
<td></td>
<td>3 trimer</td>
<td>$S_0 \rightarrow S_1$</td>
<td>432 (2.87)</td>
<td>2.3571</td>
<td>HOMO-1→LUMO+1</td>
</tr>
<tr>
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<td></td>
<td>$S_0 \rightarrow S_2$</td>
<td>429 (2.89)</td>
<td>1.6096</td>
<td>HOMO-1→LUMO+2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S_0 \rightarrow S_3$</td>
<td>418 (2.97)</td>
<td>1.6509</td>
<td>HOMO-2→LUMO</td>
</tr>
</tbody>
</table>

$^a$ Only the selected low-lying excited states are presented

$^b$ Oscillator strength

$^c$ Only the main configurations are presented.

$^d$ The CI coefficients are in absolute values.
Figure 3-15 Calculated frontier molecular orbitals HOMO (H) and LUMO (L) for P5 and P7 with one to three repeat units (monomer, dimer and trimer)

Table 3-4 Emission data and fluorescence decays of excited states of selected cyanostilbene-based polymers (P5 and P7) in THF/water mixture

<table>
<thead>
<tr>
<th>$f_w$ (vol %)</th>
<th>$\lambda_{em}$ (nm)$^a$</th>
<th>$\tau_1$ (ns)$^b$</th>
<th>$\lambda_{em}$ (nm)$^a$</th>
<th>$\tau_1$ (ns)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>609</td>
<td>0.9645±0.0045</td>
<td>614</td>
<td>0.6241±0.0041</td>
</tr>
<tr>
<td>90</td>
<td>593</td>
<td>1.337±0.0055</td>
<td>605</td>
<td>1.258±0.0053</td>
</tr>
</tbody>
</table>

$^a$ Wavelength for emission maximum in THF and THF/water mixture at 298 K

$^b$ Dynamic parameter determined from $I = A_1 \exp(-t/\tau_1)$, where $\tau_1$ is the lifetime of the excited species. Excitation wavelength: 460 nm
3.6 Concluding Remarks

In summary, this chapter has outlined the preparation of a series of new cyanostilbene-based ligands and polymers, which have been well characterized by $^1$H NMR and FT-IR spectroscopy and their molecular weight properties were determined by gel permeation chromatography (GPC). Thermal gravimetric analysis reveals that both organic and platinum-containing polymers are thermally stable with the decomposition temperature ($T_d$) exceeding 300 °C. From the examination of the AIE behavior of these cyanostilbene-based ligands and polymers, we find that the diacetylene ligands and Pt-containing polymers exhibit the typical AIE phenomenon with the PL intensity enhanced by around 15-fold in their aggregation state as compared to the isolated form. In addition, there is a noticeable red-shift of emission spectra for the Pt-containing polymers with respect to their corresponding ligands, suggesting that the $\pi$-conjugation system have been extended effectively through the connection of trans-[Pt(PBu$_3$)$_2$] unit to the AIE-active ligands. However, an ACQ problem has occurred on the aromatic-ring-linked polymers, including the benzene and fluorene linker, where the emission intensities of these polymers have dropped to the minimum with the generation of aggregated by a high fraction of water. Inconsistence with the optical behavior of the diacetylene ligands, the organic polymers (P1 – P4) are strongly emissive even in their diluted solution as the
polymerization process has tied up the AIE-active ligand tightly and given rise to the planarization of the molecular conformation to a certain extent. The further shrinkage of its molecular volume in the aqueous condition has brought the aromatic rings together in an even closer distance. At that point, the aromatic rings experience a strong $\pi - \pi$ stacking interaction between aromatic rings and hence the formation of excimers is induced, leading to a reduction of emission intensity. On the other hand, the electron-rich Pt unit provides an obstruction in the $\pi-\pi$ stacking interaction and renders the Pt-containing polymer enjoying strong fluorescence in the condensed phase. Meanwhile, the DFT calculation on the Pt-containing polymer and the blue shift of emission spectra in high water content give the evidence that the AIE phenomenon arises from the elimination of the non-radiative intramolecular charge transfer (ICT) process.
References


Chapter 4 Synthesis, Characterization and Study of Intramolecular Charge Transfer (ICT) and Aggregation Induced Emission of Phenothiazine-Cyanostilbene-Based Luminogens

4.1 Introduction

The development of red-emitting materials is a high demanding field in the application of electroluminescent devices, fluorescent sensor and bioimaging.\textsuperscript{1-11} The traditional strategy to red-shift the emission is achieved by narrowing the band gap by prolonging the $\pi$-conjugation system through introduction of additional aromatic rings to the structure or connection of strong electron-donating (D) and -withdrawing (A) unit with the luminogens. However, most of the fluorophores with large and fused aromatic ring suffer from the notorious aggregation-caused emission quenching (ACQ) effect.\textsuperscript{12} In addition, intramolecular charge transfer (ICT) arising from the dipole-dipole interaction between D-A system activates the non-radiative decay channel and is the origin of fluorescence quenching.\textsuperscript{13-15} The discovery of an opposite behavior to ACQ effect, which is known as aggregation-induced emission phenomenon, has solved the problems generated by ACQ effect, such as the limitation of fluorophore concentration in the real-world application and obstacle in utilizing the luminogen in electroluminescence device.

Recently, for a series of D-A molecules, boron dipyrromethene (BODIPY) has
been used to study the optical properties with the AIE behavior. BODIPY derivatives are found to have dual photoresponses to solvent polarity and aggregation of molecules. Along with the increase of solvent polarity, a large bathochromic shift and quenching of emission band could be observed, illustrating the polar solvent molecules has brought the luminogens from local excited (LE) to twisted intramolecular charge transfer (TICT) state. On the other hand, the large amount of water in the solution stimulates the formation of aggregates and hence slightly blue-shift and boost the emission.\textsuperscript{16} The reports on this V-shape behavior with a back and fore fashion of emission intensity are quite rare, due to the lack of a guideline to the molecular design and the relationship studies on the structure and properties.

Herein, we are encouraged to design and synthesize a series of luminogens with D-A system, which optical performance is under investigation with respect to the variation of solvent polarity and water content. In our previous work, cyanostilbene moiety is believed to possess the AIE properties, including small molecules and polymers, which could also be regarded as the electron-withdrawing unit in the structure. Associated with different electron-donating unit, a number of compounds with D-A system could be developed. In the previous chapter, two donor groups (triphenylamine and carbazole) have been connected with the cyanostilbene moiety; however, it is less likely for us to recognize the dual photoresponses to the aggregate
formation and solvent polarity in these D-A molecules. Therefore, phenothiazine is introduced and employed as the electron donating group and the backbone of the luminogens in this chapter. The electron-rich properties with high first oxidation potential of phenothiazine is favorable for the OLED applications serving as electrophore probes in supramolecular assemblies and sensor studies,\textsuperscript{17-19} which offer us an avenue for the continuous studies on the potential utilization of these phenothiazine-containing cyanostilbene-based molecular materials. From photoluminescence measurements of these luminogens, a comparable emission phenomenon to the BODIPY derivatives can be detected and an alternate mechanism to RIR process could be employed in the explanation of the unusual AIE performance.

4.2 Synthesis of Phenothiazine-Cyanostilbene-Based Luminogens

The synthetic methods of the phenothiazine-containing aldehyde and the cyanostilbene-based luminogens are shown in Scheme 4-1 to Scheme 4-3. As shown in Scheme 4-1, the N-alkylation of phenothiazine is obtained from the reaction of 10\textit{H}-phenothiazine, alkylating agent (1-bromohexane) and a strong base (KOH powder) which is used to deprotonate the hydrogen atom on the nitrogen atom. After the preparation of 10-hexyl-10\textit{H}-phenothiazine, a freshly prepared of the chloroiminium ion, which is called as Vilsmeier reagent, is first prepared from the
reaction of a substituted amine (dimethylformamide) with phosphorus oxychloride in a very dry condition. Then, the electron-rich arene, 10-hexyl-10H-phenothiazine in this case, is introduced and allowed to react with Vilsmeier reagent. In the workup procedure, water is poured into the mixture in order to hydrolyze the initial iminium ion to the corresponding aldehyde product, CHO10. Subsequently, CHO10Br is obtained by the bromination of CHO10 with the aid of N-bromosuccimide (NBS) in the absence of light. Then, the Pd-catalyzed Suzuki coupling reaction between CHO10Br and the appropriate boronic acid, such as phenylboronic acid and (4-methoxyphenyl)boronic acid afford CHO11 and CHO12, respectively.

Scheme 4-1 Synthetic route of CHO10 – CHO12 and CHO10Br
Taking advantage of the benzyl cyanide derivatives in Chapter 3, C1 – C3 can be readily given from the nucleophilic addition of the active hydrogen compounds to the carbonyl group of CHO10, followed by the dehydration reaction where a water molecule is eliminated (Scheme 4-2). Following the same pathway, C4 – C6 and C7 – C9 are successfully synthesized from the Knoevenagel condensation reaction between CN1 – CN3 and CHO11 and CHO12, respectively (Scheme 4-3).

**Scheme 4-2** Synthetic route of C1 – C3
Scheme 4-3 Synthetic route of C4 – C9
4.3 Spectroscopic Characterization of Phenothiazine-Cyanostilbene-Based Luminogens

All newly synthesized phenothiazine-cyanostilbene compounds are found to be soluble in common organic solvents, such as CH$_2$Cl$_2$, CHCl$_3$ and THF and fully characterized by $^1$H and $^{13}$C NMR spectroscopy. All the NMR data are summarized in the experimental part of Chapter 7.

As depicted in Fig. 4-1, the sharp singlet signal from aldehydic proton of the phenothiazine aldehyde, CHO10, is observed at the downfield region with $\delta = 9.8$ ppm, which provides the information for the carboxyl group insertion to the phenothiazine unit. On the other hand, the CH$_3$ protons of the methoxy group for C6 – C9 give rise to a strong singlet at $\delta = 3.8$ ppm, which has overlapped with the triplet from the hexyl group on the nitrogen atom of phenothiazine to get a combined integral of 5 (CH$_3$ of methoxy and CH$_2$ of n-C$_6$H$_{13}$). All the aromatic protons are illustrated with the accurate integrals. The selected $^1$H NMR spectra are shown in Figs. 4-1 to 4-3.
Figure 4-1 $^1$H NMR spectrum of CHO10 in CDCl$_3$.

Figure 4-2 $^1$H NMR spectrum of C7 in CDCl$_3$. 
Figure 4-3 $^1$H NMR spectrum of C9 in CDCl$_3$.

The $^{13}$C NMR spectra of the phenothiazine-cyanostilbene-based compounds represent the unequal chemical environments of every carbon with the structure by inductive effect. While the signals corresponding to aromatic carbon are located in downfield region, the upfield region displayed the peaks arose from the hexyl group for all alkylated phenothiazine and methoxy group specified for in C7 – C9
Figure 4-4 $^{13}$C NMR spectrum of C1 in CDCl$_3$.

Figure 4-5 $^{13}$C NMR spectrum of C9 in CDCl$_3$. 
4.4 Electrochemical Properties of Phenothiazine-Cyanostilbene-Based Luminogens

The electrochemical behavior of phenothiazine-cyanostilbene-based derivatives was examined by cyclic voltammetry (CV) in 0.1 M ([Bu₄N]PF₆) in MeCN solution as the supporting electrolyte using ferrocence as the internal standard. All measurements were carried out in a set up composing a thin film of sample on glassy carbon working electrode, Ag/Ag⁺ reference electrode and platinum wire counter electrode at a scan rate of 100 mV s⁻¹. The HOMO and LUMO energy levels of all cyanostilbene-based derivatives were determined by the following equations: $E_{\text{HOMO}} = -(E_{\text{onset, ox}} + 4.73)$ eV and $E_{\text{LUMO}} = -(E_{\text{onset, red}} + 4.73)$ eV, where the unit of potential is V versus Ag/AgCl.

The energy gaps of all phenothiazine-cyanostilbene-based derivatives determined from the difference between HOMO and LUMO energy level in the CV measurement are in the range of 2.04 – 2.24 eV, which are in agreement with the optical band gaps discussed in the following part. From the measurement, the influence of the introduction of electron-donating/-withdrawing group to the different position on the phenothiazine-cyanostilbene unit was investigated. In the comparison of C1 and C2, the attachment of electron-donating diphenylamine group on the cyanostilbene unit makes C2 more difficult to be reduced. On the other hand, it is
easier for C2 to be oxidized by the addition of this electron-donating group to the structure. As the destabilization effect on LUMO energy level is more effective than that on HOMO energy level through the insertion of electron-rich unit on the cyanostilbene unit, C2 exhibits an increase of energy band gap towards C1. On the contrary, binding of an electron-withdrawing CF3 group to the benzene ring near cyano group leads to more accessible way for the reduction. Similar to C2, it is more obvious in the stabilization on the LUMO energy level than that on HOMO energy level, illustrating a lowering in the band gap for C3. Moreover, the variation on the electrochemical properties in the series of C4 – C6 and C7 – C9 is found to be similar to the previous observation.

From another point of view, the band gap can be modified through connecting electron-donating/-withdrawing group to the phenothiazine side of the structure to cause a (de)stabilization of HOMO/LUMO level. C4 – C6 are the products of the attachment of the electron-donating benzene ring to the 7th position of phenothiazine moiety (3rd position to cyanostilbene part). Expectedly, the inclusion of the electron-rich element to the structure has caused the destabilization in the LUMO energy level and stabilization in HOMO energy level as the reduction is less likely to occur and oxidation is more readily to take place. C4 has illustrated a reduction in the magnitude of band gap instead. It is possible that the fastening of the benzene ring to
the phenothiazine directly could promote a more significant destabilization to the HOMO energy level than to LUMO energy level. For the sake of verifying the previous hypothesis, another set of models (C7 – C9) has been established with the cooperation with 4-methoxylbenzene ring of higher electron-donating power. From the set of measurements and calculations, a larger decline in the band gap in C7 as compared with C1 and C4 is collected, which supports to our argumentation. According to these results, the HOMO and LUMO energy levels of the phenothiazine-cyanostilbene-based derivatives could be adjusted by simply changing the substituent on either phenothiazine side or cyanostilbene unit. Based on this strategy, it offers not only a fine tuning on the color of the emission but also a tailor-made HOMO/LUMO level for these potential emissive layer to better fit the energy levels of the OLEDs components in order to achieve a more efficient charge transportation.
### Table 4-1 Electrochemical properties of cyanostilbene-based compounds (C1 – C9)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox}}$ (V)(^a)</th>
<th>$E_{\text{HOMO}}$ (eV)(^b)</th>
<th>$E_{\text{red}}$ (V)(^a)</th>
<th>$E_{\text{LUMO}}$ (eV)(^b)</th>
<th>$E_g$ (eV)(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.96</td>
<td>-5.69</td>
<td>-1.27</td>
<td>-3.46</td>
<td>2.23</td>
</tr>
<tr>
<td>C2</td>
<td>0.96</td>
<td>-5.69</td>
<td>-1.29</td>
<td>-3.44</td>
<td>2.25</td>
</tr>
<tr>
<td>C3</td>
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<td>-1.25</td>
<td>-3.48</td>
<td>2.22</td>
</tr>
<tr>
<td>C4</td>
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<td>-5.68</td>
<td>-1.27</td>
<td>-3.46</td>
<td>2.22</td>
</tr>
<tr>
<td>C5</td>
<td>0.95</td>
<td>-5.68</td>
<td>-1.29</td>
<td>-3.44</td>
<td>2.24</td>
</tr>
<tr>
<td>C6</td>
<td>0.95</td>
<td>-5.68</td>
<td>-1.25</td>
<td>-3.48</td>
<td>2.21</td>
</tr>
<tr>
<td>C7</td>
<td>0.94</td>
<td>-5.67</td>
<td>-1.27</td>
<td>-3.46</td>
<td>2.21</td>
</tr>
<tr>
<td>C8</td>
<td>0.941</td>
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<td>-1.29</td>
<td>-3.44</td>
<td>2.23</td>
</tr>
<tr>
<td>C9</td>
<td>0.95</td>
<td>-5.68</td>
<td>-1.26</td>
<td>-3.47</td>
<td>2.20</td>
</tr>
</tbody>
</table>

\(^a\) Obtained from the onset oxidation and reduction potentials

\(^b\) HOMO = -(E_{\text{ox}} + 4.73) (eV); LUMO = -(E_{\text{red}} + 4.73) (eV)

\(^c\) $E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$

### 4.5 Optical Properties of Phenothiazine-Cyanostilbene-Based Luminogens

#### 4.5.1 Absorption properties

The absorption properties of the phenothiazine-cyanostilbene-based luminogens were recorded in THF at 298 K. In Fig. 4-6, the intense absorption spectra below 350 nm are dominated by the spin-allowed $\pi-\pi^*$ transition due to the contribution of the phenothiazine moiety and benzene rings on the substituents. Furthermore, the moderately intense bands at the longer wavelength within the visible region of 350 – 500 nm correspond to the intramolecular charge transfer between donor and acceptor unit.
Figure 4-6 UV-Vis absorption spectra of phenothiazine-cyanostilbene-based fluorophores (C1 – C9) in THF (298 K)
4.5.2 Solvent effect

The emission properties of phenothiazine-cyanostilbene-based compounds were investigated in different solvents with a broad range of polarity. Upon the excitation of UV light, the hexane solution of C1 emits a strong green light, while its toluene and 1,4-dioxane solutions emit a yellow light. In relatively polar media, such as ethyl acetate, tetrahydrofuran and dichloromethane, the color of emissive light is yellow to orange, whereas in highly polar solvents, such as ethanol, acetonitrile and methanol, it has changed to red and nearly invisible. Therefore, the fluorescence spectroscopy was performed to investigate the transformations of the emission features quantitatively (Fig. 4-8). The recognizable bathochromic shifts of emission maxima with ~80 nm were observed with the increase of solvent polarity. In constrast, the UV-Vis spectra show only a narrow discrepancy as compared to emission one, in which the shift in absorption peaks has a magnitude of ~20 nm (Fig. 4-8).
**Figure 4-7** Photographs showing the emission color of C1 under UV illumination in different solvents: (A) Hexane, (B) toluene, (C) 1,4-dioxane, (D) ethyl acetate, (E) THF, (F) dichloromethane, (G) ethanol, (H), acetonitrile and (I) methanol.

