Metal-organic compounds of iridium(III) and platinum(II): synthesis, characterization and optoelectronic applications

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Metal-Organic Compounds of Iridium(III) and Platinum(II): Synthesis, Characterization and Optoelectronic Applications

WU Hao

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 and characterization of a series of ligands and the corresponding novel iridium(III) or platinum(II) complexes are discussed in this thesis. Their photophysical and electrochemical properties, the applications in organic light-emitting diodes (OLEDs), dye-sensitized solar cells (DSSCs), aggregation induced emission (AIE) and time-resolved infrared (TRIR) study are also investigated.

Chapter 1 generates a brief overview of the background, principle, and development of OLEDs, DSSCs, AIE materials and the involvement of the TRIR technique.

Chapter 2 describes the synthesis, spectroscopic, photophysical and electrochemical characterization of a series of cationic iridium(III) complexes. Strong electron-withdrawing carboxylic acid substituted bipyridyl was involved in the ligand system and the intra-ligand charge transfer character of diphenylamino containing ligand further shift the dominant absorption band to the lower energy region. Some of them were applied for DSSC device fabrication.

Chapter 3 presents the synthesis, spectroscopic, photophysical and electrochemical characterization as well as OLED application of a group of cyclometalated iridium(III) complexes by using 2-substituted 9-benzylcarbazolyl,
9-phenylcarbazolyl or 2-methyl-7-phenylcarbazolyl groups as the ligands. They show significant bathochromatic shift from those using 3-substituted ligands. And this can be explained by the fact that more electron density is located at 2-position of carbazole moiety and make them suitable candidates for deep red OLED application.

Chapter 4 delivers the synthesis, spectroscopic, photophysical and electrochemical characterization of a series of platinum(II) acetylide complexes for AIE study. All of the complexes contain \([4-(1,2,2\text{-triphenylethenyl})\text{phenyl}]\text{ethynyl}\) ligand, which is designed from AIE active building block tetraphenylamine (TPE). Some of these metal complexes show AIE behavior.

Chapter 5 outlines the synthetic methodology and characterization of another series of cyclometalated iridium(III) and platinum(II) complexes, containing TPE or carbazole units. It is very interesting to find out that there is hardly any emission in all of the TPE-containing cyclometalated complexes, nor any signs of AIE behavior. Meanwhile, for carbazole-containing platinum(II) complexes, remarkable AIE results could be generated, which is believed to be important for further organometallic AIE active material development.

Chapter 6 describes the synthetic methodology and characterization of a series of symmetric or asymmetric platinum(II) acetylides. Some of them were
further applied for TRIR analysis to generate detailed experimental information of the electron transitions during excitation. The results demonstrate that both localized and delocalized metal ligand orbital mixing could be generated according to the variations in electronegativity of the ligand system.

Chapter 7 and 8 present the concluding remarks and summarize the experimental details of all of the previous chapters.
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I would like to express my deepest gratitude and sincere thanks to my supervisor Prof. Raymond Wong Wai Yeung for his invaluable guidance, encouragement and support throughout my study and research, as well as his precious and uninterrupted suggestions, comments and corrections on the accomplishment of this thesis. His hardworking and devoted attitude has impressed me a lot and truly made my study and research a rewarding experience.

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<th>Definition</th>
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<tr>
<td>M</td>
<td>Transition metal</td>
</tr>
<tr>
<td>Ar</td>
<td>Aryl</td>
</tr>
<tr>
<td>′Bu</td>
<td><em>tert</em>-Butyl</td>
</tr>
<tr>
<td>′′Bu</td>
<td><em>n</em>-Butyl</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
</tr>
<tr>
<td>OMe</td>
<td>Methoxy</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>R</td>
<td>Alkyl</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilyl</td>
</tr>
<tr>
<td>X</td>
<td>Halogen</td>
</tr>
<tr>
<td>AcOH</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>Chloroform</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>CO</td>
<td>Carbonyl</td>
</tr>
<tr>
<td>DMF</td>
<td><em>N</em>,<em>N</em>-Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>Et₂O</td>
<td>Diethyl ether</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>NBS</td>
<td><em>N</em>-Bromosuccinimide</td>
</tr>
<tr>
<td>NEt₃</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Energy gap</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>ppm</td>
<td>Part per million</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>dd</td>
<td>Doublet of doublet</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>br</td>
<td>Broad</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>Matrix-assisted laser desorption ionization / time-of-flight</td>
</tr>
<tr>
<td>$M^+$</td>
<td>Molecular ion</td>
</tr>
<tr>
<td>$m/z$</td>
<td>Mass to charge ratio</td>
</tr>
<tr>
<td>acac</td>
<td>Acetylacetone</td>
</tr>
<tr>
<td>bipy</td>
<td>Bipyridine</td>
</tr>
<tr>
<td>ppy</td>
<td>2-Phenylpyridine</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>TRIR</td>
<td>Time-resolved infrared</td>
</tr>
<tr>
<td>UV/Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>AIE</td>
<td>Aggregation induced emission</td>
</tr>
<tr>
<td>DSSCs</td>
<td>Dye-sensitized solar cells</td>
</tr>
<tr>
<td>OLEDs</td>
<td>Organic light-emitting diodes</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaics</td>
</tr>
<tr>
<td>LMCT</td>
<td>Ligand-to-metal charge transfer</td>
</tr>
<tr>
<td>MLCT</td>
<td>Metal-to-ligand charge transfer</td>
</tr>
<tr>
<td>ca.</td>
<td>Calculated</td>
</tr>
<tr>
<td>$S_0$</td>
<td>Singlet ground state</td>
</tr>
<tr>
<td>$S_1$</td>
<td>Singlet excited state</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>$T_1$</td>
<td>Triplet excited state</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight-average molecular weight</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>r. t.</td>
<td>Room temperature</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>Short-circuit current density</td>
</tr>
<tr>
<td>$FF$</td>
<td>Fill factor</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
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</table>
List of Symbols

°C  
Degree Celsius

ν  
Wavenumber in cm$^{-1}$

δ  
Chemical shift

$\phi_p$  
Phosphorescence quantum yield

$\lambda$  
Wavelength

$\lambda_{abs}$  
Absorption wavelength

$\lambda_{em}$  
Emission wavelength

$\varepsilon$  
Molar absorptivity/molar extinction coefficient
Chapter 2

Formula Index

\[ L_1 \]

\[ L_4 \]

\[ L_6 \]

\[ L_8 \]

\[ L_5 \]

\[ L_7 \]

R = CH₃, \( L_2 \)
R = CF₃, \( L_3 \)
R = H, 1  
R = CH₃, 2  
R = CF₃, 3
Chapter 3

\[ R = \text{Me, } L_9 \]
\[ R = \text{CF}_3, \ L_{10} \]

\[ L_{11} \]

\[ L_{12} \]

\[ L_{13} \]

\[ L_{14} \]
Chapter 4

L_{15}  

L_{16}  

L_{17}  

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18

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xxxvii
Chapter 5

\[ L_{18} \]

\[ L_{19} \]

\[ L_{20} \]

\[ 20 \]

\[ 21 \]

xxxviii
Chapter 6

L_21

L_22

L_23

FPtF

NFpNF
R = \begin{align*}
29 & \quad \text{[Chemical structure]} \\
30 & \quad \text{[Chemical structure]} \\
31 & \quad \text{[Chemical structure]} \\
32 & \quad \text{[Chemical structure]} 
\end{align*}
Chapter 1

Introduction

In the past decades, Ir(III) and Pt(II) complexes as well as their derivatives play important roles in optical applications, among which luminescence materials in organic light emitting diodes (OLEDs) and light harvesting materials in dye sensitized solar cells (DSSCs) have been widely studied, and their photophysical and photochemical properties have been well investigated.\textsuperscript{[1]} Meanwhile, many efforts are still being made to further explore their undercover characteristics, recently a special kind of aggregation-induced emission (AIE) materials draw very much attention because of their novel photophysical behavior in the solid state.\textsuperscript{[2]} At the same time, new complimentary analytical techniques are being introduced as well, to help fully understand the microscopic molecular interactions especially in the excited states.\textsuperscript{[3]}

1.1 Background and Principle of Organic Light-Emitting Diodes (OLEDs)

1.1.1 Background of OLEDs

The development of OLEDs has shown tremendous progress.\textsuperscript{[4]} Their advantages, such as flexible, thin, light-weight, fast-response, wide-viewing-angle,
high-contrast and low-operation voltage,\textsuperscript{[5]} made them as the leading materials for the new generation of full-color displays and low power consumption lighting sources.

The first phenomenon of electroluminescence was observed under 100V driving voltage, when 5 mm anthracence crystal evaporated film was utilized. This is the first organic semiconductor which was designed by Pope et al. in 1963.\textsuperscript{[6]} The next breakthrough was made in 1987, when Tang and VanSlyke of Kodak reported efficient low voltage (less than 10 V) electroluminescence with external quantum efficiency as high as 1%. This two-layer organic thin-film device, fabricated by vacuum thermal sublimation technique, shows that EL materials have potential to be commercialized.\textsuperscript{[7]} Moreover, after polymer-based light-emitting diode (PLED), which was manufactured by spin-coating method with conjugated polymer poly(phenylenevinylene) (PPV), was introduced by Burroughes and coworkers at Cambridge University,\textsuperscript{[6]} large area full-color display application drives the eyes of both academic and industrial research groups.\textsuperscript{[8]} Today, OLEDs materials and the fabrication technology are already industrialized. They are believed to the suitable solution for low carbon illumination as well as the best candidate for advanced displays in mobile phones, car stereos, digital cameras, but also in large area full-color display.\textsuperscript{[9]}

Based on device structure and emission layer material, OLED could be divided into three types: small-molecule OLEDs (SMOLEDs),\textsuperscript{[9]} which use small
molecule compounds as emitters; PLEDs, as mentioned above, functionalized polymers were involved for light emission\(^{[10]}\); and light-emitting electrochemical cells (LECs), which usually contain highly-emissive transition metal complexes in the middle of a simple structures\(^{[11]}\).

Although pure organic light-emitting devices already have plenty of advantages, there is still one major issue that cannot be ignored. Most pure organic light-emitting materials are based on fluorescence, which significantly limit the internal quantum efficiency up to 25%, because of the spin forbidden rule\(^{[12]}\). In that case, by using organometallic compounds containing heavy metal atoms to emit phosphorescence, in which strong spin–orbit coupling occurs and leads to efficient triplet formation, a maximum internal quantum efficiency of 100% can be achieved theoretically\(^{[13]}\).

Among all the heavy metals, organometallic iridium(III) complexes have been widely studied in the development of highly efficient OLEDs\(^{[14]}\). Meanwhile, the emission wavelength of iridium(III) based phosphors can also be finely tuned through modifying the properties of the cyclometalated ligands; the phosphorescence lifetime of these complexes is less than 1 μs, which reduces the energy loss and leads to further improvement of efficiency. These advantages render iridium(III) complexes excellent phosphorescent emitters\(^{[3(c), 15]}\).
1.1.2 Basic Principle of OLEDs

Jablonski Diagram

The Jablonski Diagram could display the possible electron transitions of excited state. As described below, the electronic states of a molecule are illustrated by energy differences and spin multiplicity. In such a diagram, the electron transitions in the absorption, fluorescence, and phosphorescence could be demonstrated.

Upon excitation, the molecule absorbs energy ($h\nu_0$) and transfers from ground state ($S_0$) to excited state ($S_1$). After that, the energy is released through relaxation. The excited electron may radiatively ($h\nu_1$) go back to the ground state ($S_0$) from the singlet state ($S_1$); or it can undergo intersystem crossing to a triplet state ($T_1$), then further transferred back to ground state ($S_0$) through releasing of a photon ($h\nu_2$).

Figure 1.1: The Jablonski Diagram
The photons (hν₁) released from S₁-S₀ are defined as fluorescence while those (hν₂) released from T₁-S₀ are called phosphorescence.

**Photoluminescence (PL) and Electroluminescence (EL)**

Both of PL and EL are related to the light emission. However, they are excited by different types of energy. PL is the radiative decay after the absorption of photons; while EL is the light emission produced when exposing to an electric field without thermal energy generation. Therefore, for one molecule, theoretically the energy absorbed and emitted (hν) of PL and EL should be the same.\(^\text{[16]}\)

**Spin Selection Rule**

This definition describes that transitions only occur among energy states sharing the same spin multiplicity, in other words, transitions are forbidden between energy states with different spin multiplicity. However, the spin-orbit coupling between organic ligands and metal core may provide a situation overcoming this rule.\(^\text{[17]}\)

**Transitions for Transition Metal Complexes**

As shows below, in a transition metal complex, there are mainly four
possible types of transitions during excitation. In UV/Vis spectra of heavy metal complexes, a series of relatively intense absorption may be observed at much lowered energy region than the ligand absorption bands (> 400 nm), which are normally located in the late UV region and may further extend to visible region. At most of the cases, they are charge-transfer (CT) bands. The transition of electron may be transferred from ligand to metal (L → M), on the opposite (M → L), within metal (MC) or ligand (IL).