**Figure 4-8** The normalized emission spectra and absorption spectra of solution of C1 in solvent with variation of polarity ($\Delta f$).
The influence of the solvent on the optical properties has been studied by the relationship of the Stokes shifts of absorption and emission maxima and Lippert–Mataga solvent polarity parameter \( \Delta f \), equation 1), and the experiment data are summarized in Table 4-2.

\[
\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 - 1}
\]

(1)

where \( \varepsilon \) and \( n \) are the permittivity (or dielectric constant) and the refractive index of the solvent, respectively.

In non-polar solvent, hexane \( (\Delta f \approx 0) \), **C1** has shown a single and sharp emission peak at 530 nm. In toluene with a slight increase of polarity \( (\Delta f = 0.013) \) than hexane, the emission band has migrated to the yellow spectral region with a shift of emission maximum of 36 nm. With the further escalation of the solvent polarity, **C1** has even a redder emission, accompanied with a drop of emission intensity. In the highly polar solvent of acetonitrile and methanol \( (\Delta f \approx 0.3) \), the quantum efficiency of **C1** is only one eighth of that in hexane, with a large degree of shift of emission maximum.

Similarly, the emission spectra of entire phenothiazine-cyanostilbene-based luminogens \( \textbf{C2} - \textbf{C9} \) have exhibited a significant bathochromic shift and decline in intensity with the promotion of solvent polarity (Fig 4-9). From these results, it has indicated that the emission behaviors of all phenothiazine-cyanostilbene-based luminogens are intensively sensitive to the polarity of the solvent, which means they display a positive solvent solvatochromism. In the comparison of **C1** to **C4** and **C7,**
however, the degree of the decrease on the quantum efficiency in high polarity solvent (ethanol, acetonitrile and methanol) of $\text{C}_4$ and $\text{C}_7$ is much larger than that of $\text{C}_1$. It is suggested that $\text{C}_4$ and $\text{C}_7$ have more rotatable joints than $\text{C}_1$ and thus the conformational twisting of the excited species is more significant, accounting for the larger extent in light emission quenching.
### Table 4-2 Absorption maxima (\(\lambda_{\text{abs}}\) in nm) of C1 – C9 in different solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\Delta f^a)</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>C9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>~0</td>
<td>406</td>
<td>406</td>
<td>413</td>
<td>417</td>
<td>422</td>
<td>423</td>
<td>423</td>
<td>421</td>
<td>423</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.013</td>
<td>413</td>
<td>410</td>
<td>418</td>
<td>427</td>
<td>427</td>
<td>432</td>
<td>433</td>
<td>429</td>
<td>433</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>0.025</td>
<td>411</td>
<td>402</td>
<td>416</td>
<td>426</td>
<td>424</td>
<td>433</td>
<td>432</td>
<td>423</td>
<td>427</td>
</tr>
<tr>
<td>EA</td>
<td>0.201</td>
<td>405</td>
<td>402</td>
<td>410</td>
<td>417</td>
<td>417</td>
<td>421</td>
<td>427</td>
<td>428</td>
<td>427</td>
</tr>
<tr>
<td>THF</td>
<td>0.210</td>
<td>422</td>
<td>421</td>
<td>423</td>
<td>431</td>
<td>431</td>
<td>431</td>
<td>431</td>
<td>433</td>
<td>438</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
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<td>422</td>
<td>422</td>
<td>425</td>
<td>429</td>
<td>429</td>
<td>434</td>
<td>433</td>
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<td>413</td>
<td>418</td>
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<td>428</td>
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<td>405</td>
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<td>419</td>
<td>414</td>
<td>424</td>
<td>424</td>
<td>416</td>
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### Table 4-3 Emission maxima (\(\lambda_{\text{em}}\) in nm) of C1 – C9 in different solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\Delta f)</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
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<th>C9</th>
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<tr>
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<td>576</td>
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<td>570</td>
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<td>590</td>
<td>607</td>
<td>601</td>
<td>603</td>
<td>609</td>
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<tr>
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<td>617</td>
<td>627</td>
<td>625</td>
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</table>

### Table 4-4 Quantum efficiencies (\(\phi_E^a\) in %) of C1 – C9 in different solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\Delta f)</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>C9</th>
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<td>66.8</td>
<td>81.7</td>
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<td>67.6</td>
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<td>99.7</td>
<td>78.3</td>
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<td>64.0</td>
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<td>73.5</td>
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\(^a\) Measured with 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran as standard (\(\phi = 82\%\) in dimethylformamide)
Figure 4-9 Photographs showing the emission color of C2 – C9 under UV illumination in different solvents: (A) Hexane, (B) toluene, (C) 1,4-dioxane, (D) ethyl acetate, (E) THF, (F) dichloromethane, (G) ethanol, (H), acetonitrile and (I) methanol.
**Figure 4-10** The normalized emission spectra (right) and absorption spectra (left) of solution of C2 – C9 in solvent with variation of polarity (Δf).
4.5.3 Intramolecular charged transfer process

Molecules consisting of donor–acceptor (D–A) structures usually own solvatochromism effect; the emission is strongly dependent on solvent polarity. In the Franck–Condon state or local excited (LE) state, the molecules adopt a planar conformation. In non-polar solvent, the coplanar excited states could be stabilized by the electronic conjugation and is in equilibrium with the surrounding solvent molecules. Therefore, LE state is the lowest excited state in non-polar solvent and the emission intensity mainly comes from LE state, producing a sharp emission spectrum. In polar solvent environment, the planar conformation is no longer stable and the excited fluorophores are not in equilibrium with the solvent molecules. The intramolecular rotation of the molecule causes a twisted conformation and the total charge separation of the orbital of donor and acceptor, leading to the charge transfer between donor and acceptor. As a result, a new equilibrium ICT state with a larger dipole moment is stabilized by the surrounding polar solvent molecules. The elevating of HOMO energy level will narrow the band gap possessing a red-shifted emission spectrum; however, the non-radiative quenching pathway for the transformation of LE state to ICT state will diminish the emission intensity.

To have a better understanding of the ICT effect of the cyanostilbene derivatives, the polarity of solvent was varied systemically through the mixing of THF, non-polar
hexane and polar methanol together with particular fractions and the optical properties in particular ratios of solvent mixtures were examined. As depicted in Fig. 4-11, increasing the hexane fraction in solvent mixture has led to the blue shift of the emission spectra with the emission color switching from orange to yellow, along with the growth of emission quantum efficiency. On the other hand, the gradual addition of methanol in solvent brings an opposite effect on the luminescent response to the THF/hexane mixture. The quantum efficiency in methanol fraction of 90% has dropped to a one fourth of that in $f_m = 0\%$ and emission intensity maximum has been red-shifted by $\sim 20$ nm. The systematical increase of the polarity of the solvent mixture (hexane$\rightarrow$THF$\rightarrow$methanol) has shown a red-shift manner in the emission spectra, which is originated to the transition from LE state in the equilibrium with non-polar solvent molecules to ICT state stabilized by polar solvent molecules. To estimate whether the solvatochromism is a specific case for C1, the other phenothiazine-cyanostilbene-based derivatives also revealed similar trend analogous to C1. From Fig. 4-15 to Fig. 4-17, it is clear that the quantum efficiencies have declined gradually accompanied by the noticeable red-shifted emission band through the rise of solvent polarity, indicating that the optical response to the variation of solvent polarity is a general phenomenon observed in this series of luminogens.
Figure 4-11 Photographs showing the emission color of C1 under UV illumination in THF/hexane mixture with $f_h = 0 \text{ – } 90\%$.

Figure 4-12 A) Emission spectra of C1 in THF/hexane mixture ($f_h = 0 \text{ – } 90\%$). B) Plot of emission intensity maximum and quantum yield of C1 against hexane fraction ($f_h$) in THF/hexane mixture.
Figure 4-13 Photographs showing the emission color of C1 under UV illumination in THF/methanol mixture with $f_m = 0 – 90\%$.

Figure 4-14 A) Emission spectra of C1 in THF/methanol mixture ($f_m = 0 – 90\%$). B) Plot of emission intensity maximum and quantum yield of C1 against methanol fraction ($f_m$) in THF/methanol mixture.
Figure 4-15 Photographs showing the emission color of C2 – C9 under UV illumination in THF/hexane mixture with $f_h = 0 - 90\%$ and in THF/methanol mixture with $f_m = 0 - 90\%$. 
Figure 4-16 (Left) Emission spectra of C2 – C9 in THF/hexane mixture ($f_h = 0$ – 90%). (Right) Plot of emission intensity maximum and quantum yield of C2 – C9 against hexane fraction ($f_h$) in THF/hexane mixture.
Figure 4-17 (Left) Emission spectra of C2 – C9 in THF/methanol mixture ($f_m = 0 – 90\%$). (Right) Plot of emission intensity maximum and quantum yield of C2 – C9 against methanol fraction ($f_m$) in THF/methanol mixture.
4.5.4 AIE phenomenon

Apart from examining the emission properties at different solvent polarity, the influence of aggregation of molecules on the emission behavior of these cyanostilbene compounds are under investigation through the thorough study of their optical properties in THF/water mixture. Fig. 4-18 shows the photographs of cyanostilbene compound in THF/water mixture with defined fraction taken under UV illumination. When the THF solution of C1 emits a yellow light, the color of emission has switched to a redder region in the aqueous mixture at \( f_w \leq 60\% \) with the depreciation of the light intensity. However, the emission of C1 is restored after a larger portion of water is admixed with THF (\( f_w > 70\% \)), instead of the further bathochromic shift and decline in light emission.

In addition, the transformation of the emission behavior of C1 is quantified by the spectrometric measurements. Upon excitation at 430 nm, an emission band with a fluorescence maximum at 590 nm is achieved for the THF solution of C1. With the gradual increase of water content in the THF/water mixture, it has generated a bathochromic shift with a magnitude of 22 nm and a noticeable decrease of light emission with only one fourth of the photoluminescence intensity in \( f_w = 60\% \) relative to that in THF solution. Similar to the visual observation, the light emission is renovated and further intensified when more water is introduced (Fig. 4-19). However,
the emission of C1 could not be recovered to its highest value in the largest portion of water in THF/water mixture. From both visual observation and quantitative result, C1 has illustrated an unusual behavior as compared to most cyanostilbene compounds, in which the photoluminescence intensity will boost gradually in pace with water fraction and hold its maximum with \( f_w = 80 \text{–} 90\% \). In Fig. 4-19B, a V-shape graph is developed when the water fraction is plotted against the photoluminescence intensity maxima, which is in contrast to a successive climb of fluorescence intensity in the ordinary cyanostilbene compounds. Moreover, while a red-shifted emission is usually acquired from the extended conjugation of molecules established by the planarization of the twist conformation in most cyanostilbene compounds in condensed phase, an unusual back and forth shift in emission maximum is recognized for C1.

This particular phenomenon is originated from both the solvatochromism through the presence of ICT process in low water content and the limitation of the non-radiative transformation of LE to ICT state process by the formation of aggregates at high water content. In low water fraction, the addition of “small” amount of water increase the polarity of solvent mixture, similar to the situation in highly polar solvent such as acetonitrile and methanol, and initiates excited species transforming from LE state to ICT state. The fraction of ICT state is dominant with the reduction of LE state in low water content, which provokes a red-shift and decline
in emission. On the other hand, the solubility of these cyanostilbene compounds is worsened in “large” amount of water and the formation of aggregates is encouraged to begin. With the bend shape of phenothiazine and bulky cyano moiety, the excimer formation and its non-radiative decay process is restricted. Additionally, as the distance between excited molecules and the surrounding polar solvent is lengthened, effective solvent polarity inside aggregates is reduced and a less polar environment of inner phase inside aggregates is created. The ICT state of excited molecules in the inner domain is destabilized and non-radiative transition process from LE to ICT state is eliminated. Thus the LE state is more preferable in high water content, which leads to an enhancement and blue-shift in emission spectrum and AIE phenomenon is observed.
Figure 4-18 Photographs showing the emission color of C1 under UV illumination in THF/water mixture with $f_w = 0 – 90\%$.

Figure 4-19 A) Emission spectra of C1 in different THF/water fractions. B) Plot of photoluminescence intensity and emission intensity maximum of C1 versus water fraction ($f_w$).
In order to have a comprehensive understanding on the mechanism of the emission enhancement, another solvent mixture pair, methanol/water was chosen in the ongoing experiment. With the high polarity of methanol solution, the introduction of water could hardly create an effect on the resultant polarity. The origin of the emission in pure methanol solution of the cyanostilbene compounds mainly arises from ICT state, instead of LE state. The interference (solvatochromism) in both emission maximum and intensity by the change in solvent polarity, which is detected in THF/water mixture, on the study of emission enhancement in aggregation could be eliminated by employing methanol/water solvent pair. The emission spectra of C1 in methanol/water mixture are presented in Fig. 4-20. In methanol solution, weak fluorescence intensity could be detected and is somewhere constant when a small amount of water is added. However, the light emission has escalated starting from $f_w = 40\%$ and reached its maximum at 90\%. Meanwhile, the emission spectra show a blue-shifted pattern. In respect to the outcome in THF/water solvent mixture, a similar trend at high water content region in THF/water solvent system was observed for the methanol/water solution of the cyanostilbene compounds. In other words, these cyanostilbene compounds have the ability to enhance their emission through the formation of aggregates by suppression of the non-radiative process after photoexcitation.
Figure 4-20 A) Emission spectra of C1 in different methanol/water fractions. B) Plot of photoluminescence intensity and emission intensity maximum of C1 versus water fraction ($f_w$).
To check whether this emission behavior is a general phenomenon for cyanostilbene-based luminogens with similar structure, the optical properties of the series of C4 – C6 and C7 – C9 were further studied by the identical experimental condition to that of C1. All the emission spectra in various pair of solvent mixture in defined ratio are displayed in Fig. 4-22. The trend of the performance in the photophysical measurements, including absorption and emission, are approximately equivalent to those for the cyanostilbene model, C1. In THF/water solvent mixture, the forward and reverse shift in emission maximum and the V-shape pattern for the derivation in light intensity could also be collected in all cyanostilbene fluorophores. Consistent to C1, the emission intensities of C2 – C9 are weakened with the expansion of water fraction at low water fraction region and the weakest light emission is attained at $f_w = 60\%$. On the other hand, the formation of aggregates with further addition of water has reversed the direction of the change in emission intensity, which is in agreement with C1. Among these cyanostilbene luminogens, only the series of C7 – C9 is more emissive in its condensed phase than that in its dissolved solution. It is likely the methoxy group on the phenyl moiety has promoted the hydrophobicity and the proportion of aggregates of C7 – C9 in high water content, which will facilitate to eliminate the non-radiative process and hence the maximum fluorescence is achieved at $f_w = 90\%$. On the other hand, the emission of C4 and C7
in all condition are red-shifted as compared to that of C1, suggesting that the 
\(\pi\)-conjugation could be extended and could be reached by attachment of the aromatic 
ing ring on the phenothiazine moiety. The red-shifted emission spectra could also be 
encountered in comparing C5 and C8 to C2 and C6 and C9 to C3. In addition, the 
increase in the emission maximum could be received by fastening the 
electron-accepting unit, -CF\(_3\), to cyanostilbene unit (C3, C6 and C9) with respect to 
phenyl ring counterpart (C1, C4 and C6, respectively) which is the outcome of the 
smaller band gap by the larger effect on destabilization of HOMO than that of LUMO.
Figure 4-21 Photographs showing the emission color of C2 – C9 under UV illumination in THF/water mixture with $f_w = 0 – 90\%$. 
Figure 4-22 (Left) Emission spectra of C2 – C9 in methanol/water mixture ($f_w = 0 – 90\%$). (Right) Plot of emission intensity maximum and quantum yield of C2 – C9 against water fraction ($f_w$) in methanol/water mixture.
4.6 Concluding Remarks

In this chapter, investigation has been focused on achieving the red-emitting phenothiazine-cyanostilbene-based luminogens. We have successfully designed and afforded nine new chromophores with donor (D) – acceptor (A) system prepared with phenothiazine (D) and cyanostilbene (A) units. Additionally, the substituents with electron-withdrawing/donating moiety has been attached to either/both phenothiazine or/and cyanostilbene part to examine their electrochemical and photophysical properties.

In the study of electrochemistry, the introduction of the electron-donating unit to the structure could lift both HOMO and LUMO energy levels. However, the substitution of the diphenylamino unit to the hydrogen atom on the cyanostilbene part is more effective in elevating HOMO than LUMO energy level, leading to an increase in the band gap of C2, C5 and C8 to C1, C4 and C6, respectively. On the other hand, the attachment of benzene or 4-methoxyphenyl ring to the phenothiazine part directly will lead to a lower band gap as the influence on the destabilization of LUMO is greater than HOMO energy level. On the contrary, the electron-withdrawing group makes the molecules easier to be reduced and stabilizes the LUMO energy level. As a result, the electron-withdrawing group on the cyanostilbene moiety renders a greater influence on the LUMO energy level and the narrower band gap for C3, C6 and C9.
To present the optical behavior of phenothiazine-cyanostilbene-based derivatives, their response to the variation of solvent polarity was firstly investigated. \( \text{C1} - \text{C9} \) have exhibited a positive solvatochromism and color tunability by changing the polarity of solvent and LE-ICT transition. In non-polar solvents, the strong emission of cyanostilbene-based derivatives arises from the relaxation of LE excited state, whereas the red-shifted and weaker emission comes from the ICT state in polar solvents. To investigate the AIE properties of this class of luminogens, water is introduced to trigger the aggregation of molecules. However, the phenothiazine-cyanostilbene derivatives exhibit a V-shape fashion of emission intensity transformation, which is inconsistent to typical AIE phenomenon of the conventional cyanostilbene compounds with a successively climb up of photoluminescence intensities in response to enlargement of water proportion in the solvent mixture. When a “small” amount of water was being introduced, the emission of chromophores started to quench due to the influence of growth of solvent polarity overstepping the aggregation of molecules. On the other hand, the addition of a “large” amount of poor solvent induced the aggregate formation. A less polar local environment is created and thus suppresses the non-radiative transition to the ICT state, causing a blue shift in the emission color and a boost of emission efficiency.