- Metal-to-ligand charge transfer (MLCT) transition: it is the electron transition from a metal based orbital to a ligand counted orbital. After that, the metal is essentially oxidized. Thus the transition energy is largely related to the ionization potential of the metal ion, and MLCT usually occurs between electron rich complexes and ligands with good π electron accepting properties or even empty π* orbital.[18]

\[ L\text{--}M \xrightarrow{hv} L^-\text{--}M^+ \text{ (MLCT)} \]

- Ligand-to-Metal Charge Transfer (LMCT): upon excitation, an electron is donated from a principally ligand-based orbital and essentially reduces the metal atom. Therefore, the LMCT transition energy has a large relationship with the reduction potential of the metal ion, and the transition usually happens between ligands with good reducing property and metals with good electron withdrawing character.
Metal-centered Charge Transfer (MCCT): an electron is mostly moving round the metal core, usually transferring from the non-bonding $d\pi$ orbital to the anti-bonding $d\sigma$ orbital. And MCCT is favored by filled-d-shell metals.

Intraligand Charge Transfer (ILCT): the electron transition is mainly located around the ligand. It may be transferred from a $\pi$ bonding or non-bonding orbital to an anti-bonding $\pi^*$ orbital.

1.1.3 Basic Structure of OLEDs

An OLED is a light-emitting diode (LED) using organic materials to compose the film in electroluminescent layer.

![Diagram of OLED configuration](image)

Figure 1.2: A single layer OLED configuration
Among which, the single layer OLED has the simplest configuration, which consists cathode, anode, and an electroluminescent layer sandwiched in between. It has straightforward working principle. When bias is applied, holes are injected from the anode and electrons are injected from the cathode, both of them travel towards the EL layer. An exciton is produced when an electron and a hole combines, and excite the emissive material from ground state to the singlet and triplet states. The relaxation of excitons results in the emission of photons.\textsuperscript{[16]} The emission color of single layer OLED is determined by the energy difference between the HOMO and LUMO of the molecules in the EL layer, and it can be simply adjusted by the modification of the electronegativity and conjugation length of the EL compound.

However, one major shortage of this kind of OLED is that the charge carriers are difficult to conduct to the EL simultaneously since the distribution of pure organic molecules is disordered. In addition, if the charge carriers form space charges and stay at any of the electrodes, further hole and electron injection will be prevented and may even stop the whole process.\textsuperscript{[16]}

Therefore, multi-layered OLED was invented to deal with the above disadvantages. With the help of electron injection layer (EIL), hole injection layer (HIL), electron transport layer (ETL), and hole transporting layer (HTL), the injection of the carriers to the emission layer (EML) is much enhanced since the energy barrier between the electrodes and the adjacent organic materials is
minimized. As shown in Figure 1.3, when an external voltage is applied, similar as single layer OLED, the holes are injected from the anode while electrons are injected from the cathode. After that, the holes migrate through HIL and HTL gradually while the electrons pass through EIL and ETL. When holes and electrons arrive at EML, they will combine and form excitons with excess energy. And the energy will release as photons (EL) after the molecules relax to the ground state. Both fluorescence ($S_1$ to $S_0$) and phosphorescence ($T_1$ to $T_0$) may be observed. And unavoidably some energy will be lost through radiationless decay.

Figure 1.3 A multilayer OLED configuration
1.1.4 Basic Parameters of OLED Performance

To better describe the overall performance of OLED devices, several parameters, which are commonly used, are listed below. Since OLEDs are one kind of the most competitive new generation light source, the measurements are mainly based on the parameters that can indicate the reflection of human eyes, usually using traditional light sources such as candles or bulbs as the reference.

**Luminance** \((L)\) describes the light quantity falling inside a given angle, which is produced by or passes through a particular area. It is one of the photometric measurement calculated by putting the light luminous intensity over area, i.e. light intensity per unit area per current injected. The unit of it is candela per square meter \((\text{cd/m}^2)\).\(^{[20(a)]}\)

**Luminance Intensity** describes the power of emitted light through a particular direction or solid angle. It is quantified by candela (cd), which is the luminescent power generated from one common candle light.\(^{[20(b)]}\)

**Luminance Efficiency** \((\eta_L)\) shows the capability of visible light produced by unit electricity current.\(^{[20(c)]}\) It is calculated by putting the amount of luminance over electricity applied, thus the unit of it is candela per ampere \((\text{cd/A})\).

**Power Efficiency** \((\eta_P)\) demonstrates the light power generated in the forward direction of unit electric power consumed. It is the ratio of forward light power emitted over the electrical power required for the OLED at a particular
voltage.\textsuperscript{[20(d)]}\textsuperscript{42} Therefore the unit is lumen per watt (lm/W), and is a factor involved in electricity consumption.

**External Efficiency** ($\eta_{ext}$) is calculated by the ratio of total number of photons emitted over the number of electrons injected through the viewing direction of the OLED.\textsuperscript{[20(d)]}

**Turned-on Voltage** ($V_{\text{turn-on}}$) by definition is the least voltage at which the electroluminescence of an OLED device starts to satisfy the lowest limitation of a recording equipment.

1.2 Background and Principle of Dye-Sensitized Solar Cells (DSSCs)

1.2.1 Background of DSSCs

A dye-sensitized solar cell (DSSC) is a photo-electrochemical system based on a semiconductor formed between a photo-sensitized anode and an electrolyte.\textsuperscript{[18]} The idea was first introduced in the late 1970's but it did not draw the world's attention until Swiss photochemist, Michael Grätzel, reported a newly invented version of a dye solar cell in a Nature paper in 1991, which achieved 7% efficiency.\textsuperscript{[19]} After that Grätzel and co-workers quickly pushed the efficiency to 10% in 1993.\textsuperscript{[20]} Recently the record was brought up to \textasciitilde13% along with continuous improvements both chemically and physically.\textsuperscript{[21+science]} Moreover, a lot of relevant literature papers has been published, which keeps broadening the
scientific experience of electrochemistry, photophysics, and materials chemistry.\cite{22}

DSSCs are currently the most efficient solar power technology.\cite{18} They have attracted great attention as a potential low-cost, simple assembled technology as well as high-power-conversion-efficiency photovoltaic paradigm. The efficiencies of typical thin-film technologies range from 5% to 13%, while those of traditional low-cost commercialized silicon panels are between 12% and 15%.\cite{18} As a result DSSCs are considered to be suitable replacement for existing solar energy applications in "low density" fields such as rooftop solar collectors. Also, the robustness and light weight of the glass-less DSSCs are their major advantages.\cite{23} The mechanical robustness makes them possible to work at high temperatures and remain at high efficiency, and the thin layer structure allows them to radiate away heat easily. The flexibility of DSSCs is another advantage as well.\cite{23}

The manufacture of DSSCs is pretty less expensive than older solid-state cell designs.\cite{21} Moreover, there is still potential to further reduce the cost by limiting the usage of noble materials such as platinum and ruthenium. Although the conversion efficiency of DSSCs is still lower than the best thin-film cells as mentioned above, they have very high price/performance ratios (kWh/(m²·annum·dollar)) which are good enough to compete with the fossil fuel electrical generation.\cite{24,25}
1.2.2 Basic Principle of DSSCs

As described below in Figure 1.4, there are five components in a typical DSSC: nanocrystalline semiconductor oxide film electrode (e.g. nanoporous TiO$_2$ film), dye sensitizer, electrolyte, counter electrode and transparent conducting substrate.

Figure 1.4 shows the structure and operating principle of DSSCs. The process is as follows: when sunlight passes through the transparent conducting substrate and reaches the dye on the surface of TiO$_2$, photons with enough energy strike the dye to the excited state (D $\rightarrow$ D*), from which an electron can be generated and "injected" directly into the conduction band of the semiconductor electrode (D* $\rightarrow$ D$^+$ + e$^-$). After that the electron transfers to the electrode and passes through the circuit. When the electron reaches the electrolyte, the reductant is regenerated (Ox + e$^-$ $\rightarrow$ Red), and it can further reduce the dye to the ground state (D$^+$ + e$^-$ $\rightarrow$ D). After the whole process the dye is subsequently recovered, usually the last step was carried out in the solution of an organic solvent or ionic liquid solvent containing the I$_3^-/I^-$ redox system. It is a very quick process, as compared to that of electron injection to recombine with the oxidized dye.
1.2.3 Development of DSSCs

In the past decades, great effort has been made to optimize the performance
of DSSCs such as variation of ligands, heavy metals and other substituent groups in metal complexes.\textsuperscript{[25]} Heavy metals commonly mentioned are Ru(II), Os(II), Pt(II), Re(I), Cu(I), Fe(II), and Ir(III).\textsuperscript{[20b, 25]}

Recently, researches are mainly focused on developing new types of stable and efficient dyes as well as their DSSCs. In order to functionalize the molecules smoothly, the dyes in DSSCs need to fulfill the following requirements: firstly they must bond strongly to TiO$_2$ through anchoring groups, which could be carboxylic, phosphonic and/or sulfonic acid groups. This property can prevent gradual leaching of the electrolyte and is necessary for efficient electron injection into TiO$_2$ conducting band. Secondly, the LUMO of the dye should be high enough in energy while maintaining efficient regeneration of oxidized dye by HTM and the HOMO of that must be sufficiently low in energy. Also, to enable efficient light harvesting, the dye materials must have large molar extinction coefficients as well as wide absorption bands which cover as much of the visible spectrum as possible and even extend to the near-infrared region. Moreover, it has to be more rapid for the electrons transferring from the dye to TiO$_2$ than the dye decay to the ground state. In addition, thinner film can reduce the dye molecules aggregation on the glass surface and help to avoid nonradiative decay to consume the excited state energy.\textsuperscript{[26]}
1.2.4 Basic Parameters of DSSC Performance

DSSC has been explored exclusively in the last decades. To have better description of the performance of DSSC devices, some terms have to be defined below.

**Current Density-Voltage Curve** (*J-V Curve*) is a simple plot of current density over voltage of the fabricated DSSC device, as shown in Figure 1.5, from which one can find the maximum voltage (*V*\textsubscript{max}) and current (*J*\textsubscript{max}), and the theoretical maximum power (*P*\textsubscript{max}), where

\[ P_{\text{max}} = V_{\text{max}} \times J_{\text{max}} \]

The ideal case will be represented by the outer square shell of Figure 1.5, However in the real case, there are always energy lost.

**Short-Circuit Current Density** (*J*\textsubscript{sc}) describes the unit area current density value of the device when no external voltage is applied on. It indicates the photo generation ability of charge carriers. The commonly used units for *J*\textsubscript{sc} are mA/cm\textsuperscript{2} and A/cm\textsuperscript{2}. This value can be enlarged by using dye materials with large solar absorption coverage, high coefficient and relatively high diffusion length, and also lower reflection at the device surface.

**Open-Circuit Voltage** (*V*\textsubscript{oc}) is the maximum voltage that can be measured in a solar cell, which directly depends on the energy gap between HOMO and
LUMO level of the dye materials. Apart from that it can also be enlarged by restricting recombination rates in the diffusion zone.

**Power Conversion Efficiency** (PCE) can be calculated according to the following equation. It describes the ratio of device energy output over solar energy input and is a common parameter used to compare two devices' performance.

\[
PCE = \frac{P_{\text{max}}}{P_{\text{in}}} \times 100\% = \frac{J_{\text{max}}*V_{\text{max}}}{P_{\text{in}}} \times 100\% = \frac{J_{\text{sc}}*V_{\text{oc}}*\text{FF}}{P_{\text{in}}}
\]

**Incident Photon to Electron Conversion Efficiency** (IPCE) / **External Quantum Efficiency** (EQE) can be obtained through the following calculation. It is another way to demonstrate the DSSC device performance and represents the percentage of photons that are converted to electrons. This value depends on the molar extinction coefficient of the dye, amount of materials used, efficiencies of charge injection and transportation during the working process as well as the energy loss through reflection.

\[
\text{IPCE (EQE)} = \frac{N_{\text{charge}}}{N_{\text{photon}}} = \frac{1024*J_{\text{sc}}}{\lambda*P_{\text{light}}}
\]

**Fill Factor** (FF) is another important parameter normally used to describe the efficiency of a DSSC device and is defined by the equation shown below. It
reflects the amount ratio of photo-generated charge carriers to those which uncounted at the electrode. The value is largely affected by the charge carrier recombination during charge transport processes.

\[
FF = \frac{J_{\text{max}} V_{\text{max}}}{J_{\text{sc}} V_{\text{oc}}} = \frac{P_{\text{max}}}{J_{\text{sc}} V_{\text{oc}}}
\]

Figure 1.5 An example of \( J-V \) curve of DSSC device

1.3 Aggregation Induced Emission (AIE) Effects

1.3.1 Background of AIE

Aggregation induced emission (AIE) is an opposite phenomenon of aggregation-caused quenching (ACQ). ACQ relates to a quantitative increase of non-radiative excited state decay among aggregated molecules.\textsuperscript{[27]} This kind of
Weakened photoluminescence (PL) was discovered by Förster and Kasper in 1950s. They observed that the PL intensity of pyrene went down while its concentration increased.\textsuperscript{[28]} Not long afterwards, it was well recognized that this property was also shared among many other aromatic materials.\textsuperscript{[29, 30]} And the existence of non-radiative pathway was realized as a major reason responsible for this concentration-quenching effect, which was caused by a collisional induced formation of sandwich-shaped excimers and exciplexes.\textsuperscript{[29]} In 1970, Birks summarized this phenomenon inside his book \textit{Photophysics of Aromatic Molecules}.\textsuperscript{[28]} in other words, the planar aromatic rings of the neighbouring fluorophores experience strong $\pi-\pi$ stacking interactions.