To satisfy the high demand on red emitting chromophores in numerous
applications, we are encouraged to design a rational method to shift the emission color of our compounds with high emission efficiency. Based on the traditional approach, the lengthening of \( \pi \)-conjugation and red shift of the emission color through the incorporation of fused and large aromatic rings into our structure has initiated the non-radiative relaxation process and ACQ expression, which is contrary to the original intention of this project. In this work, we have successfully generated a group of new AIE luminogens built on D – A system with the emission color spread to the red region. In the inspection of the emission enhancement and color of the phenothiazine-cyanostilbene-based luminogens, \( C_7 \) – \( C_9 \) are the group of derivatives which are more emissive in their aggregated state than that in the solution. The methoxy group on the phenyl moiety directly attached to phenothiazine is believed to reinforce the hydrophobicity and enlarge the degree of aggregate formation in high water content, facilitating the elimination of the non-radiative process and enhancement of emission. In addition, the 4-methoxyphenyl unit on phenothiazine unit together with 4-trifluoromethylphenyl ring on cyanostilbene side was found to have the greater reduction of band gap on altering the energy level of HOMO and LUMO. As a consequence, \( C_9 \) has combined both electron-donating and withdrawing effect and thus its emission color is the most red-shifted one. Evidently, enhancement and color of emission could be accomplished through the fine modification on the
structure or substituent of cyanostilbene compound. It demonstrates the great
tunability on the optical properties of the cyanostilbene fluorophores and possibility to
create the numerous luminogens with desired emission color and high emission
efficiency through a comprehensive structural design.
References


Chapter 5 Synthesis and Characterization of A Highly Selective Cadmium (II) Chemosensor Based on a Pyridyl-Functionalized Cyanostilbene-Based Compound with Aggregation-Induced Emission Characteristics

5.1 Introduction

The design and development of sensors in detecting cadmium ion have been of considerable interest in recent years due to the detrimental and toxic effects of cadmium ion on human health. The U.S. Environmental Protection Agency has listed cadmium as one of the 126 priority pollutants and the half-life of cadmium in human body are estimated to be 15 – 20 years.1 In addition, the FAO/WHO Joint Expert Committee on Food Additives recommends the maximum intake of cadmium of 1.0 – 1.2 μg kg⁻¹ body mass per day.2 The excessive exposure to cadmium will cause serious health problem, including pulmonary cancer, prostatic and renal cancers.3-5 The most common method in the analysis of cadmium involves the use of atomic absorption (AA) or inductively coupled plasma (ICP) atomic emission spectroscopy. In spite of their highly sensitivity and selectivity in metal ion detection, they usually require numerous complicated laboratory preconcentration procedures and are relatively expensive.6-9

In fact, a great number of fluorescent metal ion sensors based on the optical
response of luminogens have been studied owing to its operational simplicity, real-time detection and high selectivity.\textsuperscript{10-11} However, there are only a few cadmium ion fluorescent sensors reported as the greatest challenge of finding a suitable cadmium ion sensor is the difficulty in differentiating zinc ion and cadmium ion or the interference of zinc in detection of cadmium in the sample.\textsuperscript{12-16} Considering zinc and cadmium belonging to the same group, they own similar properties and cause indistinguishable spectral change, such as fluorescent intensity and maximum wavelength of emission and absorption through the interaction of these metal ions and the sensing materials.\textsuperscript{17-19} While the selectivity is one of the important criteria to become an eligible metal ion sensor, the development of a novel cadmium ion chemosensor distinguishing cadmium ion from zinc ion is an imperative demand.

To evaluate the metal ion content, water is usually the working platform for the preparation and investigation of the unknown sample, such as polluted food, soil or water. Although the conventional organic luminogens hold a high fluorescence in the dilute solution, they suffer from the aggregation-caused quenching (ACQ) effect in condensed phase or dispersion in aqueous media. The decline in the emission of this class of materials comes from the strong $\pi - \pi$ stacking interaction and the formation of excimer or exciplexes, hampering the utilization of these ordinary luminescent materials in metal ion sensing.\textsuperscript{20-23} Up to now, aggregation-induced emission (AIE)
phenomenon, which is an exactly opposite behavior against ACQ effect, has been extensively examined and numerous of compounds, for example tetraphenylethene (TPE)\textsuperscript{24-25} and cyanostilbene derivatives,\textsuperscript{26-27} have been employed in difference areas, such as organic light-emitting diodes (OLEDs) and bioprobes. Through the proper molecular design, these classes of compounds could be evolved to be a potential candidate in sensitive probes for the detection of metal ion.

For the sake of enduring a metal-coordinating ability, in this chapter, we have designed and synthesized a pyridine-containing cyanostilbene-based compound, C11, which have been functionalized (Z)-2-([1,1'-biphenyl]-4-yl)-3-phenylacrylonitrile (P-bPCN, Scheme 5-1), with a pyridine moiety in the view of its strong metal chelating capacity.\textsuperscript{28} Being insoluble in aqueous media, C11 forms an aggregate and turns on its emission with greenish-blue light. When the mixture comprising the aggregate of C11 is exposed to cadmium(II) ion, it experiences a noticeable escalation and bathochromic shift of the emission spectra, demonstrating its potential ability to be a satisfactory cadmium ion sensor in aqueous condition.

\begin{center}
\textbf{Scheme 5-1} The chemical structure of (Z)-2-([1,1'-biphenyl]-4-yl)-3-phenylacrylonitrile (P-bPCN)
\end{center}
5.2 Synthesis of Pyridyl-Functionalized Cyanostilbene-Based Compounds

Scheme 5-2 shows the chemical structures and the synthetic strategies to the intermediates and the target pyridyl-functional cyanostilbene compound, C11. The attachment of the pyridine moiety to P-bPCN was accomplished in three-step stage via an ethylene unit connection. In the first step, C10 was obtained from the Knoevenagel condensation reaction between CN1 in chapter 3 and 4-methylbenzaldehyde. On the methyl group placed in the benzylic position of C10, the reactivity has been increased and it is ready to undergo photochemical bromination in converting the methyl group to benzyl chloride precursor using benzoyl peroxide (BPO) as radical initiator. Through the reaction of triphenylphosphine with the alkyl halide (C10Br), the phosphonium ylide (Wittig reagent) has been prepared which was treated with a strong base to undergo Wittig olefination with picolinaldehyde to obtain the target product, C11.

Scheme 5-2 Synthetic route of C11
5.3 Spectroscopic Characterization of Pyridyl-Functionalized Cyanostilbene-Based Compounds

All the newly synthesized compounds are air-stable and can be stored without any special precautions. They have all been well characterized by common spectroscopic techniques including $^1$H and $^{13}$C NMR spectroscopy. $^1$H and $^{13}$C NMR analyses have clearly illustrated a well-defined structure for each compound. Figs. 5-1 to 5-3 have demonstrated the selected proton spectra for the compounds, C10, C10Br and C11. While the proton signals located at the downfield region correspond to the aromatic proton, the CH$_3$ protons of the methyl group on aromatic position give rise to the sharp singlet at $\delta = 2.4$ ppm. After the free radical bromination on the methyl group, one proton has been replaced which is illustrated in the $^1$H NMR spectrum of C10Br. Not only is the integral of the proton signal in the upfield region reduced by 1, but also the chemical shift of the singlet is increased ($\delta = 4.5$ ppm) due to the insertion of the higher electronegative neighbor atom, Br. For the pyridyl-functionalized derivative, a characteristic downfield signal with $\delta = 8.6$ ppm from the proton on the pyridyl ring can be observed in $^1$H NMR spectrum of C11, suggesting the successful attachment of pyridine ring to the cyanostilbene-based compound.
The entire carbon signal observed in the $^{13}$C NMR spectra is consistent with their structure. All the signals corresponding to the aromatic carbon are located in the downfield region and the spectroscopic data are summarized in the experimental section in Chapter 7. The selected $^{13}$C NMR spectra are depicted in Figs. 5-4 and 5-5.

![Figure 5-1 $^{1}$H NMR spectrum of C10 in CDCl₃.](image_url)
Figure 5-2 $^1$H NMR spectrum of C10Br in CDCl$_3$.

Figure 5-3 $^1$H NMR spectrum of C11 in CDCl$_3$. 
Figure 5-4 $^{13}$C NMR spectrum of C10 in CDCl$_3$.

Figure 5-5 $^{13}$C NMR spectrum of C11 in CDCl$_3$. 
5.4 Optical Properties of Pyridyl-Functionalized Cyanostilbene-Based Compound

5.4.1 AIE properties

The AIE feature of C11 was studied with the variation of water fractions. C11 could be well dissolved in common organic solvents, such as chlorinated solvent and tetrahydrofuran (THF) and acetone but dissolve poorly in water. From Fig. 5-6, a dilute THF solution of C11 shows a weak luminescence peaking at 456 nm when photoexcited at 360 nm. With a gradual increment of water fraction of the mixture, intense fluorescence spectra accompanied by a bathochromic shift were observed and the magnitude of photoluminescence intensity and wavelength has reached its maximum in THF/water mixture with 90% vol. The delocalization of the electron cloud from pyridine moiety throughout the molecule has rigidified the structure to a certain extent and it has created a more planar conformation as compared to the conventional cyanostilbene compound, leading to a weak luminescence at lower water fractions. When the water fraction is larger than 70%, the solvating power of the solution mixture is worse and the molecules of C11 are promoted to form aggregates. At this aggregated state, the partially twisted conformation of the molecule originating from the steric effect of bulky cyano group is planarized and a red-shifted and boosted emission spectra with an increase of photoluminescence intensity of 18-times was
consequently achieved at high water content (Fig. 5-7).

**Figure 5-6** Emission spectra of C11 in THF/water mixtures of various water fractions.

**Figure 5-7** The variation on $I/I_0 - 1$ of C11 with water fraction in the THF/water mixtures.
5.4.2 Metal Ion Sensing Properties

Owing to the coordinating properties of pyridyl moiety to metal ion, the metal chelating property of C11 was being investigated and verified to be a potential candidate in metal ion sensing. The sensory experiments for C11 were carried out in its aggregated form with THF/water mixture (1:9 = v/v) as the metal salt dissolved completely in aqueous solution and the high water content environment could imitates the realistic situation in our cells, which increases the accuracy and reproducibility of this model of the experiment.

Figs. 5–8 to 5–9 depict the fluorescence response of C11 aggregates to different metal cations (Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), Ca\(^{2+}\), Mn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\) and Hg\(^{2+}\)) of the same concentration at \(f_w = 90\%\). The alkali metal cation (Na\(^{+}\), K\(^{+}\)) and alkaline earth metal cation (Mg\(^{2+}\), Ca\(^{2+}\)) do not exhibit any variation in the position and magnitude of the emission maximum, suggesting that the soft pyridyl does not coordinate to these hard metal cations. A slight increase in the emission intensity is caused by deterioration of the solvating power of the solvent with addition of metal salts, generating more aggregates in the solution mixture. Upon the addition of Zn\(^{2+}\) to the solution of C11, it does not illustrate an obvious change in the fluorescence spectrum unexpectedly, as compared to the spectrum before the addition of Zn\(^{2+}\), as Zn\(^{2+}\) has a strong affinity in the coordination to pyridine and should induce an evident
transformation in the emission profile. Furthermore, different transition metal cations were chosen and examined to verify the metal ion sensing capability of C11. The emission spectra representing C11 with the other transition metal cations in the same period as Zn$^{2+}$ ion, such as Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ ions could not show any discrepancy against that of the solution with free and uncoordinated molecules of C11. Besides, the presence of Fe$^{2+}$ ion and Cu$^{2+}$ ion has expressed that they are more efficient fluorescent intensity quencher as compared to other metal ions. To further investigate the enhancement in fluorescent of C11 from metal ion, it was observed that, instead of the first row transition metal cations, the introduction of second row transition metal cations in the same group of Zn$^{2+}$ ion Cd$^{2+}$ ion, has manifested a noticeable red-shift in emission maximum together with a boost in fluorescence intensity. Though another metal ion in the same group of Zn$^{2+}$ ion, Hg$^{2+}$ ion, could also induce the change of the emission maximum, indicates the difference from the fluorescence intensity, for which the existence of Hg$^{2+}$ ion incite the emission quenching. For practical applications, however, fluorescence sensors with “turn-on” features in the presence of analyte are superior to those with “turn-off” properties, for the sake of avoiding the background noise or interferences. From the photoluminescence measurement of C11 in aggregated state and its response to various metal cations, it is believed that C11 could be the promising metal ion sensor by mean of its AIE features and
distinguishable transformation of its emission profile in the presence of Cd$^{2+}$.

**Figure 5-8** Emission spectra of C11 in the presence of different metal ion at $f_w = 90\%$. [C11] = 50 $\mu$M; [metal ion] = 100 $\mu$M.

**Figure 5-9** Column diagram of the photoluminescence ratio ($I_{573}/I_{486}$ and $I_{573}/I_{514}$) corresponding to C11 in the absence and presence of each metal cation in THF/water mixture. The data are extracted from Fig 5-8.
In order to acquire comprehensive information of the sensing ability of Cd$^{2+}$ ion by C11, the photoluminescence changes of C11 with different concentration of Cd$^{2+}$ ion (0 – 1000 μM) were monitored. From Fig. 5-10, it has revealed the decline of photoluminescence intensity at 486 nm and 514 nm, corresponding to the peaks of the emission spectrum of the free C11 solution, when Cd$^{2+}$ ion is once introduced into the solution. Meanwhile, a new redder emission band grows with the increase of concentration of Cd$^{2+}$ ion, which becomes to be visually observable at [Cd$^{2+}$] = 200 μM and dominant when [Cd$^{2+}$] is larger than 300 μM. The plot of the fluorescence intensity ratio ($I_{573}/I_{486}$ and $I_{573}/I_{514}$) in Fig. 5-11 presents unequivocal information in the response and detection of Cd$^{2+}$ ion by using C11 as a metal ion sensor.

The bathochromic shift and enhancement of C11 could be ascribed to the intramolecular charger transfer (ICT) effect between C11 and metal cation. Upon the complexation with Cd$^{2+}$ ion, the electron-withdrawing ability of pyridine group is intensified and hence the ICT process between electron-donating phenyl group and pyridine-Cd$^{2+}$ moiety is triggered. Owing to the electron-withdrawing properties of pyridine, the stabilization of the lowest unoccupied molecular orbital (LUMO) is more significant than that of the highest occupied molecular orbital (HOMO) by the complexation of metal cation, resulting in a narrower band gap and red-shift in emission. On the other hand, the extension of the conjugated system with the
formation of C11-Cd$^{2+}$ complex could also be another possibility to account for the bathochromic shift of the emission spectra.

**Figure 5-10** PL spectra of C11 in THF/water mixture solution with different concentration of Cd$^{2+}$ ion ([Cd$^{2+}$]). [C11] = 50 µM

**Figure 5-11** Plot of $I_{573}/I_{486}$ (Left) and $I_{573}/I_{514}$ (Right) versus [Cd$^{2+}$]. The data are extracted from Fig. 5-10.
Similarly, Fig. 5-12 demonstrates a new absorption peak at 355 nm at a concentration of Cd$^{2+}$ ion of 500 $\mu$M, which is red-shifted by 55 nm as compared to that in the absence of Cd$^{2+}$ ion (300 nm), providing an alternate evidence to prove the formation of a narrower band gap by ICT process. At [Cd$^{2+}$] = 500 $\mu$M, a hybrid of these two bands was observed, along with the mixture of free and metal-coordinated C11 in the solution. A competing conversion of the absorption band starting with [Cd$^{2+}$] = 700 $\mu$M has confirmed that most C11 molecules is binded with Cd$^{2+}$ ion and the absence of free C11, which is consistent with the level-off behavior in its emission spectra at the same concentration range (700 $\mu$M – 1000 $\mu$M).

**Figure 5-12** UV-Vis absorption spectra of C11 in THF/water mixture solution with different concentration of Cd$^{2+}$ ion. [C11] = 50 $\mu$M.
To better understand the metal-ion sensing ability of C11 in different surrounding environment, the experiment for C11 in various water fractions at the same concentration of Cd$^{2+}$ ion has been performed. From Fig. 5-13, it has implied that the magnitude variation of both emission maxima and photoluminescence intensity are the most noticeable for $f_w = 90\%$. In low water content, the polarity of the solvent is relatively low, dampening the ICT process through the destabilization of the partially polarized complex, C11-Cd$^{2+}$. On the other hand, the aggregates of C11 molecules are well developed and the polar water molecules more or less aid the build of the partially polarized C11 molecules in high water content. The stabilization of the resultant complexes by polar water molecules and encouragement of ICT process between C11 and Cd$^{2+}$ ion led to the red-shift and intensification of emission spectra with the introduction of Cd$^{2+}$ ion in high water fraction of solution. As a result, the hypothesis of ICT process as the origin of the bathochromic shift and enhancement in emission by Cd$^{2+}$ ion are further consolidated by the discrepancy of the response of C11 to Cd$^{2+}$ ion in low and high fraction of water.
**Figure 5-13** Emission spectra of C11 in THF/water mixtures of various water fractions at \([\text{Cd}^{2+}] = 500 \, \mu\text{M}\). \([\text{C11}] = 50 \, \mu\text{M}, \lambda_{\text{ex}} = 350 \, \text{nm}\).