For many years great efforts have been made to develop more efficient luminescent materials.\textsuperscript{[31]} However, the efficiency of most organic materials which work in optical devices has been restricted due to ACQ effect in solid state.\textsuperscript{[32]} To alleviate this shortage, chemical, physical as well as engineering approaches have all been explored.\textsuperscript{[32]} For instance, attaching bulky rings, spiro kinks and dendritic chains, encapsulation of surfactant or doping into non-conjugated transparent polymers such as poly(methyl methacrylate) (PMMA) are common processes to prevent aggregate formation.\textsuperscript{[33]}

However, in most of the cases, aggregation was only partially or temporarily dismissed,\textsuperscript{[33, 34]} since it is a natural process and exists spontaneously for molecules in a condensed phase. Therefore, aggregation-induced emission (AIE)
has drawn great attraction for scientists in further development of new luminescent materials\textsuperscript{[35]} since the first report by Tang’s group in 2001.\textsuperscript{[36]}

AIE describes the exhibition of more efficient emission in aggregated phase than that in solution.\textsuperscript{[31e, 35b]} In other words, AIE active materials conquer the major part of ACQ shortages. Instead of trying to prevent aggregation formation, one can take advantages of it. Apart from developing high-efficiency light-emitting materials, it may also be applied in bio-imaging process and switchable lighting materials.\textsuperscript{[35]}

In 2009, Tang’s group further defined the phenomenon “emissions of some luminescent molecules are enhanced by aggregation” as an aggregation-induced emission enhancement (AIEE) effect.\textsuperscript{[35]}

In the past decade, great effort has been made to design, synthesize as well as theoretically study luminescent AIE materials.\textsuperscript{[32]} Apart from Tang’s group, Park and other groups also reported AIE active molecules based on cyanostilbene derivatives.\textsuperscript{[37]}

1.3.2 Principle of AIE

One widely accepted AIE mechanism is that the non-radiative decay in solution, which mostly contributed by energy consuming intramolecular rotations, can be blocked in aggregation states because of the restriction of movements.\textsuperscript{[38]}
This process can be further assisted by supramolecular packing like J-aggregation,\textsuperscript{39} dimer stacking,\textsuperscript{35b} herringbone stacking,\textsuperscript{40} and even weakly coupled H-aggregation,\textsuperscript{41} resulting in strong luminescence in solid state. Moreover, there exists a special kind of AIE active compounds and draws significant attention, which are intramolecular charge transfer (ICT) materials.\textsuperscript{37,42} For ICT luminophors, several mechanisms are possible including restricted twisted ICT\textsuperscript{42c} and intermolecular charge-transfer,\textsuperscript{43} formation of dimer\textsuperscript{44} or a combination of these.

\textit{Restriction of intramolecular rotation (RIR)}

![Restriction of Intramolecular Rotation (RIR)](image)

Figure 1.6: Structural presentation of AIE processed for pyrene and HPS\textsuperscript{35}
Hexaphenylsilole (HPS) was used as an example to demonstrate AIE mechanism in the reviews of Tang’s group.\cite{35} Structural characterization indicates that comparing to common luminophores such as the disc-like planar perylene, HPS is a propeller shaped non-planar molecule (Chart 1) instead. According to the well accepted concept that the emission behavior corresponds to the molecular structure, in a dilute solution, six phenyl rings in an HPS molecule dynamically rotate against their silacyclopentadiene or silole center, which is a non-radiative annihilation that consumes the released energy from excited states. As a result, the compounds are non-luminescent in solution. In solid state, due to the propeller-shaped construction, HPS molecules do not suffer from $\pi-\pi$ stacking process and the intramolecular rotations are mostly restricted. Since RIR process blocks the non-radiative pathway, energy can radiate through photons, i.e. HPS molecules become emissive in the aggregate state.\cite{35}

HPS is one of the first silole derivatives that helped to discover the AIE phenomenon. For a typical AIE luminogen, the intramolecular rotations exist in solutions, which consume energy of excitons and serve as a relaxation pathway to non-radiative decay. In solid state, the intramolecular rotations are restricted, which save excitons from the non-radiative channel and contributes to the emissive pathway.\cite{35}
Planarity and rotatability

It is found that the emission performance of a molecule can be tuned through modulating its conformational stability.\cite{45}

Tang’s group demonstrates the relationship among geometrical planarity and intramolecular motion with luminescence behaviour by a graphic model below.\cite{35} Assuming that a luminescent molecule is constructed by units A and B, which are linked by a rotatable bond. As shown in Figure 1.7, $\psi$, $\theta$, and $\omega$ represent “the dihedral angle between units A and B, the extent of intramolecular rotation/torsion, and the vibrational frequency”, respectively (Figure 1.7). It means that $\psi$ indicates the planarity of the luminophore, while $\theta$ and $\omega$ describes its rigidity.\cite{35}

If $\psi \approx 0$, as shown in the left panel of Figure 1.7, A and B are parallel to each other, the model molecule A-B achieves a maximal conjugation together with a minimal potential energy. Their electrons can delocalize through the C–C linkage and render it some double-bond character, which strengthens the molecular conformation and improves the resistance against intramolecular rotations. Therefore A and B may still vibrate in small amplitudes ($\theta$) but the low-frequency motions are too weak to quench the PL process. Thus, it is the high-frequency ($\omega$) vibration that dominates the molecular motions and results in a deeper potential energy surface. Because of the high molecular rigidity, the luminophore has small possibilities to reorganize, which enables energy saving and gives high fluorescence quantum yields in solutions.\cite{35}
On the other hand, if the steric interactions make A and B twist more perpendicularly to each other, as shown in the right panel of Figure 1.7, i.e. $\psi' > 0$, the electrons are restricted to overlap between units A’ and B’, leading to much weaker overall $\pi$-conjugation. Therefore the single bond linkage between A’ and B’ has more freedom to undergo intramolecular rotations. In other words, only much lower energy is required. Thus it is the low-frequency ($\omega'$) vibrations that dominate the molecular motions and result in a shallower potential energy surface. Because of the small energy barrier of conformational change, the rotations between A’ and B’ could be larger, i.e. the $\theta'$ values can be varied among $0^\circ$–$90^\circ$ theoretically. As a result much more energy is consumed by twisting motions, leading to small photoluminescence quantum yields in solutions.\cite{35}

According to the presented model above, photoluminescence properties in solutions has much relationship with molecular rigidity and can be predicted from vibrations, i.e. $\psi$ (or planarity) and $\theta$ (or rotatability).\cite{35}

According to the presented model above, photoluminescence properties in solutions has much relationship with molecular rigidity and can be predicted from vibrations, i.e. $\psi$ (or planarity) and $\theta$ (or rotatability).\cite{35}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.7.png}
\caption{Relationship among geometrical planarity and intramolecular motion with luminescence behaviour}
\end{figure}
**Intramolecular Restriction**

As shown in Figure 1.7, it suggests that a covalent linkage can strengthen the molecular conformation and enhance its emission intensity in solutions by limiting intramolecular rotation.\textsuperscript{[35]} At the same time, molecular conformation can be influenced by interactions among different molecules as well. For instance, PL intensity can be increased by elevating viscosity and pressure or decreasing temperature, which restrains the molecular vibrations externally.\textsuperscript{[35,45]}

Meanwhile, there are also other intramolecular interactions that may work together with AIE behavior and demonstrate interesting results.\textsuperscript{[35]}

**Twisted Intramolecular Charge Transfer (TICT)**

A donor-acceptor (D-A) fluorophore usually demonstrates the phenomenon that the emission color is red shifted and the intensity is dropped while the solvents polarity is increased\textsuperscript{[46]}.

![Diagram of intramolecular rotation](image)

In a nonpolar solvent system  
In a polar solvent system

**Figure 1.8: Intramolecular rotation**
In a nonpolar system, the excited D-A fluorophore is in equilibrium with the surrounding solvent molecules. Thus a planar molecular conformation is much more preferred since it is stabilized by the enlarged conjugation length and stronger electron delocalization. As a result sharp luminescence can be observed in this solution. On the other hands in a polar system, the D-A charge separation is greatly actuated since the fluorophore interacts with the surrounding polar molecules until the twisted D-A molecules get equilibrium with and stabilized by the surrounding solvent system. As a result the exited molecule is further transferred to a TICT state by intramolecular rotation. The twisting angles are different among all the D-A molecules which directly affect their emission properties and as a result a broad emission band can be observed. In contrast to planar conformation, a twisted D-A molecule destabilizes the HOMO level and results in a narrow band gap, and thus a red-shift can also be observed. However, the TICT state usually suffers from nonradiative quenching process, which may sufficiently weaken the emission intensity.\textsuperscript{[42c]}

By attaching an AIE active unit to a TICT parent, the emission properties can be finely tuned. For example in a THF/H\textsubscript{2}O matrix, as water fractions start going up, the solvent polarity will increase and the transformation of the TICT state will lead to dramatically weakened emission intensity and bathochromically shifted emission color. However, when the molecules start to aggregates, the PL intensity climbed up with increasing water concentration mostly due to the RIR process
discussed above. Meanwhile, the PL peak was gradually red-shifted because of the TICT character.\cite{42a}

**Intermolecular charge transfer**

For a D-A material, an intermolecular charge transfer state\cite{46} can also be formed as the molecules undergo aggregation. It is mostly originated from overlapping of the donor moiety of one molecule and the acceptor moiety of its adjacent molecules. This process further facilitates the aggregation and enlarge the particle size.\cite{47} Similar to the TICT mechanism above, intermolecular charge transfer contributes to charge separation and results in larger molecular dipole moment, which further strengthens the intermolecular overlap and stabilizes itself as well. Therefore both red-shifted absorption and emission can be observed.\cite{48}

For instance, J-aggregation is one typical molecular packing mode which may cause AIE effect.\cite{35a}

J-aggregation corresponding to head-to-tail alignment of the D-A molecules with large red-shifted and enhanced emission after monomers undergoes aggregation.\cite{43} Materials after J-aggregation usually show bathochromically shifted absorption band,\cite{49} indicating that charge transfers in exited state of the molecules are significantly altered after aggregation. Further studies proved that excited states of J-aggregates are located at coherently coupled adjacent
monomers’ transition dipoles.\textsuperscript{[39]}

In a THF/water matrix, at higher water ratio, the intermolecular charge transfer state of the aggregates mainly shows a broad emission band.\textsuperscript{[50]} However, one important reason for an emission enhancement after J-aggregation is the planar conformations of the molecules.\textsuperscript{[31c]} It is possible that some compounds may still remain in twisted structure in the ICT state after aggregation, resulting in slightly different luminescence wavelength and relatively lower intensity.\textsuperscript{[37]}

1.3.3 Development of AIE

Ever since discovered by Tang's group for silole molecules in 2001,\textsuperscript{[36]} AIE materials have drawn great attention both in theoretical study and practical applications.\textsuperscript{[35]}

Tang's group identified one basic mechanism to explain this phenomenon - restriction of intramolecular rotation (RIR)\textsuperscript{[35]}. Based on that, a large variety of AIE luminogens, which contain conjugated stators together with aromatic rotors, were developed and demonstrated in the application as chemosensors, bioprobes and solid-state emitters\textsuperscript{[51]}. Moreover, some newly synthesized AIE active simple organic molecules can form phosphorescent crystals at room temperature, which broke the common principle that under ambient conditions phosphorescence of pure organic materials can be hardly observed.\textsuperscript{[52]}
Rapid growth of AIE exploration provides a large number of products, which can be further divided into hydrocarbon, heterocyclic, supramolecular, polymeric and organometallic materials based on their structural features. For hydrocarbon AIE materials, 8,8-dihydrocyclopenta[a]indene derivatives with remarkable AIE effects were reported by Wu et al., and together with many other related studies, it showed that AIE property is determined by the propeller shape rather than the conformation of its olefin unit of hydrocarbon luminophores. In addition, because of lack of planarity, the cis isomers are found to be deviated from π-π stacking in the crystallization process and easily result in highly-emissive aggregates by Ma et al. Moreover, the introduction of large aromatic rings instead of phenyl rings in the terminals is reported to be useful as well, since the steric effect induced conformational twists can help prevent ACQ in the corresponding luminogen solution.

As for heteroatom-containing materials, their AIE properties are largely related to the intramolecular charge transfer (ICT) interaction which can significantly alter the photophysical properties of D-A type luminogens. Along this line of consideration, many kinds of molecules were developed. Since nitrogen has both lone pair electrons and a empty p-orbital, nitrogen-containing compounds can be tuned from electron-donating to electron-withdrawing property by adjusting molecular structure. Among which, triphenylamine (TPA) and carbazole units are often applied as donor part of a D-A molecule, whose color
can be finely tuned by attaching different acceptor.[56] In addition, the planar conformation of carbazole units as well as the parallel conformation of TPA units also helps the restriction in the solid state which can further enhance the luminescence.[57] On the other hand, aromatic nitrogen-containing groups such as pyridine unit often play an important role as acceptor in a D-A molecule as well. An AIE system based on pyridinium salts was published by Tao' group.[58] Besides nitrogen, sulphur- or phosphor-containing materials have also drawn great attention.[59] Among these, benzobis(thiadiazole) (BTA) is famous for its strong electron-withdrawing property.[59] Wang et al. have synthesized an AIE active molecule containing both BTA and TPA units which produce a strong ICT effect and shift the PL peak to the near-IR region.[59] Meanwhile, a large quantity of AIE luminogens containing cyano groups have been developed,[60] because of their high dipole moment and rigidity induced by the C-H…N≡C hydrogen bonds formed between two adjacent molecules.[61]

Hydrogen bonding is regarded as another important non-covalent bond which can improve the molecular rigidity and herein strengthen RIR processes, i.e. increase the AIE phenomenon.[62] The excited-state intramolecular proton transfer (ESIPT) is one important process for this kind of AIE materials.[35] Many examples have been published to demonstrate the formation of intramolecular hydrogen bonds during excitation in the solid or crystalline state, which blocks the non-radiative path way and turns on luminescence.[35] Apart from solids, many
gels formed by intermolecular hydrogen bonding also show interesting AIE properties. Park et al.\(^{[63]}\) and Bo et al.\(^{[64]}\) reported gelation-induced emission in 2003 and 2007, respectively.