**Figure 5-14** Column diagram of the change in emission maxima (\(\lambda_{\text{max}}\)) and that in photoluminescence maxima (\(I_{\text{max}}\)) corresponding to C11 in the absence and presence of the same concentration of Cd\(^{2+}\) ion in THF/water mixture. The data are extracted from Fig. 5-6 and Fig. 5-13.
5.5 Concluding Remarks

In summary, a pyridyl-functionalized cyanostilbene-based compound (C11) has been designed and synthesized. The key intermediate and the target compounds have been well characterized by common spectroscopic methods. In the examination of the AIE features of C11, it possesses a weak photoluminescence in its dilute solution in THF. It is believed that the electron delocalization of pyridine moiety within the molecule has probably rigidified the structure, which created a planar conformation as compared to the well-known AIE luminogens. The transformation of non-luminescent behavior in solution state to highly emissive one has demonstrated C11 to possess an AIE characteristic.

Comprising a metal-chelating pyridine unit in C11, the typical optical and sensing properties to various metal cations at \( f_w = 90\% \) have been investigated to imitate the genuine sensing situation and increase both accuracy and reproducibility. From the experimental data, C11 can serve as a metal ion chemosensor in high water content. With the introduction of Cd\(^{2+}\) ion, a manifest bathochromic shift (67 nm) and boosting \( (I_{573}/I_{486} = 12.5) \) of emission intensity with respect to other metal cations were observed and deduced to be initiating from the ICT process between C11 and Cd\(^{2+}\) ion, permitting the discrimination of Cd\(^{2+}\) ion from other metal ions.
References


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Chapter 6 Concluding Remarks and Future Work

A series of new cyanostilbene-based compounds were successfully designed, synthesized and well characterized by common spectroscopic methods. In addition, the photophysical properties of all cyanostilbene-based luminogens were investigated deeply. Through the variation of the substituent attaching to the cyanostilbene moiety, different aggregation-induced emission properties of the cyanostilbene-based compounds have been observed and discussed in this work. At the beginning of this work, L1 is the first cyanostilbene-based luminogen possessing the abnormal AIE effect. From the photoluminescence measurement of L1 in various water fractions in THF/water fraction, its emission has been raised about two-fold in the aggregation state. To enlarge the AIE system in the field of cyanostilbene derivatives, replacing triphenylamine unit by carbazole and insertion of the thiophene group has been performed. On the other hand, the extension of the \( \pi \)-conjugation system accompanied by the increase in rotatable joints has been accomplished. With the modification of the groups attached to the cyanostilbene moiety, their AIE features can successfully be retained and even the AIE effect has been magnified. In the report on the quantification of the AIE luminogens, L8 owns the highest enhancement ratio with a value of 1128, which means the photoluminescence intensity of L8, has been increased by 1128-times in aggregated form as compared to that in the isolated state.
With the strong emissive properties in their aggregated state or in water, the utilization of this AIE active cyanostilbene-based fluorophores in live cell imaging, chemical vapor and electroluminescence devices has been demonstrated. From the overlay fluorescent image of HeLa cell, the strong fluorescence intensity by cyanostilbene-based derivatives are located within cytoplasm instead of nucleus or membrane. It suggests that these AIE luminogens illustrate good cell permeability and biocompatibility, promoting them to play a role as the bioprobe in bioimaging studies. Moreover, the reversible switch-off/on capability in the presence/absence of common volatile organic solvents (VOCs) of the cyanostilbene-based compounds recommends that they are capable as a fluorescence detector for the chemical vapor. Being a strong solid emitter with high decomposition temperature, the utilization of the cyanostilbene-based luminogens as the emissive layer in the electroluminescence devices has been considered. Among the selected compounds, the best device performance has been achieved by L8 based device with the luminous efficiency of 3.38 cd/A, power efficiency of 3.08 lm/W and external quantum efficiency of 2.84%.

With the primary studies and researches on the AIE features in cyanostilbene system in the early stage, further development based on the cyanostilbene framework should be carried out to expand the territory. Organic conjugated polymers with high molecular weight, excellent thin-film form ability and AIE characteristics are one of
our interests as it is efficient to remedy the weaknesses of low-molecular-weight luminogens, where the fabrication method of these luminogens into thin solid film for practical applications is relatively expensive and not applicable in large-area devices. On the other hand, simple and inexpensive fabrication processes, for example, spin-coating or ink-jet printing, can be applied in the formation of large-area thin film at ambient condition. Therefore, the high-molecular-weight cyanostilbene-based polymers have been acquired and reported. Unexpectedly, the binding of the AIE diacetylene cyanostilbene-based monomers (L9 – L11) with the organic spacers, benzene and fluorene unit (P1 – P4), has created the ACQ problem to the aromatic-ring-linked cyanostilbene-based polymers. On the contrary, the platinum-linked polymers (P5 – P7) through the connection of the diacetylene monomer with trans-[Pt(PBu₃)₂] unit exhibit and preserve the AIE feature of their corresponding cyanostilbenes. From the examination of the optical behavior of the organic polymers, they are strongly emissive in the diluted solution as the polymerization process has tied up the AIE-active ligand tightly and given rise to the planarization of the molecules conformation to a certain extent. In aggregated state, further shrinkage of their molecular volume has gathered the aromatic rings in an even closer distance, where they experience strong $\pi-\pi$ stacking interaction between aromatic rings and hence formation of excimer is induced. Besides, the electron-rich
Pt unit with widespread electron cloud provides the barrier to the $\pi-\pi$ stacking interaction and renders the Pt-linked polymer enjoying the strong fluorescence in condensed phase. Furthermore, the high emission intensity of the Pt-linked polymer in the condensed state is contributed to the elimination of the non-radiative intramolecular charge transfer (ICT) process, as evident by the blue shift of their emission spectra with the increase of water fraction and the DFT calculation.

Attempt on tuning the emission color to the red region has been made to satisfy the high demand on the red-emitting materials in the applications of electroluminescent devices, fluorescent chemosensor and bioprobes. In this research, a new system of chromophores ($\text{C1} - \text{C9}$) with donor (D) – acceptor (A) system derived from phenothiazine (D) and cyanostilbene (A) units have been prepared. With the change of the solvent polarity, $\text{C1} - \text{C9}$ illustrate a positive solvatochromism, in which the red shift and quenching of emissions are observed with the increase of solvent polarity. It is believed that the strong emission of cyanostilbene-based derivatives arises from the relaxation of LE excited state in non-polar solvent and the red-shifted and weaker emission from the ICT state in polar solvent is due to the involvement of non-radiative transition process from LE to ICT state. On the other hand, $\text{C1} - \text{C9}$ exhibit a V-shape fashion of emission intensity transformation in response to the enlargement of water proportion in the solvent mixture, which is
inconsistent to the traditional AIE cyanostilbene compounds with a successively climb up of PL intensities in the same situation. The emissions of C1 – C9 are found to quench at the beginning when “small” amount of water is introduced, owing to the influence of growth of solvent polarity overstepping the effect from the molecules aggregation. Afterwards, the addition of “large” amount of poor solvent induced the formation of large amount of aggregates and hence transcended solvatochromism effect. In the microscopic view of the aggregates, a less polar local environment is created and it will suppress the non-radiative transition to the ICT state, causing a blue shift in the emission color and a boosting of emission efficiency. In this work, we have successfully generated a series of new AIE luminogens built on D – A system with the emission color extended to the redder region.

Based on the comprehensive study on the AIE feature of cyanostilbene-based derivatives, functionalization through the attachment of pyridine ring to these luminogens is done to enrich this research in the real application by employing these novel compounds. A metal-ion chelating capability of cyanostilbene-based compound (C11) was therefore studied and the responses to numerous metal cations by the aggregate of C11 were investigated. To be a switch-on AIE-active metal-ion sensor, the optical properties of C11 in different water volume have been examined. A weak emission was observed in the diluted solution of C11, which is explained by the
partial planarization of the conformation through the electron delocalization from pyridine moiety along the whole structure. With the formation of aggregates in the high proportion of a bad solvent, further planarization accounts for the highly emissive behavior of C11 in 90% water fraction. In the examination of response to different metal cation of C11, the aggregate state instead of the free state is being chosen as the working platform to increase the accuracy and reproducibility in the real measurement of the water samples. Among the selected metal cation, both Hg$^{2+}$ and Cd$^{2+}$ ions create a red shift of emission spectra noticeably. However, only Cd$^{2+}$ ion reinforce the emission intensity as compared to the free aggregates. With the turn-on feature of C11 in the presence of Cd$^{2+}$ ion, it is believed that C11 is a promising candidate as metal ion sensor for unknown water sample.

Through the sensible structural design, the AIE luminogens comprising cyanostilbene moiety can be tailored to serve different purpose through the incorporation of bio-components to the structure covalently. For example, from the attachment of the maleimide (MI) group to cyanostilbene unit, the protein labeling could be carried out through the exclusive thiol-ene click reaction of cysteine, allowing the differentiation from other amino acids. In this research, the basic idea of the AIE properties of the cyanostilbene-based luminogens was obtained; the studies on the functionalization of these compounds will be focused to further explore their
high-tech applications, such as bioprobes, so as to widen and unearth the map of AIE system.
Chapter 7 Experimental Section

7.1 General Procedures

7.1.1 General information

All the reactions were performed under nitrogen atmosphere and magnetically stirred. Solvents were dried carefully by appropriate drying agents under N₂ prior to use. All commercially available reagents were used without further purification unless otherwise stated. All the reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated aluminum foil sheet. Flash column chromatography were carried out on silica gel from Merck (0.063 – 0.200 mesh). The NMR spectra were measured with deuterated solvent on Bruker Ultrashield 400 MHz FT-NMR spectrometer, with \(^1\)H and \(^{13}\)C\{\(^1\)H\} chemical shifts quoted relative to tetramethylsilane (Me₄Si) internal standard and \(^{31}\)P chemical shifts relative to an 85% H₃PO₄ external reference.

7.1.2 Physical Measurements

The Fourier transform infrared (FT-IR) spectra were reported on Perkin Elmer Paragon 1000 PC FTIR spectrometer, using KBr pellets for solid state spectroscopy. The UV-Vis spectra were collected with a Hewlett Packard 8453 spectrophotometer and the photoluminescence (PL) properties were obtained on a Perkin Elmer LS55B
spectrofluorometer. The fluorescent quantum yield ($\Phi_F$) of all compounds in different solvent mixture were determined at 298 K against 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran as a reference in (methanol) ($\Phi_F = 43\%$). Electrochemical measurement was carried out on a CH Instruments Model 600 D Series Potentialstat in a three-electrode cell with a glassy carbon working electrode, a Ag/AgCl reference electrode and a platinum wire counter electrode. All the measurements were performed as the thin film on glassy carbon working electrode at a scan rate of 100 mV s$^{-1}$ under a nitrogen atmosphere with 0.1 M tetrabutylammonium hexafluorophosphate ($\text{tBu}_4\text{NPF}_6$) in MeCN as the supporting electrolyte. All potential values recorded were quoted with reference to the ferrocene-ferrocenium (Fc/Fc$^+$). The value of onset oxidation potential ($E_{\text{onset, ox}}$) and reduction potential ($E_{\text{onset, red}}$) were used to determine HOMO and LUMO energy levels from the equations $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.73)$ (eV) and $E_{\text{LUMO}} = -(E_{\text{red}} + 4.73)$ (eV), respectively. Thermal analyses were carried out using a Perkin Elmer TGA6 thermal analyzer under nitrogen at a heating rate of 20 $^\circ$C/min. Weight- and number-average molecular weights ($M_w$ and $M_n$) and polydispersity indices ($M_w/M_n$) of polymers were examined by gel permeation chromatography (GPC) on a HP 1050 series HPLC with visible wavelength and fluorescent detected and were calibrated against polystyrene standards.
7.1.3 Preparation of Solution

The cyanostilbene-based luminogens were dissolved in THF and a stock solution were prepared. To a 3 mL solution with defined water fraction ($f_w = 0 – 90\%$), 30 μL of the stock solution was introduced with vigorous stirring and the spectral measurements of the resultant solution and aggregates were performed immediately.

7.1.4 Cell Culture

The HeLa cell line was supplied by the Institute of Biochemistry and Cell Biology, SIBS, CAS (China). The KB cells were grown in RPMI 1640 (Roswell Park Memorial Institute's Medium) supplemented with 10% FBS (Fetal Bovine Serum) at 37 °C and 5% CO$_2$. Cells (5×10$^8$/L) were plated on 18 mm glass coverslips and allowed to adhere for 24 h.

7.1.5 Two-photon Cell Imaging

Two photon confocal luminescence imaging was conducted on an Olympus IX81 laser scanning confocal microscope equipped with a 40 immersion objective lens. A semiconductor laser served as the excitation source of the HeLa cells incubated with cyanostilbene-based luminogens at 760 nm. The G & R optical spectroscopy was used to collect two-photon emission, of which G and R contains 495-540 nm and 575-630
nm bands, respectively. Cyanostilbene-based compounds were dissolved in DMSO to yield 20 μM solutions. The HeLa cells were incubated with the solution of cyanostilbene-based luminogens for 1 h at 25 °C.

7.1.6 DFT Calculation in Chapter 2

The geometries of the compounds were optimized using density functional theory (DFT) with B3LYP functional and 6-31G (d) basis set. There were no imaginary frequencies for all optimized structures. The spin density surfaces of the dyads were calculated at the B3LYP/6-31G (d) level. All these calculations were performed with Gaussian 09W.²

7.1.7 OLED Devices Fabrication in Chapter 2

The OLED devices were fabricated on pre-patterned indium tin oxide (ITO). Before the fabrication of the device, the ITO glass substrates were first cleaned in ultrasonic bath in organic solvent and followed by the ozone treatment for 20 min. Then, PEDOT:PSS film was deposited on ITO glass substrates and cured at 120 °C for 30 min. The solutions of cyanostilbene-based luminogens in chlorobenzene were prepared in gloves box and spin-coated on the top of ITO/PEDOT:PSS surface with 700 rpm for 1 min, which underwent thermal annealing at 70 °C for another 30 min.
Afterwards, a 50 nm thick layer of TPBI was thermally deposited by the vacuum evaporation as the electron transporting layer. A thin layer of LiF as the electron injection cathode and subsequently the 100 nm of Al protection layer were thermally deposited through vacuum evaporation in a vacuum chamber at the pressure less than $10^{-6}$ Pa without breaking vacuum between every vacuum deposition processes. The EL spectra and CIE coordinates were measured with a PR650 Spectra colorimeter. The J-V-L curves of the devices were obtained with a Keithley 2400/2000 source meter and the luminance was recorded by a PR650 SpectraScan spectrometer. All the experiments and measurement were performed under ambient condition at room temperature.

7.1.8 DFT and TDDFT Calculations in Chapter 3

All calculations were performed with Gaussian09 program. Ground-state geometry optimizations were carried out by DFT with the BP86 functional and RI approximation, which is widely used in large-molecule systems. To obtain a good description of the electron correlation in the excitation processes, the TDDFT method with cam-B3LYP functional was adopted to investigate the excited states of these compounds. Vertical excitation energy calculations were performed from the ground optimized structure using TDDFT method and solvent effect has included
using the integral equation formalism (IEF) version of Polarizable Continuum Model (PCM) with the dielectric constant of tetrahydrofuran (THF, $\varepsilon = 7.43$). Throughout the ground-state optimizations and excited-state studies, the SVP basis set was chosen for nonmetallic elements, and the LanL2dz and pseudopotential ECP basis sets were selected for platinum atoms.$^{5,13}$

7.1.9 Preparation for Metal ion sensing in Chapter 5

The metal ion solutions were prepared by dissolving 0.1 mmol of the corresponding metal salts in 10 mL distilled water to obtain a stock solution with concentration of 10 mM. Stock solution of cyanostilbene-based luminogens was diluted to 50 $\mu$M using water and an aliquot of different metal ion stock solution was then supplied. The final concentration of the metal ions was 100 mM unless otherwise specified.

7.2 Synthesis of Cyanostilbene-Based Arylacetylide Small Molecules for Chapter 2

7.2.1 Synthesis of CNTMS

An ice-cooled mixture of 2-(4-bromophenyl)acetonitrile (1.5 g, 7.65 mmol), Pd(OAc)$_2$ (18.5 mg, 0.09 mmol), CuI (19.8 mg, 0.09 mmol) and PPh$_3$ (56.7 mg,
0.22 mmol) in THF/NEt$_3$ was stirred for 20 min. Me$_3$SiC≡CH (1.87 g, 19.1 mmol) was added in an ice bath for another 30 min before being warmed at room temperature. After stirring for 30 min at room temperature, the mixture was heated to reflux for 12 h. The solvent was removed and the residue was purified by silica-gel column chromatography (hexane/CH$_2$Cl$_2$ = 1/2) to afford a yellow solid (1.45 g, 88%). $^1$H NMR (CDCl$_3$): $\delta$ 7.48 (d, $J = 8.36$ Hz, 2H, Ar), 7.28 (s, 1H, Ar), 7.26 – 7.25 (m, 1H, Ar), 3.75 (s, 2H, CH$_2$CN), 0.25 (s, 9H, SiMe$_3$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 132.45, 130.14, 129.69, 127.89 (Ar), 132.27 (C≡N), 104.14, 93.40 (C≡C), 23.66 (CH$_2$), 3.44 (SiMe$_3$) ppm.

7.2.2 Synthesis of CHO$_2$

A mixture of (4-(diphenylamino)phenyl)boronic acid$^{14}$ (560 mg, 1.94 mmol) and 5-bromothiophene-2-carbaldehyde$^{15}$ (336 mg, 1.76 mmol), Pd(PPh$_3$)$_4$ (101 mg, 0.08 mmol), and K$_2$CO$_3$ (0.9 mL, 4 M) in ethanol/toluene (3/1: v/v) was heated to reflux for 12 h. The solution was extracted with ethyl acetate, washed with brine and dried with Na$_2$SO$_4$. The crude product was purified by silica-gel column chromatography with hexane/CH$_2$Cl$_2$ to afford a bright yellow solid (406.6 mg, 65%). $^1$H NMR (CDCl$_3$): $\delta$ 9.85 (s, 1H, CHO), 7.70 (d, $J = 4.0$ Hz, 1H, Ar), 7.53 (d, $J = 8.8$ Hz, 2H, Ar), 7.32 – 7.28 (m, 5H, Ar), 7.15 – 7.12 (m, 4H, Ar), 7.11 – 7.07 (m, 3H, Ar), 7.05 (s,
1H, Ar) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 182.60 (CHO), 154.61, 149.18, 147.00, 141.36, 137.70, 129.50, 127.26, 126.17, 125.20, 123.89, 122.87, 122.39 (Ar) ppm.