Many series of conjugated polymers with enhanced emission intensity have been developed as well, apart from H-bonding or ICT interactions mentioned above, the polymeric molecules mostly overcome the mechanical weakness and processing disadvantage, which can be readily fabricated into large area thin film through simple processes, for instance, spin-coating or static-casting method.\(^{[65]}\)

For organometallic materials, phosphorescence is usually counted for aggregation-induced emissions and the much more complicated molecular conformation leads to more difficulties in systematic studies. Many research papers were published, for instance, Li et al.\(^{[66]}\) and Park et al.\(^{[67]}\) reported AIEE phosphorescent Ir(III) complexes, Che et al.\(^{[68]}\) reported that a Pt(II) complex and Lu et al.\(^{[69]}\) published the Re(I) complex systems. Recently, Su et al.\(^{[32]}\) found a group of AIE active Ir(III) complexes while studying piezochromic luminescence.

Much effort on the application of AIE luminophores has been devoted to utilities in optoelectronic and sensory fields.\(^{[35]}\) Together with high efficiency OLEDs, a large number of AIE active chemical and biological probes have been successfully investigated.\(^{[70]}\) In addition, the AIE effect seems highly suitable for protein fibrillogenesis study as well, since both of them are associated with aggregate formation.\(^{[71]}\)
1.3.4 Basic Parameters of AIE Study

As AIE is a relatively new concept, there are hardly any literature or systematic rule like those for OLED or DSSC to qualify this kind of behavior. One commonly used measurement is to detect the PL intensity of one compound in a series of water-organic mixture with different ratio but maintaining same concentration. The organic solvent should be highly water-miscible, in this thesis, THF is chosen because it mixes well with water and provides good solubility for most of the products.

During the above measurements, one supplementary calculation and plot can also be applied to demonstrate the intensifying PL intensity along with increasing water fractions. By comparing each intensity (I) over the initial one (I₀) measured in pure THF solution, the plot of I/I₀ can be generated and presents how far the luminescence has changed.

Other PL data such as solid photoluminescence, low-temperature photoluminescence or even crystal photoluminescence may also be detected and their variations in PL intensity and wavelength from those collected in other solvent system or aggregation states could help to have a better understanding on the AIE nature.

In addition, the typical method to determine the involvement of twisted intra-ligand charge transfer is to perform a series of UV and/or PL measurements
for the same compound in solvents with various polarity. For TICT based AIE molecules, the change of intensity and/or wavelength can partially reflect the origin of AIE behavior as well.

Moreover, for molecules with more complicated structure, like organometallic compounds, all of the above measurements may still not be enough to draw a clear conclusion for their AIE nature. Thus, many further supplementary theoretical investigations were used by scientists as well to predict the detail motivations, such as DFT calculation and single-crystal x-ray diffraction, to predict the possible transition mechanism and intermolecular interaction.

1.4 Time Resolved Infrared Analysis

Time resolved infrared spectroscopy (TRIR) is a type of transient absorption (TA) spectroscopy. As demonstrated in Figure 1.9,[72] the fundamental laser beam is generated from a mode-locked titanium sapphire oscillator combined with a regenerative amplifier.[73] This laser is split into two parts first, one pump through either a sum frequency generation (SFG) or UV/vis optical parametric amplifier (OPA) to generate the pump beam in which tunable pump pulses throughout the visible region are produced; the other beam goes through a difference frequency generation (DFG) OPA to generate the IR beam and in which mid-IR pulses (2 to 10 μm) are provided. After that Ge beam splitter further split the latter beam into a
probe and a reference beam. Both of them pass through the sample cell respectively but the pump beam only overlaps with the probe beam. Finally, both of the laser signals are analyzed by a spectrometer Triax 320 followed by detail Hg/Cd/Te array (32 elements) detectors, respectively. The pump beam passes through a chopper operating at 500 Hz, allowing the measurements of the IR absorption signals at both pump on and off conditions. And the overall signal can be calculated after comparing the probe with the reference beam results. The sample during detection is stored under N₂ atmosphere in a Plexiglas box and with a steady N₂ flow, which eliminate the influence of carbon dioxide or water vapor on the results.

TRIR spectroscopy provides signals corresponding to electron transitions at the excited state. As the dipole moment changes during excitation and relaxation, the measured IR spectrum changes in both peak position and intensity. Moreover, TRIR can provide a way to focus on one particular vibrational modes within an excited state instead of recording complicated signals without specificity. Therefore, TRIR is a common measurement to identify excited state electron delocalization especially for molecules bearing triple bonds.\textsuperscript{[74]} Because of that, it has been applied to study the excited states conformations of both organic\textsuperscript{[75]} and organometallic complexes\textsuperscript{[76]} as well as reaction intermediates\textsuperscript{[77]}. 
Similar to IR absorption spectrum, bands in TRIR spectroscopy can reflect the electron density distribution at the excited state.\cite{78} Therefore, electron transfer during excitation can cause a dramatic shift in the band comparing to that measured for the ground state of the same molecule. As mentioned above, IR bands are functionally specified, so that precise regions of the detecting molecules can be generated and analyzed.\cite{79} For a long period of time, TRIR spectroscopy has widely been used for the study of organometallic complexes containing C≡O or C≡N ligands.\cite{106} The triple bonds have large oscillator strengths and frequencies when appropriate solvent windows are chosen.\cite{78} Recently, moderately intense carbonyl (C=O) groups in ester substituted ligands of
ruthenium bipyridine complexes have also been exploited and the MLCT characters of excited stated have been closely tracked. However, in iridium complexes, the excited state locations are adjustable by varying the ligands, and TRIR can help to reveal the location of excited states as well as charge transfer properties. Also, the IR stretches of acetylene in Pt(II) complexes have also been detected and signals are provided corresponding to the ligand localized and charge transfer excited states.