7.2.3 General procedure for the synthesis of CHO5 – CHO8

To a mixture of 4-(bis(4-iodophenyl)amino)benzaldehyde$^{16}$ (1 equiv), appropriate boronic acid$^{14,17-19}$ (1 equiv), and Pd(PPh$_3$)$_4$ (5% mol) was stirred in toluene/ethanol mixture (v/v : 1:4) and 2 M K$_2$CO$_3$ (2M, 4 equiv). The resultant mixture was heated at 85 °C for 18 h under N$_2$ atmosphere. The mixture was cooled extracted with ethyl acetate, washed with brine and dried with Na$_2$SO$_4$. The solvent of the organic layer was removed under reduced pressure and the residue was obtained as crude product, which was purified with silica-gel column chromatography by using appropriate eluent to give a pure sample of CHO5 – CHO8 with 74 – 86 % product yield.

CHO5: Yield: 74%; yellow solid. $^1$H NMR (CDCl$_3$): $\delta$ 9.84 (s, 1H, CHO), 7.74 – 7.72 (m, 2H, Ar), 7.61 – 7.57 (m, 7H, Ar), 7.46 – 7.43 (m, 4H, Ar), 7.37 – 7.35 (m, 2H, Ar), 7.28 – 7.26 (m, 5H, Ar), 7.16 – 7.14 (m, 2H, Ar) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 190.48 (CHO), 145.36, 140.24, 137.88, 131.38, 128.87, 128.36, 127.34, 126.88, 126.35, 120.48 (Ar) ppm.

CHO6: Yield: 80%; yellow solid. $^1$H NMR (CDCl$_3$): $\delta$ 9.64 (s, 1H, CHO), 7.55 –
7.52 (m, 2H, Ar), 7.30 – 7.28 (m, 4H, Ar), 7.25 – 7.19 (m, 2H, Ar), 7.07 – 7.05 (m, 4H, Ar), 6.78 – 6.96 (m, 2H, Ar), 6.78 – 6.69 (m, 4H, Ar) ppm. $^{13}$C NMR (CDCl$_3$):

$\delta$ 190.42 (CHO), 163.59, 161.08, 158.59, 152.88, 145.66, 131.53, 131.38, 131.23, 130.25, 129.95, 126.52, 125.92, 125.69, 125.38, 124.56, 120.59, 111.85, 104.51 (Ar) ppm.

**CHO7**: Yield: 86%; yellow solid. $^1$H NMR (CDCl$_3$): $\delta$ 9.85 (s, 1H, CHO), 7.78 (s, 1H, Ar), 7.76 (s, 1H, Ar), 7.75 – 7.72 (m, 4H, Ar), 7.69 – 7.66 (m, 6H, Ar), 7.60 – 7.58 (m, 3H, Ar), 7.56 – 7.55 (m, 2H, Ar), 7.36 – 7.30 (m, 7H, Ar), 7.18 – 7.17 (m, 2H, Ar), 2.11 – 2.05 (m, 8H, CH$_2$), 0.39 – 0.35 (m, 12H, CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$):

$\delta$ 190.91 (CHO), 150.66, 145.15, 139.02, 128.36, 127.12, 126.91, 126.40, 125.74, 122.93, 121.19, 119.99, 119.87, 119.73 (Ar), 56.22 (fluorene C), 31.62, 8.60 (C$_2$H$_5$) ppm.

**CHO8**: Yield: 78%; yellow solid. $^1$H NMR (CDCl$_3$): $\delta$ 9.83 (s, 1H, CHO), 7.73 – 7.70 (m, 2H, Ar), 7.56 – 7.54 (m, 4H, Ar), 7.48 – 7.46 (m, 4H, Ar), 7.29 – 7.27 (m, 6H, Ar), 7.25 – 7.23 (m, 6H, Ar), 7.15 – 7.11 (m, 14H, Ar), 7.05 – 7.02 (m, 4H, Ar) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 190.61 (CHO), 147.60, 137.36, 129.30, 127.78, 127.49, 126.36, 124.48, 123.81, 123.02, 119.81, 110.45 (Ar) ppm.
7.2.4 General procedure for the synthesis of $L_1 – L_8$

Under a nitrogen atmosphere, each appropriate aldehyde precursor, CHO1 – CHO8 \(^{20-22}\) (1 equiv) was reacted with CNTMS (1 equiv) in basic ethanol (0.25 M NaOEt, 0.1 equiv) at 80 °C for 3 h. After the reaction mixture was cooled to room temperature, all the volatiles were removed under reduced pressure. The crude product was purified by silica-gel chromatography with suitable eluent system and dried under reduced pressure. Yield: 75 – 86 %.

$L_1$: Yield: 83%; pale yellow solid. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.79 (s, 1H, Ar), 7.77 (s, 1H, Ar), 7.61 – 7.52 (m, 4H, Ar), 7.43 (s, 1H, Ar), 7.34 (s, 1H, Ar), 7.32 (s, 2H, Ar), 7.30 (s, 2H, Ar), 7.17 (s, 2H, Ar), 7.15 (s, 2H, Ar), 7.13 (s, 1H, Ar), 7.05 (s, 1H, Ar), 7.03 (s, 1H CNC=CH), 3.17 (s, 1H, C≡C-H) ppm. \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 150.27, 146.51, 142.24, 132.69, 130.86, 129.61, 126.06, 125.84, 125.48, 124.55, 120.67 (Ar, C=C), 83.11, 78.74 (C≡C) ppm. IR (KBr pellet, cm\(^{-1}\)): 3282 (C≡C-H), 2212 (C≡N), 1579 and 1510 (vinyl and aromatic C=C).

$L_2$: Yield: 75%; orange solid. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.63 – 7.60 (m, 2H, Ar), 7.58 – 7.57 (m, 1H, Ar), 7.55 – 7.52 (m, 3H, Ar), 7.46 – 7.43 (m, 1H, Ar), 7.31 – 7.27 (m, 5H, Ar), 7.15 – 7.13 (m, 3H, Ar), 7.10 – 7.06 (m, 5H, Ar), 6.99 (d, \(J = 8.48\) Hz, CNC=CH), 3.18 (s, 1H, C≡C-H) ppm. \(^13\)C NMR (CDCl\(_3\)):\(\delta\) 149.93, 148.54, 147.12, 135.93, 134.86, 134.78, 134.49, 132.76, 129.44, 127.02, 126.66, 125.34, 124.97,
123.65, 122.79, 122.68, 122.33, 118.13 (Ar, C=C), 105.73 (C≡N), 83.07, 78.95 (C≡C) ppm. IR (KBr pellet, cm$^{-1}$): 3295 (C≡C-H), 2206 (C≡N), 1583 and 1488 (vinyl and aromatic C=C).

**L3:** Yield: 80%; yellow solid. $^1$H NMR (CDCl$_3$): δ 8.65 (d, $J = 1.64$ Hz, 1H, Ar), 8.16 – 8.14 (m, 2H, Ar), 7.44 (s, 1H, Ar), 7.69 – 7.67 (m, 2H, Ar), 7.58 – 7.56 (m, 2H, Ar), 7.54 (dt, $J = 15.3, 1.0$ Hz, 1H, Ar), 7.48 – 7.43 (m, 2H, Ar), 7.31 – 7.28 (m, 1H, CNC=CH), 4.36 (t, $J = 7.2$ Hz, 2H, NCH$_2$), 3.18 (s, 1H, C≡C-H), 1.92 – 1.85 (m, 2H, CH$_2$), 1.47 – 1.37 (m, 2H, CH$_2$), 0.98 (t, $J = 7.3$ Hz, 3H, CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): δ 144.07, 141.83, 141.05, 135.63, 132.71, 127.20, 126.51, 125.51, 124.53, 123.28, 122.83, 122.77, 120.75, 118.84, 109.24, 109.16 (Ar, C≡C) 106.41 (C≡N), 83.20, 78.71 (C≡C), 43.11, 31.12, 20.56, 13.88 (C$_4$H$_9$) ppm. IR (KBr pellet, cm$^{-1}$): 3304 (C≡C-H), 2208 (C≡N), 1583 and 1497 (vinyl and aromatic C=C).

**L4:** Yield: 86%; yellow solid. $^1$H NMR (CDCl$_3$): δ 8.74 (s, 1H, Ar), 8.22 (d, $J = 7.7$ Hz, 1H, Ar), 8.04 (dd, $J = 8.7, 1.8$ Hz, 1H, Ar), 7.75 (s, 1H, Ar), 7.70 – 7.68 (m, 2H, Ar), 7.64 – 7.62 (m, 2H, Ar), 7.58 – 7.56 (m, 4H, Ar), 7.46 – 7.40 (m, 3H, Ar), 7.35 (s, 1H, CNC=CH), 3.18 (s, 1H, C≡C-H) ppm. $^{13}$C NMR (CDCl$_3$): δ 143.82, 142.19, 141.66, 136.97, 135.53, 132.74, 130.08, 128.08, 127.68, 127.07, 126.82, 125.66, 125.59, 123.86, 123.14, 122.45, 122.29, 120.90, 120.69, 118.64, 110.31, 110.27 (Ar, C≡C), 107.27 (C≡N), 83.13, 78.74 (C≡C) ppm. IR (KBr pellet, cm$^{-1}$): 3304 (C≡C-H),
2210 (C≡N), 2105 (C≡C), 1581 and 1502 (vinyl and aromatic C=C).

**L5**: Yield: 75%; orange solid. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.83 (s, 1H, Ar), 7.82 (s, 1H, CNC=CH), 7.63 (s, 1H, Ar), 7.61 – 7.59 (m, 6H, Ar), 7.58 – 7.57 (m, 2H, Ar), 7.56 – 7.53 (m, 5H, Ar), 7.46 – 7.45 (m, 4H, Ar), 7.43 (s, 1H, Ar), 7.37 – 7.34 (m, 2H, Ar), 7.26 – 7.25 (m, 2H, Ar), 7.18 (s, 1H, Ar), 7.15 (s, 1H, Ar), 3.17 (s, 1H, C≡C-H) ppm.

\(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 149.95, 145.69, 142.14, 140.37, 137.29, 135.35, 132.71, 130.94, 128.85, 128.25, 127.22, 126.85, 126.56, 125.84, 125.52, 122.30, 121.34, 118.42 (Ar, C=C), 107.09 (C≡N), 83.10, 78.80 (C≡C) ppm. IR (KBr pellet, cm\(^{-1}\)): 3280 (C≡C-H), 2210 (C≡N), 2105 (C≡C), 1581 and 1502 (vinyl and aromatic C=C).

**L6**: Yield: 79%; orange solid. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.85 (s, 1H, Ar), 7.83 (s, 1H, CNC=CH), 7.64 – 7.61 (m, 2H, Ar), 7.56 – 7.54 (m, 2H, Ar), 7.48 – 7.46 (m, 5H, Ar), 7.44 – 7.40 (m, 2H, Ar), 7.28 – 7.24 (m, 4H, Ar), 7.20 – 7.17 (m, 2H, Ar), 6.99 – 6.90 (m, 4H, Ar), 3.18 (s, 1H, C≡C-H) ppm. \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 149.69, 145.94, 142.05, 135.24, 132.73, 131.16, 130.94, 130.09, 126.99, 125.55, 125.38, 122.39, 121.85, 111.76, 111.55, 107.49, 104.48 (Ar, C=C), 104.22 (C≡N), 83.06, 78.86 (C≡C) ppm. IR (KBr pellet, cm\(^{-1}\)): 3290 (C≡C-H), 2210 (C≡N), 2106 (C≡C), 1580 and 1509 (vinyl and aromatic C=C).

**L7**: Yield: 80%; orange solid. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.85 (s, 1H, Ar), 7.83 – 7.82 (m, 1H, Ar), 7.78 (s, 1H, CNC=CH), 7.76 (s, 1H, Ar), 7.73 (s, 1H, Ar) ,7.71 (s, 1H, Ar),
7.67 (s, 1H, Ar), 7.64 – 7.63 (m, 2H, Ar), 7.61 (s, 1H, Ar), 7.60 (s, 1H, Ar), 7.58 (s, 1H, Ar), 7.56 – 7.55 (m, 3H, Ar), 7.53 (s, 1H, Ar), 7.47 – 7.45 (m, 1H, Ar), 7.34 – 7.29 (m, 10H, Ar), 7.26 – 7.23 (m, 2H, Ar), 7.20 (s, 1H, Ar), 7.18 (s, 1H, Ar), 3.17 (s, 1H, C≡C-H), 2.08 – 2.07 (m, 8H, CH₂), 0.39 – 0.35 (m, 12H, CH₃) ppm. ¹³C NMR (CDCl₃): δ 150.67, 150.17, 149.98, 146.44, 145.53, 142.15, 141.16, 140.85, 139.20, 137.78, 135.38, 132.73, 130.96, 129.69, 128.27, 128.22, 126.92, 126.50, 126.29, 125.91, 125.72, 125.53, 125.44, 124.68, 122.94, 122.30, 121.21, 120.96, 120.00, 119.73, 118.45 (Ar, C=C), 107.04 (C≡N), 83.13, 78.82 (C≡C), 56.21 (flourene C), 32.84, 8.61 (C₂H₅) ppm. IR (KBr pellet, cm⁻¹): 3296 (C≡C-H), 2211 (C≡N), 2107 (C≡C), 1584 and 1492 (vinyl and aromatic C=C).

**L₈**: Yield: 76%; orange solid. ¹H NMR (CDCl₃): δ 7.83 (s, 1H, Ar), 7.81 (s, 1H, CNC=CH), 7.63 (s, 1H, Ar), 7.61 (s, 1H, Ar), 7.55 – 7.54 (m, 3H, Ar), 7.53 – 7.52 (m, 3H, Ar), 7.48 – 7.46 (m, 6H, Ar), 7.29 – 7.27 (m, 7H, Ar), 7.25 – 7.22 (m, 6H, Ar), 7.16 – 7.13 (m, 12H, Ar), 7.06 – 7.05 (m, 1H, Ar), 7.03 (m, 2H, Ar), 7.02 – 7.01 (m, 1H, Ar), 3.19 (s, 1H, C≡C-H) ppm. ¹³C NMR (CDCl₃): δ 150.27, 147.64, 144.90, 145.68, 138.87, 136.27, 130.97, 129.80, 129.27, 129.05, 128.75, 128.59, 127.68, 127.46, 126.86, 126.13, 125.95, 125.85, 125.57, 124.94, 124.44, 123.89, 123.20, 122.96 (Ar, C=C), 105.66 (C≡N), 84.73, 79.47 (C≡C) ppm. IR (KBr pellet, cm⁻¹): 3296 (C≡C-H), 2211 (C≡N), 2101 (C≡C), 1584 and 1491 (vinyl and aromatic C=C).
7.2.5 General procedure for the synthesis of D1 – D4

CuI (6.4 mg, 0.033 mmol), Pd(OAc)$_2$ (7.5 mg, 0.033 mmol) and PPh$_3$ (21.6 mg, 0.083 mmol) were added to an ice-cooled mixture of 9,9-dibutyl-2,7-diiodo-9H-fluorene$^{23}$ (122.6 mg, 0.23 mmol) in THF/NEt$_3$ under nitrogen and the mixture was stirred for 20 min. The appropriate cyanostilbene arylacetylide (2.2 equiv) was then added and the mixture was stirred for 30 min in an ice bath. After reacting for 30 min at room temperature, the mixture was heated to 75$^\circ$C for 16 h. The solvent was evaporated under reduced pressure and the crude product was purified by silica-gel column chromatography with gradient elution of hexane/CH$_2$Cl$_2$. Yield: 60 – 69 %.

**D1**: Yield 68%; orange solid. $^1$H NMR (CDCl$_3$): $\delta$ 7.80 (s, 2H, Ar), 7.70 – 7.67 (m, 4H, Ar), 7.66 – 7.65 (m, 2H, Ar), 7.62 – 7.60 (m, 4H, Ar), 7.56 – 7.53 (m, 4H, Ar), 7.47 (s, 2H, Ar), 7.34 – 7.31 (m, 8H, Ar), 7.81 – 7.82 (m, 9H, Ar), 7.13 – 7.12 (m, 3H, Ar), 7.06 (s, 2H, Ar), 7.04 (s, 2H, CNC=C$\equiv$H), 2.03 – 1.99 (m, 4H, CH$_2$), 1.13 – 1.08 (m, 4H, CH$_2$CH$_3$), 0.71 – 0.68 (t, $J$ = 7.3 Hz, 6H, CH$_2$CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 145.47, 145.40, 143.18, 140.83, 139.83, 134.12, 133.68, 132.21, 131.16, 131.07, 130.25, 129.84, 129.79, 128.57, 128.29, 127.95, 127.25, 125.13, 124.97, 124.79, 124.51, 123.48, 123.03, 122.44, 120.72, 120.60, 119..65, 119.12, 119.05, 117.52, 108.73 (Ar, C=C), 105.84(C≡N), 99.13, 88.40 (C≡C), 54.19 (fluorene C), 39.21,
D2: Yield: 61%; red solid. $^1$H NMR (CDCl$_3$): $\delta$ 7.70 – 7.65 (m, 8H, Ar), 7.63 (s, 2H, Ar), 7.61 – 7.59 (m, 8H, Ar), 7.32 – 7.28 (m, 12H, Ar), 7.15 – 7.13 (m, 6H, Ar), 7.10 – 7.06 (m, 8H, Ar), 7.03 – 6.97 (m, 2H, CNC=CH), 2.03 – 2.01 (m, 4H, CH$_2$), 1.14 – 1.09 (m, 4H, CH$_2$), 0.71 – 0.68 (m, 6H, CH$_3$), 0.62 – 0.61 (m, 4H, CH$_2$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 151.19, 148.51, 147.13, 147.05, 136.07, 134.74, 134.42, 132.51, 132.19, 130.90, 129.44, 129.41, 127.99, 127.02, 126.90, 126.71, 126.02, 125.58, 125.42, 124.97, 123.64, 122.81, 122.70, 121.74, 120.11, 118.23 (Ar, C=C), 105.91 (C≡N), 92.41, 89.53 (C≡C), 55.26 (fluorene C) 31.62, 25.93, 23.10, 22.69 (C$_4$H$_9$) ppm. IR (KBr pellet, cm$^{-1}$): 2206 (C≡N), 2096 (C≡C), 1593 and 1492 (vinyl and aromatic C=C).

D3: Yield: 69%; orange solid. $^1$H NMR (CDCl$_3$): $\delta$ 8.76 (s, 2H, Ar), 8.24 (d, $J = 7.6$ Hz, 2H, Ar), 8.07 (dd, $J = 8.8$, 1.6 Hz, 2H, Ar), 7.79 (s, 2H, Ar), 7.76 – 7.72 (m, 5H, Ar), 7.67 – 7.63 (m, 10H, Ar), 7.59 – 7.54 (m, 12H, Ar), 7.53 – 7.38 (m, 14H, Ar), 7.36 (m, 2H, CNC=CH), 2.05 – 2.01 (m, 4H, CH$_2$), 1.16 – 1.09 (m, 4H, CH$_2$), 0.72 – 0.68 (m, 4H, CH$_2$), 0.62 – 0.61 (m, 6H, CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 151.18, 143.46, 142.13, 136.95, 132.15, 130.88, 130.67, 129.09, 128.06, 127.66, 127.06, 126.80, 126.02, 125.75, 125.65, 123.85, 123.55, 123.14, 122.42, 120.88, 120.70,
120.10, 110.31 (Ar, C=C), 107.40 (C≡N), 92.17, 89.22 (C≡C), 55.26 (fluorene C), 31.62, 25.64, 22.69, 14.16 (C₄H₉) ppm. IR (KBr pellet, cm⁻¹): 2210 (C≡N), 1598 and 1502 (vinyl and aromatic C=C).

**D4:** Yield: 60%; orange solid. $^1$H NMR (CDCl₃): δ 8.67 (s, 2H, Ar), 8.17 – 8.15 (m, 4H, Ar), 7.77 – 7.69 (m, 8H, Ar), 7.66 – 7.63 (m, 4H, Ar), 7.57 – 7.55 (m, 4H, Ar), 7.52 – 7.50 (m, 2H, Ar), 7.46 – 7.43 (m, 4H, Ar), 7.32 – 7.28 (m, 2H, CNC=CH), 4.35 (t, J = 7.0 Hz, 4H, NCH₂), 2.05 – 2.01 (m, 4H, CH₂), 1.92 – 1.85 (m, 4H, NCH₂CH₂), 1.47 – 1.39 (m, 4H, NCH₂CH₂CH₂), 1.17 – 1.08 (m, 4H, CH₂), 0.99 (t, J = 7.3 Hz, 6H, NCH₂CH₂CH₂CH₃), 0.73 (t, J = 7.2 Hz, 6H, CH₃), 0.63 – 0.62 (m, 4H, CH₂) ppm. $^{13}$C NMR (CDCl₃): δ 151.86, 143.74, 141.80, 141.05, 140.87, 134.99, 132.013, 130.87, 127.17, 126.49, 126.02, 125.60, 124.65, 123.29, 122.81, 121.79, 120.75, 120.08, 119.89, 118.91, 109.23, 109.18 (Ar, C=C), 106.66 (C≡N), 92.09, 89.47 (C≡C), 55.24 (fluorene C), 40.27, 25.91, 23.09, 13.87 (C₄H₉) ppm. IR (KBr pellet, cm⁻¹): 2210 (C≡N), 1584 and 1509 (vinyl and aromatic C=C).

**7.2.6 General procedure for the synthesis of Pt1 – Pt4**

A mixture of trans-[Pt(PBu₃)₂Cl₂] (1 equiv) and the corresponding cyanostilbene arylacetylide (1 equiv) was dissolved in CH₂Cl₂/NEt₃ (50 mL, 1:1, v/v), and CuI (3.0 mg) was subsequently added. After stirring at room temperature for 15 h, the solvent
was removed under reduced pressure. The crude product was purified by silica-gel column chromatography eluting with hexane/CH$_2$Cl$_2$. Yield: 63 – 81%.

**Pt1**: Yield: 75%; orange solid. $^1$H NMR (CDCl$_3$): $\delta$ 7.77 – 7.75 (m, 4H, Ar), 7.51 – 7.50 (m, 4H, Ar), 7.38 (s, 2H, Ar), 7.33 (s, 2H, Ar), 7.31 – 7.30 (m, 6H, Ar), 7.29 – 7.28 (m, 4H, Ar), 7.17 – 7.13 (m, 8H, Ar), 7.11 – 7.09 (m, 4H, Ar), 7.05 (s, 2H, Ar), 7.03 (s, 2H, CNC=CH), 2.16 – 2.12 (m, 12H, PCH$_2$CH$_3$), 1.63 – 1.60 (m, 12H, PCH$_2$CH$_3$), 1.48 – 1.43 (m, 12H CH$_2$CH$_3$), 0.95 – 0.92 (m, 18H, CH$_2$C(CH$_3$)$_3$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 149.71, 146.72, 140.56, 131.21, 130.48, 129.55, 126.84, 125.64, 125.20, 124.27, 121.09, 118.76 (Ar, C=C), 107.98 (C≡N), 26.33, 24.43, 23.98, 13.84 (PC$_4$H$_9$) ppm. $^{31}$P NMR (CDCl$_3$): $\delta$ 3.22 ($J_{Pt-P} = 2894$ Hz) ppm. IR (KBr pellet, cm$^{-1}$): 2210 (C≡N), 2097 (C≡C), 1591 and 1508 (vinyl and aromatic C=C).

**Pt2**: Yield: 63%; red solid. $^1$H NMR (CDCl$_3$): $\delta$ 7.57 (s, 2H, Ar), 7.54 – 7.49 (m, 10H, Ar), 7.32 – 7.28 (m, 10H, Ar), 7.25 – 7.24 (m, 2H, CNC=CH), 7.15 – 7.13 (m, 8H, Ar), 7.09 – 7.06 (m, 10H, Ar), 2.14 – 2.12 (m, 12H, PCH$_2$CH$_3$), 1.62 – 1.61 (m, 12H, PCH$_2$CH$_3$), 1.48 – 1.43 (m, 12H, CH$_2$CH$_3$), 0.96 – 0.92 (m, 18H, CH$_2$C(CH$_3$)$_3$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 148.30, 147.18, 147.12, 135.35, 133.75, 131.60, 1328, 129.38, 128.84, 126.93, 126.84, 125.11, 124.84, 123.54, 122.79, 122.62, 121.89 (Ar, C=C), 105.76 (C≡N), 82.07, 79.85 (C≡C), 29.74, 26.40, 24.46, 22.69 (PC$_4$H$_9$) ppm. $^{31}$P NMR (CDCl$_3$): $\delta$ 3.13 ($J_{Pt-P} = 2893$ Hz) ppm. IR (KBr pellet, cm$^{-1}$): 2206 (C≡C),
2093 (C≡N), 1594 and 1492 (vinyl and aromatic C=C).

**Pt3**: Yield: 68%; orange solid. $^1$H NMR (CDCl$_3$): $\delta$ 8.71 (s, 1H, Ar), 8.22 (d, $J = 7.7$ Hz, 2H, Ar), 8.02 (d, $J = 7.1$ Hz, 2H, Ar), 7.70 (s, 2H, CNC=CH), 7.63 – 7.56 (m, 12H, Ar), 7.52 – 7.51 (m, 2H, Ar), 7.45 – 7.42 (m, 6H, Ar), 7.36 – 7.33 (m, 6H, Ar), 2.19 – 2.15 (m, 12H, PCH$_2$CH$_2$), 1.66 – 1.63 (m, 12H, PCH$_2$CH$_2$), 1.51 – 1.48 (m, 12H, CH$_2$CH$_3$), 0.98 – 0.94 (m, 18H, CH$_3$CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 141.86, 141.61, 137.10, 131.37, 131.25, 130.03, 127.96, 137.46, 127.07, 125.30, 123.82, 123.23, 122.00, 120.75, 120.67, 118.97, 110.20 (Ar, C=C), 108.35 (C=N), 83.3, 97.7 (C≡C), 26.42, 24.45, 24.02, 22.66 (C$_4$H$_9$) ppm. $^{31}$P NMR (CDCl$_3$): $\delta$ 3.25 ($J_{P-t-P} =$ 2894 Hz) ppm. IR (KBr pellet, cm$^{-1}$): 2208 (C≡N), 2097 (C≡C), 1596 and 1503 (vinyl and aromatic C=C).

**Pt4**: Yield: 81%; orange solid. $^1$H NMR (CDCl$_3$): $\delta$ 8.62 (s, 2H, Ar), 8.17 (d, $J = 7.7$ Hz, 2H, Ar), 8.14 (dd, $J = 8.8$, 1.7 Hz, 2H, Ar), 7.69 (s, 2H, Ar), 7.61 (s, 2H, Ar), 7.59 (s, 2H, Ar), 7.53 (dt, $J = 8.1$, 1.1 Hz, 2H, Ar), 7.45 – 7.42 (m, 4H, Ar), 7.37 (s, 2H, Ar) 7.35 (s, 2H, Ar), 7.31 (t, $J = 7.4$ Hz, 2H, CNC=CH), 4.33 (t, $J = 3.5$ Hz, 4H, N-CH$_2$), 2.20 – 2.18 (m, 12H, PCH$_2$), 1.92 (m, 4H, N-CH$_2$CH$_2$), 1.67 – 4.65 (m, 12H, PCH$_2$CH$_2$), 1.53 – 1.47 (m, 12H, CH$_2$CH$_3$), 1.44 – 1.38 (m, 4H, N-CH$_2$CH$_2$CH$_2$), 0.99 – 0.96 (m, 18H, CH$_2$CH$_3$), 0.96 (d, $J = 4.6$ Hz, 6H, N-CH$_2$CH$_2$CH$_2$CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 141.94, 141.51, 141.30, 133.11, 131.52, 131.26, 129.42, 126.98,
126.37, 125.61, 125.26, 125.08, 123.24, 122.83, 122.37, 120.72, 119.74, 119.17 (Ar, C≡C), 109.17, 109.09 (C≡C), 107.56 (C≡N), 43.09, 31.62, 31.14, 29.73, 26.44, 24.48, 24.03, 22.69, 20.57 (C₄H₉ + PC₄H₉) ppm. ³¹P NMR (CDCl₃): δ 3.25 (Jₚ–p = 2895 Hz) ppm. IR (KBr pellet, cm⁻¹): 2209 (C≡N), 2097 (C≡C), 1598 and 1504 (vinyl and aromatic C=C).

7.3 Synthesis of Cyanostilbene-based Platinum-Arylacetylide Polymers for Chapter 3

7.3.1 Synthesis of CHO9

In a suspension of 4-(bis(4-iodophenyl)amino)benzaldehyde¹⁶ (1.05 g, 2.01 mmol) in THF/NEt₃ was added CuI (15 mg), Pd(OAc)₂ (15 mg) and PPh₃ (45 mg). After cooling in ice bath for 20 min, Me₃SiC≡CH (0.99 g, 10.1 mmol) was then added into the solution in 0 °C for 30 min. The reaction mixture was warmed to room temperature for 30 min and heated to 60 °C overnight. The solvent was removed under vacuum. The crude product was purified with column chromatography with hexane/CH₂Cl₂ to afford a yellow solid in 78% yield (1.20 g) ¹H NMR (CDCl₃): δ 9.85 (s, 1H, CHO), 7.72 – 7.71 (m, 2H, Ar), 7.42 – 7.39 (m, 4H, Ar), 7.08 – 7.02 (m, 6H, Ar), 0.25 (s, 18H, SiMe₃) ppm. ¹³C NMR (CDCl₃): δ 190.46 (CHO), 152.22, 145.99, 133.41, 131.32, 130.51, 125.16, 121.49, 119.36 (Ar), 107.44, 94.73 (C≡C),
3.40 (SiMe₃) ppm.

7.3.2 General procedure for the synthesis of CN1 – CN3

A mixture of 2-(4-bromophenyl)acetonitrile (1 equiv) and corresponding phenylboronic acid (1.2 equiv)¹⁴,¹⁷,²⁴ and aqueous K₂CO₃ solution (4 equiv, 2 M) were dissolved in ethanol/toluene (1/3 : v/v) and Ph(PPh₃)₄ (3% mol) was added into the mixture under stirring. After reflux for 12 h, the reaction mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was washed with brine and dried with sodium sulfate. The solvent was evaporated under vacuum and the crude product was purified with column chromatography using hexane/dichloromethane (1:1: v/v) as eluent. Yield: 76 – 80%.

**CN1:** Yield: 80%; white solid. ¹H NMR (CDCl₃): δ 7.62 – 7.57 (m, 4H, Ar), 7.48 – 7.44 (m, 2H, Ar), 7.42 – 7.37 (m, 3H, Ar), 3.80 (s, 2H, CH₂CN) ppm. ¹³C NMR (CDCl₃): δ 129.13, 128.91, 128.39, 127.95, 127.87, 127.67, 127.10 (Ar), 117.80 (C≡N), 23.36 (CH₂) ppm.

**CN2:** Yield: 76%; pale yellow solid. ¹H NMR (CDCl₃): δ 7.58 – 7.56 (m, 2H, Ar), 7.47 – 7.43 (m, 2H, Ar), 7.38 – 7.36 (m, 2H, Ar), 7.29 – 7.25 (m, 4H, Ar), 7.14 – 7.06 (m, 6H, Ar), 7.06 – 7.02 (m, 2H, Ar), 3.78 (s, 2H, CH₂) ppm. ¹³C NMR (CDCl₃): δ 147.58, 140.56, 133.88, 129.34, 128.37, 128.23, 127.70, 127.29, 124.56, 123.72,
CN3: Yield: 78%; white solid. $^1$H NMR (CDCl$_3$): $\delta$ 7.72 – 7.67 (m, 4H, Ar), 7.63 – 7.60 (m, 2H, Ar), 7.46 – 7.44 (m, 2H, Ar), 3.81 (s, 2H, CH$_2$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 132.32, 129.91, 129.61, 129.21, 128.89, 128.61, 128.02, 127.93, 127.40, 125.87, 125.83, 122.21 (Ar), 117.29 (C≡N), 23.39 (CH$_2$) ppm.

7.3.3 General procedure for the synthesis of L9 – L10

CHO9 (1 equiv) and appropriate benzyl cyanide (CN1 – CN3) reagents (1 equiv) was dissolved in basic ethanol and heated to reflux for 3 h. The reaction mixture was concentrated under vacuum. The residue was purified with silica-gel column chromatography with hexane/CH$_2$Cl$_2$ and dried in reduced pressure. Yield: 73 – 75%.

L9: Yield: 75%; orange solid.$^1$H NMR (CDCl$_3$): $\delta$ 7.85 – 7.82 (m, 2H, Ar), 7.75 – 7.73 (m, 2H, Ar), 7.72 (s, 1H, CNC=CH) 7.68 – 7.62 (m, 3H, Ar), 7.50 – 7.47 (m, 2H, Ar), 7.44 – 7.38 (m, 6H, Ar), 7.13 – 7.11 (m, 2H, Ar), 7.09 – 7.08 (m, 2H, Ar), 7.07 – 7.05 (m, 2H, Ar), 3.08 (s, 2H, C≡C-H) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 148.60, 146.71, 141.72, 140.87, 140.03, 133.51, 130.81, 128.95, 128.37, 127.82, 127.68, 127.04, 126.20, 125.83, 124.58, 123.13, 117.55 (Ar, C≡C), 108.89 (C≡N), 83.33, 77.26 (C≡C) ppm. IR (KBr pellet, cm$^{-1}$): 3296 (C≡C-H), 2211 (C≡N), 2101 (C≡C) 1597 and 1498 (vinyl and aromatic C≡C).
L10: Yield: 73%; orange solid. $^1$H NMR (CDCl$_3$): $\delta$ 7.84 – 7.82 (m, 2H, Ar), 7.72 – 7.70 (m, 2H, Ar), 7.65 – 7.63 (m, 2H, Ar), 7.51 (s, 1H, CNC=C=C), 7.49 – 7.48 (m, 2H, Ar), 7.44 – 7.41 (m, 4H, Ar), 7.30 – 7.26 (m, 4H, Ar), 7.16 – 7.13 (m, 7H, Ar), 7.11 – 7.10 (m, 1H, Ar), 7.09 – 7.03 (m, 6H, Ar), 3.08 (s, 2H, C≡C-H) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 148.53, 147.73, 147.53, 146.73, 141.16, 140.52, 133.56, 133.50, 133.05, 130.77, 12936, 128.46, 127.64, 127.05, 126.18, 124.64, 124.56, 123.61, 123.12, 123.16, 118.45, 117.51 (Ar, C=C), 108.98 (C≡N), 83.33, 77.35 (C≡C) ppm. IR (KBr pellet, cm$^{-1}$): 3281 (C≡C-H), 2212 (C≡N), 2103 (C≡C) 1595 and 1497 (vinyl and aromatic C=C).

L11: Yield: 75%; orange solid. $^1$H NMR (CDCl$_3$): $\delta$ 7.85 – 7.83 (m, 1H, Ar), 7.82 – 7.79 (m, 1H, Ar), 7.77 – 7.76 (m, 1H, Ar), 7.72 (s, 1H, Ar), 7.69 – 7.67 (m, 1H, Ar), 7.58 – 7.51 (m, 3H, Ar), 7.44 – 7.41 (m, 6H, Ar), 7.14 – 7.07 (m, 5H, Ar), 7.06 – 7.05 (m, 2H, Ar), 3.08 (s, 2H, C≡C-H) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 146.6, 141.55, 133.52, 132.20, 133.87, 127.85, 127.32, 127.28, 126.38, 124.67, 123.00, 122.92 (Ar, C=C, CF$_3$), 117.70 (C≡N), 83.27, 77.25 (C≡C) ppm. IR (KBr pellet, cm$^{-1}$): 3288 (C≡C-H), 2211 (C≡N), 2102 (C≡C) 1594 and 1499 (vinyl and aromatic C=C).

7.3.4 Synthesis of P1

Pd(OAc)$_2$ (7.5 mg, 0.033 mmol), CuI (6.4 mg, 0.033 mmol) and PPh$_3$ (21.6 mg,
0.083 mmol) were added to an ice-cooled mixture of 1,4-diiodobenzene (201 mg, 0.61 mmol) in THF/NEt$_3$ under nitrogen and stirred for 20 min. L9 (253 mg, 0.51 mmol) was then added and the mixture was stirred for 30 min in an ice bath. After reacting for 30 min at room temperature, the mixture was heated to 75 °C for 6 h. The solvent was evaporated under reduced pressure. The residue was redissolved in CH$_2$Cl$_2$ and filtered through a silica-gel column with the same eluent. After removal of the solvent under vacuum, an orange solid was obtained and it was then washed with MeOH and hexane in 75% yield (218 mg). $^1$H NMR (CDCl$_3$): δ 7.87 – 7.83 (m, 1H, Ar), 7.76 – 7.75 (m, 1H, Ar), 7.74 (s, 1H, CNC=CH), 7.68 – 7.60 (m, 2H, Ar), 7.57 – 7.53 (m, 3H, Ar), 7.52 – 7.50 (m, 3H, Ar), 7.49 – 7.45 (m, 4H, Ar), 7.41 – 7.36 (m, 4H, Ar), 7.34 – 7.28 (m, 5H, Ar), 7.15 – 7.08 (m, 2H, Ar) ppm. IR (KBr pellet, cm$^{-1}$): 2109 (C≡N), 2092 (C≡C)1585 and 1503 (vinyl and aromatic C=C).

7.3.5 General procedure for the synthesis of P2 – P4

An ice-cooled mixture of 9,9-dibutyl-2,7-diiodo-9H-fluorene$^{23}$ (1 equiv), CuI (19.8 mg, 0.09 mmol), Pd(OAc)$_2$ (18.5 mg, 0.09 mmol) and PPh$_3$ (56.7 mg, 0.22 mmol) in THF/NEt$_3$ was stirred for 20 min. The appropriate cyanostilbene arylacetylide compound (1 equiv) was then added and stirred in an ice bath for 30 min before being warmed at room temperature. After reacting for 30 min at room temperature, the
mixture was heated to 70 °C for 6 h. The reaction mixture was cooled to room temperature and all the volatile component was removed under vacuum. The crude product was redissolved in CH\textsubscript{2}Cl\textsubscript{2} and filtered by a silica-gel column with same eluent. The filtrate was concentrated and then washed with MeOH and hexane to afford a pure product. Yield: 57 – 70%.

**P2:** Yield: 70%; orange solid. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta\) 7.88 – 7.82 (m, 2H, Ar), 7.75 (s, 1H, CNC=CH) 7.74 – 7.73 (m, 1H, Ar), 7.69 – 7.66 (m, 3H, Ar), 7.64 – 7.59 (m, 4H, Ar), 7.55 – 7.50 (m, 5H, Ar), 7.49 – 7.47 (m, 3H, Ar), 7.40 – 7.37 (m, 2H, Ar), 7.32 – 7.31 (m, 1H, Ar), 7.30 (s, 1H, CNC=CH), 7.17 – 7.14 (m, 2H, Ar), 7.12 – 7.10 (m, 2H, Ar), 6.95 – 6.89 (m, 2H, Ar), 1.99 (b, 4H, CH\textsubscript{2}), 1.13 – 1.08 (m, 4H, CH\textsubscript{2}), 0.72 – 0.68 (m, 6H, CH\textsubscript{3}), 0.61 (b, 4H, CH\textsubscript{2}) ppm. IR (KBr pellet, cm\textsuperscript{-1}): 2212 (C≡N), 2094 (C≡C), 1587 and 1505 (vinyl and aromatic C=C).

**P3:** Yield: 65%; orange solid. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta\) 7.87 – 7.76 (m, 3H, Ar), 7.71 – 7.67 (m, 5H, Ar), 7.59 – 7.47 (m, 12H, Ar), 7.39 – 7.35 (m, 4H, Ar), 7.32 – 7.28 (m, 4H, Ar), 7.24 (s 1H, CNC=CH), 7.19 – 7.14 (m, 5H, Ar), 7.07 – 7.04 (m, 3H, Ar), 1.98 (b, 4H, CH\textsubscript{2}), 1.11 – 1.10 (m, 4H, CH\textsubscript{2}), 0.72 – 0.69 (m, 6H, CH\textsubscript{3}), 0.60 (b, 4H, CH\textsubscript{2}) ppm. IR (KBr pellet, cm\textsuperscript{-1}): 2211 (C≡N), 2096 (C≡C), 1587 and 1506 (vinyl and aromatic C=C).

**P4:** Yield: 57%; orange solid. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta\) 7.88 – 7.83 (m, 2H, Ar), 7.77 –
7.66 (m, 4H, Ar), 7.58 – 7.51 (m, 8H, Ar), 7.48 – 7.45 (m, 4H, Ar), 7.38 – 7.31 (m, 3H, Ar), 7.21 (s, 1H, CNC=CH), 7.15 – 7.10 (m, 5H, Ar), 1.98 – 1.94 (m, 4H, CH₂), 1.11 – 1.09 (m, 4H, CH₂), 0.71 – 0.65 (m, 6H, CH₃), 0.64 – 0.58 (m, 4H, CH₂) ppm.

IR (KBr pellet, cm⁻¹): 2211 (C≡N), 2095 (C≡C), 1589 and 1504 (vinyl and aromatic C=C).

7.3.6 General procedure for the synthesis of P5 – P7

A mixture of trans-[PtCl₂(PBu₃)₂] (1 equiv) and the appropriate cyanostilbene arylacetylide derivatives (1 equiv) in NEt₃/THF (50 mL, 1:1, v/v) was reacted with the presence of CuI (5 mg) at room temperature for 15 h. The reaction mixture was evaporated to dryness. The residue was redissolved in CH₂Cl₂ and undissolved substance was filtered with a silica gel column using the same eluent. After removing the solvent, it was washed with MeOH and hexane to obtain a pure solid. Yield: 64 – 67%.

P5: Yield: 65%; orange solid. ¹H NMR (CDCl₃): δ 7.79 – 7.72 (m, 3H, Ar), 7.66 – 7.65 (m, 2H, Ar), 7.62 – 7.59 (m, 2H, Ar), 7.49 – 7.36 (m, 5H, Ar), 7.21 – 7.19 (m, 3H, Ar), 7.06 – 6.93 (m, 6H, Ar), 6.91 (s, 1H, CNC=CH), 2.17 – 2.13 (m, 12H, PCH₂), 1.62 (m, 12H, PCH₂CH₂), 1.50 – 1.42 (m, 12H, CH₂CH₃), 0.95 – 0.90 (m, 18H, CH₃CH₂) ppm. ³¹P NMR (CDCl₃): δ 2.89 (Jₚₚ = 2906 Hz) ppm. IR (KBr pellet,
cm$^{-1}$): 2211 (C≡N), 2088 (C≡C), 1579 and 1497 (vinyl and aromatic C=C).

**P6:** Yield: 67%; orange solid. $^1$H NMR (CDCl$_3$): $\delta$7.78 – 7.76 (m, 3H, Ar), 7.71 – 7.61 (m, 2H, Ar), 7.51 – 7.45 (m, 3H, Ar), 7.30 – 7.25 (m, 5H, Ar), 7.21 – 7.12 (m, 10H, Ar), 7.07 – 7.00 (m, 7H, Ar), 7.00 (s, 1H, CNC=CH), 2.17 – 2.13 (m, 12H, PCH$_2$), 1.61 (m, 12H, PCH$_2$CH$_2$), 1.47 – 1.43 (m, 12H, CH$_2$CH$_3$), 0.95 – 0.90 (m, 18H, CH$_2$CH$_3$) ppm. $^{31}$P NMR (CDCl$_3$): $\delta$2.85 ($J_{P-P}$ = 2906 Hz) ppm. IR (KBr pellet, cm$^{-1}$): 2211 (C≡N), 2096 (C≡C), 1584 and 1497 (vinyl and aromatic C=C).

**P7:** Yield: 64%; orange solid. $^1$H NMR (CDCl$_3$): $\delta$7.76 – 7.70 (m, 4H, Ar), 7.68 – 6.66 (m, 1H, Ar), 7.56 – 7.49 (m, 3H, Ar), 7.39 – 7.32 (m, 2H, Ar), 7.21 – 7.04 (m, 10H, Ar), 7.00 (s, 1H, CNC=CH), 2.15 – 2.14 (m, 12H, PCH$_2$), 1.61 (m, 12H, PCH$_2$CH$_2$), 1.49 – 1.43 (m, 12H, CH$_2$CH$_3$), 0.95 – 0.90 (m, 18H, CH$_2$CH$_3$) ppm. $^{31}$P NMR (CDCl$_3$): $\delta$2.88 ($J_{P-P}$ = 2906 Hz) ppm. IR (KBr pellet, cm$^{-1}$): 2209 (C≡N), 2093 (C≡C), 1590 and 1496 (vinyl and aromatic C=C).

### 7.4 Synthesis of Phenothiazine-Cyanostilbene-Based Luminogens for Chapter 4

#### 7.4.1 Synthesis of CHO10

A mixture of phosphoryl chloride (1.26 mL, 13.6 mmol) and dimethylformamide (1.32 mL, 17.0 mmol) was allowed to stir for 20 min in an ice bath and the mixture was warmed to room temperature for another 30 min. 10-hexyl-10H-phenothiazine$^{25}$
(0.96 g, 3.39 mmol) in CH$_2$Cl$_2$ was then added and heated to 90 °C for 12 h. The reaction mixture was allowed to cool to room temperature and extracted with CHCl$_3$ for three times. The organic layer was washed with brine, dried with Na$_2$SO$_4$ and filtered. All the solvent were removed under reduced pressure and the crude product was purified with silica-gel column chromatography eluting with hexane/CH$_2$Cl$_2$ to yield a yellow oily product with 80% yield (1.32 g). $^1$H NMR (CDCl$_3$): $\delta$ 9.79 (s, 1H, CHO), 7.64 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.9$ Hz, 1H, Ar), 7.58 (d, $J = 1.92$ Hz, 1H, Ar), 7.18 – 7.14 (m, 1H, Ar), 7.12 – 7.10 (m, 1H, Ar), 6.98 – 6.94 (m, 1H, Ar), 6.90 – 6.87 (m, 2H, Ar), 3.88 (t, $J = 7.2$ Hz, 2H, NCH$_2$), 1.85 – 1.77 (m, 2H, CH$_2$), 1.48 – 1.40 (m, 2H, CH$_2$), 1.32 – 1.28 (m, 4H, CH$_2$), 0.90 – 0.86 (m, 3H, CH$_3$) ppm.

7.4.2 Synthesis of CHO10Br

A mixture of CHO10 (0.69 mg, 2.22 mmol) and N-Bromosuccinimide (0.40 mg, 2.22 mmol) in 1:1 molar ratio in CHCl$_3$ (50 mL) was allowed to react in the absence of light for 12 h. The solvent was removed under reduced pressure and the crude product was purified with silica-gel column chromatography eluting with hexane/CH$_2$Cl$_2$ to get a yellow solid with 76% yield (0.87 g). $^1$H NMR (CDCl$_3$): $\delta$ 9.80 (s, 1H, Ar), 7.66 – 7.64 (m, 1H, Ar), 7.57 (d, $J = 1.92$ Hz, 1H, Ar), 7.26 – 7.22 (m, 2H, Ar), 6.90 (d, $J = 8.4$ Hz, 1H, Ar), 6.72 (d, $J = 8.6$ Hz, 1H, Ar), 3.85 (t, $J = 7.2$ Hz, 2H, NCH$_2$), 1.85 – 1.77 (m, 2H, CH$_2$), 1.48 – 1.40 (m, 2H, CH$_2$), 1.32 – 1.28 (m, 4H, CH$_2$), 0.90 – 0.86 (m, 3H, CH$_3$) ppm.
Hz, 2H, NCH₂), 1.82 – 1.75 (m, 2H, CH₂), 1.44 – 1.41 (m, 2H, CH₂), 1.31 – 1.26 (m, 4H, CH₂), 0.90 – 0.86 (m, 3H, CH₃) ppm. ¹³C NMR (CDCl₃): δ 189.92 (CHO), 150.35, 142.93, 142.68, 131.30, 130.25, 129.82, 128.62, 128.49, 117.09, 115.82, 115.01, 114.27 (Ar), 48.11, 31.34, 26.62, 26.45, 22.56, 13.97 (C₆H₁₃) ppm.

7.4.3 Synthesis of CHO11

Pd(PPh₃)₄ (50 mg) was added into the mixture of CHO10Br (866 mg, 2.22 mmol), phenylboronic acid¹⁷ (297 mg, 2.42 mmol) and 2 M aqueous K₂CO₃ in toluene/ethanol (40 mL, 3:1, v/v) in the protection of nitrogen atmosphere. The resultant mixture was heated to reflux for 18 h. After cooling to room temperature, the mixture was poured into water and extracted with ethyl acetate. The organic layer was further washed with brine and dried with Na₂SO₄. The filtrate was concentrated and the residue was purified on a silica-gel column chromatography by gradient elution of hexane/ethyl acetate (3:1, v/v) to afford a yellow solid. (67%, 0.86 g). ¹H NMR (CDCl₃): δ 9.73 (s, 1H, CHO), 7.57 – 7.55 (m, 1H, Ar), 7.51 – 7.50 (m, 1H, Ar), 7.49 – 7.47 (m, 2H, Ar), 7.39 – 7.35 (m, 2H, Ar), 7.33 – 7.30 (m, 1H, Ar), 7.28 – 7.26 (m, 2H, Ar), 3.80 (t, J = 7.3 Hz, NCH₂), 1.78 – 1.73 (m, 2H, CH₂), 1.42 – 1.38 (m, 2H, CH₂), 1.29 – 1.25 (m, 4H, CH₂), 0.88 – 0.85 (m, 3H, CH₃) ppm. ¹³C NMR (CDCl₃): δ 189.89 (CHO), 150.34, 142.50, 139.53, 136.59, 131.06, 130.22, 128.89, 128.29,
The compound was prepared following with the similar procedure as described above of CHO11 with replacing phenylboronic acid by (4-methoxyphenyl)boronic acid\textsuperscript{26}. Elution the column with hexane/ethyl acetate (3:1, v/v) gave a yellow solid (68%, 0.79 g). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta\) 9.72 (s, 1H, CHO), 7.56 – 7.54 (m, 1H, Ar), 7.51 – 7.50 (m, 1H, Ar), 7.42 – 7.40 (m, 2H, Ar), 7.28 – 7.26 (m, 1H, Ar), 7.23 – 7.22 (m, 1H, Ar), 6.92 – 6.90 (m, 2H, Ar), 6.83 – 6.78 (m, 2H, Ar), 3.80 – 3.78 (m, 5H, NCH\textsubscript{2} and OCH\textsubscript{3}), 1.78 – 1.74 (m, 2H, CH\textsubscript{2}), 1.43 – 1.35 (m, 2H, CH\textsubscript{2}), 1.29 – 1.25 (m, 4H, CH\textsubscript{2}), 0.89 – 0.82 (m, 3H, CH\textsubscript{3}) ppm. \textsuperscript{13}C NMR (CDCl\textsubscript{3}): \(\delta\) 189.85 (CHO), 159.18, 150.39, 141.87, 136.28, 132.04, 130.97, 130.22, 128.22, 127.50, 125.65, 125.33, 124.44, 123.94, 116.09, 114.60, 114.31 (Ar), 55.31 (OCH\textsubscript{3}), 48.05, 31.65, 26.69, 26.55, 22.73, 14.21 (C\textsubscript{6}H\textsubscript{13}) ppm.

7.4.5 General procedure for the synthesis of C1 – C3

All phenothiazine-based cyanostilbene compounds were synthesized by reacting CHO10 and the corresponding benzyl cyanide (CN1 – CN3) in 1:1 molar ratio in a
basic ethanol solution (0.25 M NaOEt, 0.1 equiv). The mixture was heated to reflux for 3 h and then cooled to room temperature. The solvent was removed and purified with column chromatography in a gradient elution of hexane and CH₂Cl₂. Yield: 69 – 76%

**C1**: Yield : 76%; orange solid. ¹H NMR (CDCl₃): 7.75 – 7.73 (m, 1H, Ar), 7.64 – 7.62 (m, 2H, Ar), 7.58 – 7.55 (m, 4H, Ar), 7.47 – 7.46 (m, 1H, Ar), 7.42 – 7.38 (m, 2H, Ar), 7.34 – 7.30 (m, 1H, Ar), 7.28 (s, 1H, CNC=CH), 7.12 – 7.08 (m, 1H, Ar), 7.06 – 7.03 (m, 1H, Ar), 6.90 – 6.86 (m, 1H, Ar), 6.79 – 6.74 (m, 2H, Ar), 3.75 (t, J = 7.20 Hz, 2H, NCH₂), 1.78 – 7.70 (m, 2H, CH₂), 1.40 – 1.36 (m, 2H, CH₂), 1.29 – 1.25 (m, 4H, CH₂), 0.89 – 0.85 (m, 3H, CH₃) ppm. ¹³C NMR (CDCl₃): 147.06, 143.88, 141.43, 140.43, 133.67, 132.16, 129.36, 129.00, 128.51, 127.95, 127.60, 127.53, 127.29, 127.03, 126.72, 127.36, 126.36, 126.16, 125.98, 125.79, 124.59, 123.63, 123.13, 118.56, 115.61, 115.07 (Ar, C=C), 107.95 (C≡N), 47.83, 31.71, 26.75, 26.67, 22.78, 14.15 (C₆H₁₃) ppm.

**C2**: Yield : 69%; orange solid. ¹H NMR (CDCl₃): 7.86 – 7.83 (m, 1H, Ar), 7.71 – 7.69 (m, 2H, Ar), 7.65 – 7.63 (m, 2H, Ar), 7.57 – 7.56 (m, 1H, Ar), 7.54 – 7.51 (m, 2H, Ar), 7.38 (s, 1H, CNC=CH), 7.33 – 7.29 (m, 4H, Ar), 7.20 – 7.19 (m, 4H, Ar), 7.17 – 7.16 (m, 3H, Ar), 7.14 – 7.12 (m, 1H, Ar), 7.11 – 7.07 (m, 2H, Ar), 6.98 – 6.94 (m, 1H, Ar), 6.88 – 6.86 (m, 2H, Ar), 3.86 (t, J = 7.1 Hz, 2H, NCH₂), 1.87 – 1.80 (m, 2H,
CH$_2$), 1.49 – 1.44 (m, 2H, CH$_2$), 1.37 – 1.33 (m, 4H, CH$_2$), 0.96 – 0.93 (m, 3H, CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): δ 147.70, 147.57, 147.03, 143.92, 140.92, 140.10, 133.60, 133.10, 129.43, 128.65, 128.51, 128.03, 127.67, 127.51, 127.00, 126.16, 124.66, 123.67, 123.24, 123.11, 118.55, 115.59, 115.11 (Ar, C=C), 108.12 (C≡N), 47.83, 31.70, 26.79, 26.69, 22.78, 14.29 (C$_6$H$_{13}$) ppm.

C3: Yield : 73%; orange solid. $^1$H NMR (CDCl$_3$): δ 7.80 – 7.71 (m, 1H, Ar), 7.73 – 7.70 (m, 1H, Ar), 7.69 – 7.68 (m, 5H, Ar), 7.63 – 7.60 (m, 2H, Ar), 7.53 – 7.52 (m, 1H, Ar), 7.36 (s, 1H, CNC=CH), 7.16 – 7.12 (m, 1H, Ar), 7.09 – 7.06 (m, 1H, Ar), 6.94 – 6.92 (m, 1H, Ar), 6.84 – 6.81 (m, 2H, Ar), 3.81 (t, $J$ = 7.1 Hz, 2H, NCH$_2$), 1.80 – 1.76 (m, 2H, CH$_2$), 1.43 – 1.40 (m, 2H, CH$_2$), 1.33 – 1.26 (m, 4H, CH$_2$), 0.90 – 0.83 (m, 3H, CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): δ 147.34, 143.92, 143.49, 140.93, 139.84, 134.76, 129.87, 129.55, 128.77, 128.55, 127.77, 127.50, 127.27, 126.29, 15.82, 124.68, 123.58, 123.16, 118.37, 115.60, 115.06 (Ar, C=C, CF$_3$), 107.63 (C≡C), 47.82, 31.46, 26.74, 26.61, 22.65, 14.04 (C$_6$H$_{13}$) ppm.

7.4.6 General procedure for the synthesis of C4 – C6

To a mixture of CHO11 (1 equiv) and appropriate benzyl cyanide (1 equiv) was added to basic ethanol solution (0.25M NaOEt, 0.1 equiv). The mixture was allowed to heat to reflux for 3 h and then cooled to room temperature. All the volatile were
removed by rotatory evaporator and the crude products were purified on silica-gel column chromatography with hexane/CH$_2$Cl$_2$ (1:1, v/v). Yield: 73 – 79%

**C4:** Yield: 79%; red solid. $^1$H NMR (CDCl$_3$): δ 7.87 – 7.84 (m, 1H, Ar), 7.73 – 7.71 (m, 2H, Ar), 7.67 – 7.62 (m, 5H, Ar), 7.58 – 7.57 (m, 1H, Ar), 7.55 – 7.53 (m, 2H, Ar), 7.49 – 7.44 (m, 3H, Ar), 7.42 – 7.40 (m, 4H, Ar), 7.38 – 7.35 (m, 3H, Ar), 7.33 (s, 1H, CNC=CH), 6.93 – 6.89 (m, 2H, Ar), 3.90 (t, $J = 7.28$ Hz, 2H, NCH$_2$), 1.86 – 1.84 (m, 2H, CH$_2$), 1.52 – 1.46 (m, 2H, CH$_2$), 1.37 – 1.33 (m, 4H, CH$_2$), 0.91 – 0.88 (m, 3H, CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): δ 147.32, 143.71, 141.32, 135.03, 132.70, 128.93, 128.86, 128.83, 128.63, 128.55, 127.77, 127.64, 127.59, 127.48, 127.16, 127.03, 126.52, 126.16, 126.11, 125.89, 125.52, 125.25, 124.59, 123.51, 123.16, 122.39, 118.20, 115.70, 115.09 (Ar, C=C), 108.32 (C≡N), 47.89, 31.46, 26.77, 26.63, 22.64, 14.14 (C$_6$H$_{13}$) ppm.

**C5:** Yield: 73%; red solid. $^1$H NMR (CDCl$_3$): δ 7.83 – 7.81 (m, 1H, Ar), 7.68 – 7.65 (m, 2H, Ar), 7.61 – 7.59 (m, 2H, Ar), 7.54 – 7.54 (m, 2H, Ar), 7.50 – 7.48 (m, 2H, Ar), 7.47 (s, 1H, CNC=CH), 7.42 – 7.38 (m, 2H, Ar), 7.38 – 7.34 (m, 2H, Ar), 7.32 – 7.28 (m, 3H, Ar), 7.26 – 7.23 (m, 3H, Ar), 7.14 – 7.12 (m, 6H, Ar), 7.06 – 7.02 (m, 2H, Ar), 6.89 – 6.84 (m, 2H, Ar), 3.85 (t, $J = 7.4$ Hz, 2H, NCH$_2$), 1.88 – 1.76 (m, 2H, CH$_2$), 1.49 – 1.42 (m, 2H, CH$_2$), 1.34 – 1.30 (m, 4H, CH$_2$), 0.90 – 0.87 (m, 3H, CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): δ 147.71, 147.57, 146.78, 143.11, 141.00, 140.05, 139.75, 136.15,
133.62, 133.11, 129.38, 128.86, 128.59, 128.10, 127.66, 127.18, 127.01, 126.52, 126.15, 125.87, 124.65, 124.38, 124.05, 123.66, 123.21, 118.50, 115.70, 115.08 (Ar, C=C), 108.27 (C≡N), 47.90, 31.64, 26.77, 26.66, 22.71, 14.19 (C₆H₁₃) ppm.

C₆: Yield : 74%; red solid. ¹H NMR (CDCl₃): δ 7.87 – 7.84 (m, 1H, Ar), 7.75 – 7.73 (m, 2H, Ar), 7.72 – 7.71 (m, 4H, Ar), 7.66 – 7.65 (m, 2H, Ar), 7.59 – 7.58 (m, 1H, Ar), 7.54 – 7.52 (m, 2H, Ar), 7.43 – 7.41 (m, 3H, Ar), 7.37 (s, 1H, CNC=C), 7.34 – 7.32 (m, 2H, Ar), 6.93 – 6.88 (m, 2H, Ar), 3.89 (t, J = 7.4 Hz, 2H, CH₂), 1.87 – 1.83 (m, 2H, CH₂), 1.49 – 1.45 (m, 2H, CH₂), 1.36 – 1.31 (m, 4H, CH₂), 0.92 – 0.88 (m, 3H, CH₃) ppm. ¹³C NMR (CDCl₃): δ 147.06, 143.02, 140.93, 139.67, 139.72, 136.25, 134.68, 128.4, 128.75, 128.67, 127.81, 127.30, 127.19, 126.51, 126.34, 126.13, 125.89, 124.39, 123.99, 118.33, 115.73, 115.09 (Ar, C=C), 107.81 (C≡N), 47.91, 31.46, 26.76, 26.62, 22.63, 14.02 (C₆H₁₃) ppm.

7.4.7 General procedure for the synthesis of C7 – C9

The mixture of CHO12 (1 equiv) and appropriate benzyl cyanide (CN1 – CN3) were reacted in basic ethanol solution (0.25 M, 0.1 equiv) and heated to reflux for 3 h. The reaction mixture was concentrated and the crude product was purified with silica-gel column chromatography with a gradient elution of hexane and CH₂Cl₂. Yield: 70 – 79%.
C7: Yield: 76%; red solid. $^1$H NMR (CDCl$_3$): $\delta$ 7.86 – 7.84 (m, 1H, Ar), 7.73 – 7.71 (m, 2H, Ar), 7.66 – 7.65 (m, 1H, Ar), 7.64 – 7.63 (m, 2H, Ar), 7.62 – 7.61 (m, 1H, Ar), 7.58 – 7.57 (m, 1H, Ar), 7.48 – 7.47 (m, 2H, Ar), 7.46 – 7.45 (m, 2H, Ar), 7.40 – 7.38 (m, 2H, Ar), 7.34 – 7.32 (m, 1H, Ar), 7.30 (s, 1H, CNC=CH), 6.97 (s, 1H, Ar), 6.95 (s, 1H, Ar), 7.90 – 6.88 (m, 2H, Ar), 3.88 (t, $J$ = 7.4 Hz, 2H, NCH$_2$), 3.84 (s, 3H, OCH$_3$), 1.88 – 1.81 (m, 2H, CH$_2$), 1.49 – 1.43 (m, 2H, CH$_2$), 1.35 – 1.33 (m, 4H, CH$_2$), 0.92 – 0.87 (m, 3H, CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 159.08, 146.98, 142.53, 141.56, 140.45, 140.07, 135.90, 137.72, 132.44, 128.93, 128.63, 128.59, 128.38, 127.94, 127.85, 127.77, 127.63, 127.55, 127.30, 127.09, 127.03, 126.16, 125.63, 125.46, 124.35, 124.00, 118.47, 115.70, 115.02, 114.28 (Ar, C=C), 108.10 (C≡N), 55.38 (OCH$_3$), 47.88, 31.61, 26.77, 26.63, 22.68 14.15 (C$_6$H$_{13}$) ppm.

C8: Yield: 79%; red solid. $^1$H NMR (CDCl$_3$): $\delta$ 7.80 – 7.78 (m, 1H, Ar), 7.65 – 7.63 (m, 2H, Ar), 7.59 – 7.57 (m, 2H, Ar), 7.51 – 7.50 (m, 1H, Ar), 7.47 – 7.45 (m, 2H, Ar), 7.44 – 7.42 (m, 2H, Ar), 7.32 (s, 1H, CNC=CH), 7.30 – 7.23 (m, 6H, Ar), 7.13 – 7.11 (m, 6H, Ar), 7.05 – 7.01 (m, 2H, Ar), 6.93 – 6.91 (m, 2H, Ar), 6.84 – 6.80 (m, 2H, Ar), 3.83 – 3.80 (m, 5H, NCH$_2$ and OCH$_3$), 1.82 – 1.78 (m, 2H, CH$_2$), 1.45 – 1.41 (m, 2H CH$_2$), 1.32 – 1.29 (m, 4H, CH$_2$), 0.90 – 0.86 (m, 3H, CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 159.08, 147.76, 147.59, 146.83, 142.48, 140.94, 140.07, 135.83, 133.62, 133.13, 132.32, 129.41, 128.66, 128.55, 128.00, 127.67, 127.55, 127.00, 126.15, 125.63,
125.41, 124.66, 124.41, 124.23, 123.95, 123.67, 123.23, 118.55, 115.71, 115.00, 114.33 (Ar, C=C), 108.12 (C≡N), 55.40 (OCH$_3$), 47.88, 31.51, 26.76, 26.68, 22.67, 14.10 (C$_6$H$_{13}$) ppm.

**C9**: Yield: 70%; red solid. $^1$H NMR (CDCl$_3$): $\delta$ 7.85 – 7.82 (m, 1H, Ar), 7.74 – 7.70 (m, 6H, Ar), 7.65 – 7.63 (m, 2H, Ar), 7.57 – 7.56 (m, 1H, Ar), 7.46 – 7.44 (m, 2H, Ar), 7.40 (s, 1H, CNC=C), 7.33 – 7.31 (m, 1H, Ar), 7.28 – 7.27 (m, 1H, Ar), 6.96 – 6.94 (m, 2H, Ar), 6.89 – 6.85 (m, 2H, Ar), 3.88 – 3.86 (m, 2H, NCH$_2$), 3.84 (s, 3H, OCH$_3$), 1.87 – 1.79 (m, 2H, CH$_2$), 1.47 – 1.42 (m, 2H, CH$_2$), 1.37 – 1.31 (m, 4H, CH$_2$), 0.91 – 0.88 (m, 3H, CH$_3$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ 159.06, 147.09, 143.51, 142.38, 140.92, 139.88, 135.91, 134.66, 132.26, 129.88, 129.56, 128.75, 128.62, 127.78, 127.73, 127.52, 127.28, 126.30, 125.88, 125.84, 125.63, 125.41, 124.28, 123.86, 118.37, 115.71, 114.98, 114.27 (Ar, C=C), 107.63 (C≡N), 55.38 (OCH$_3$), 47.89, 31.48, 26.75, 26.64, 22.66, 14.06 (C$_6$H$_{13}$) ppm.

### 7.5 Synthesis of Pyridyl-Functionalized Cyanostilbene-Based Compounds for Chapter 5

#### 7.5.1 Synthesis of C10

CN1 (0.98 g, 5.08 mmol) was allowed to react with 4-methylbenzaldehyde (0.61 g, 5.08 mmol) in basic ethanol solution. The mixture was heated to 80 °C for 3 h and
then cooled to room temperature. All the volatile components were removed under reduced pressure. The crude product was purified through silica-gel column chromatography eluting with hexane/CH₂Cl₂ to afford a yellow solid with 80% yield (1.5 g). ¹H NMR (CDCl₃): δ 7.84 (s, 1H, Ar), 7.82 (s, 1H, CNC=CH), 7.76 – 7.74 (m, 2H, Ar), 7.64 – 7.62 (m, 2H, Ar), 7.55 (s, 1H, Ar), 7.49 – 7.45 (m, 2H, Ar), 7.41 – 7.38 (m, 1H, Ar), 7.30 – 7.28 (m, 2H, Ar), 2.43 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃): δ 141.97 (C=C-Ph), 141.84, 141.20, 140.05, 133.59, 131.08, 129.73, 129.36, 128.93, 127.81, 127.67, 127.05, 126.32 (Ar), 118.21 (C≡N), 110.08 (C=C-CN), 21.60 (CH₃) ppm.

7.5.2 Synthesis of C10Br

C10 (0.86 g, 2.91 mmol) and N-bromosuccinimide (NBS, 0.52 g, 2.91 mmol) were dissolved and stirred in 50 mL of carbon tetrachloride (CCl₄) and a small amount of benzoyl peroxide was introduced as an initiator. The reaction mixture was heated to 60 °C for 12 h. After cooling to room temperature, the undissolved white salt was filtered and the crude product was concentrated under reduced pressure. The light yellow colored solid was obtained with precipitation with hexane (698 mg, 65% yield). ¹H NMR (CDCl₃): δ 7.90 – 7.88 (m, 2H, Ar), 7.77 (s, 1H, CNC=CH), 7.76 – 7.74 (m, 1H, Ar), 7.64 – 7.63 (m, 2H, Ar), 7.58 – 7.56 (m, 1H, Ar), 7.52 – 7.46 (m,
5H, Ar), 7.41 – 7.38 (m, 1H, Ar), 4.53 (s, 2H, CH$_2$Br) ppm.

7.5.3 Synthesis of CII

A mixture of C10Br (0.53 g, 1.42 mmol) and triphenylphosphine (0.74 g, 2.84 mmol) was stirred and refluxed in toluene for 48 h. The reaction mixture was allowed to cool and the resulting light yellow precipitate was filtered, washed with toluene and used without further purification. A cooled mixture of the dried phosphonium salt (681 mg, 1.22 mmol) and potassium tert-butoxide (13.7 mg, 0.12 mmol) in dry THF was stirred for 30 min. Isonicotinaldehyde (117 mg, 1.34 mmol) was then introduced to the solution and allowed to react at room temperature for 12 h. The solvent was evaporated and the purification was accomplished by the silica-gel column chromatography with a gradient elution with hexane/ethyl acetate and the product was obtained with 70% yield (329 mg). $^1$H NMR (CDCl$_3$): 8.61 – 8.60 (m, 2H, Ar), 7.95 – 7.93 (m, 2H, Ar), 7.78 (s, 1H, CNC=CH), 7.75 (m, 1H, Ar), 7.69 – 7.67 (m, 2H, Ar), 7.64 – 7.62 (m, 4H, Ar), 7.56 (s, 1H, Ar), 7.49 – 7.45 (m, 2H, Ar), 7.41 – 7.38 (m, 3H, Ar), 7.33 (m, 1H, Ar), 7.12 – 7.08 (m, 1H, Ar) ppm. $^{13}$C NMR (CDCl$_3$): δ 150.31 (C=N), 144.15(C=C-Ph), 142.16, 140.83, 139.90, 138.26, 133.96, 133.28, 132.07, 129.89, 128.97, 127.92, 127.80, 127.72, 127.50, 127.05, 126.42, 122.00 (Ar, C=C), 118.03 (C≡N), 111.32 (C=C-CN) ppm.
References


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CURRICULUM VITAE

Academic qualification of the thesis author, Miss LAU Wai Sum:

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