1.5 Molecular Design

Cyclometalated Ir(III) and Pt(II) compounds are famous d⁶ and d⁸ complexes. They have strong spin-orbital coupling characters and can easily achieve high phosphorescence efficiency together with relatively long lifetime since MLCT process releases the spin-forbidden phosphorescence and opens the radiative relaxation channel of the triplet state. Also the emission colors of these kinds of materials can be finely tuned by simply varying the ligand field.

Based on the above properties, Ir(III) complexes have been widely used in the application of organic light-emitting diodes (OLEDs), luminescence sensors, and biological labeling reagents.

The relatively long-lived triplet excited state makes Ir(III) complexes promising DSSC candidates as well since it leads to efficient photo-induced
charge separation for solar energy conversion.\textsuperscript{[83]} However, the Ir(III) based complexes always suffer from low absorptivity and narrow absorption band in the visible region.\textsuperscript{[83]} Recently, a series of cationic heteroleptic complexes, [Ir(C^N)\textsubscript{2}(N^N)]\textsuperscript{+} (C^N = substituted phenylpyridine or benzothiazole ligands, N^N = 2,2'-bipyridine-4,4'-dicarboxylate) have been reported as attractive materials for photosensitizer applications which can efficiently absorb visible light and maintains highly energetic charge-separated excited states.\textsuperscript{[1]} This provides a direction to further explore the solar application of Ir(III) complexes.

Oligomeric or polymeric Pt(II) acetylide compounds containing tertiary phosphine ligands have strong absorptivity, good transparency, tunable luminescence properties, and acceptable electrical conductivities. They have been widely used in optical applications such as bulk heterojunction (BHJ) solar cells, DSSCs and optical power limiting (OPL).

Although there are a bunch of remarkable properties and decades of developments of Ir(III) and Pt(II) luminophores, in the majority of the cases they still suffer from ACQ processes and as a result their device results can be substantially limited by intrinsic excited-state self-quenching and triplet–triplet annihilation.

Compounds containing fluorenyl or carbazolyl units demonstrate interesting chemical and physical behaviors since their biphenyl moiety show rigid planar property.\textsuperscript{[17]} The planar configuration allow electrons delocalized through and
therefore much enlarge the conjugation length, which may improve the orbital mixing and increase the luminescence efficiency. And it makes them suitable candidates for emissive materials development. For instance, the PL quantum yield of ter(9,9-diarylfluorene)s in ethyl acetate reaches as high as 80%.\textsuperscript{[27]}

However, also because of the planar conformation of fluorenyl or carbazolyl units, organic materials containing them usually suffer from several problems. One of them is ACQ process during aggregation, π-π stacking or formation of excitmers may happen, the excitation energy may lose through non-radiation pathway or relax through lower energy excitmer traps, leading to lower efficiency device fabrication or red-shifted EL wavelength.\textsuperscript{[28]}

Therefore, reduction or elimination of the ACQ effects is a possible way to improve OLED device performance. To date, apart from increasing the disorder of conjugation and decreasing the close chain molecules packing by the involvement of bulky substituent, introduction of AIE property is regarded as a alternative solution.

Tetraphenylethylene (TPE) has been largely investigated, not only because it is a typical AIE material but also a powerful building block which can manipulate other molecules to become AIE active. The common mechanism is the blocking of non-radiative channel by RIR process and parallel molecular conformation of TPE unit.
1.6 Motivation and Aim of the Thesis

Cyclometalated Ir(III) and Pt(II) complexes can achieve excellent PL efficiencies with tunable emission color and good physical/chemical stabilities, and attract intensive research interest for new materials development in many different fields. However, there is still large room not only in the improvement of the existing materials' performance but also in exploring their new practical utility. Herein, to make full usage of the strong spin-orbital coupling characters of these heavy metal complexes, we design and synthesize a series of anchor-containing zwitterionic Ir(III) complexes, which containing substitutable C\(^{\equiv}\)N ligands and 2,2'-bipyridine-4,4'-dicarboxylate ligand, and thus they maintain the photophysical adjustability while become suitable candidates for DSSC fabrication. And their device results have also been investigated. Meanwhile, to further improve the OLED performance in deep red region, we synthesize and characterize a series of 2-substituted N-benzylcarbazolyl pyridine based Ir(III) complexes. Moreover, to catch up with and explore the updated advanced properties, TPE units are introduced to a group of Pt(II) acetylide and Ir(III) cyclometalated complexes to explore and verify the influence and chemical nature of AIE behaviors. Furthermore, two cyclometalated Pt(II) complexes with substantial ILCT characters at the excited state are studied and their AIE properties were characterized and discussed in this thesis as well. In addition, to fully understand the excited stated nature, a valuable TRIR technique was used to
characterize the strong and identical C≡C IR absorption bands in Pt(II) acetylide complexes.
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Chapter 2

Synthesis and Characterization of Charged Cyclometalated Iridium(III) Complexes Containing Carboxyl Group Substituted Bipyridine Ligands

2.1 Introduction

For Ir(III) complexes, efficient intersystem crossing between singlet and triplet excited states due to strong spin–orbit coupling, contributes to long-lived emitting states and high luminescence efficiencies.\textsuperscript{[1]} Because of these remarkable photoluminescence properties, Ir(III) complexes have drawn great attention\textsuperscript{[2]} and shown valuable application in organic light-emitting diodes (OLEDs),\textsuperscript{[3]} unimolecular oxygen sensors\textsuperscript{[4]}, biological labeling reagents,\textsuperscript{[5]} and photocatalysts for hydrogen production.\textsuperscript{[6]}

Through decades, it was well established that the emission color of Ir(III) phosphors can be tuned from red to blue by varying ligand groups.\textsuperscript{[7]} At the same time, harvesting and conversion of solar energy attracts much attention as well since it is a relatively environmental friendly way to meet the growing energy demand.\textsuperscript{[8]} Among which, dye-sensitized solar cells (DSSCs) received considerable attention because of various advantages such as easy fabrication
process, high performance efficiency and low material cost. Apart from the well studied ruthenium based series, the exploration of suitable DSSC candidates also extends to cationic heteroleptic iridium complexes, since they have potential advantages such as highly tunable electro-optical properties that arise from metal to ligand charge transfer (MLCT) states and good photo-induced charge separation caused by long-lived triplet excited states.  

Campagna et al. and Grätzel et al. studied the possibilities of anchoring metal complexes containing this kind of ligands to a semiconductor surface in dye-sensitized solar cells (DSSCs). Mayo et al. presented Ir(III) dyes with PF₆⁻ counter ions which can be used as sensitizers in DSSCs. They possess quantum yields approaching unity for conversion of absorbed photons to current, indicating current production resulting from ligand to ligand charge-transfer (LLCT) states rather than typical metal to ligand charge-transfer (MLCT) states as in ruthenium-based cells. Ning et al. synthesized novel Ir(III) complexes with carboxyl pyridyl ligand and improved the power conversion efficiency of DSSC to 2.86%. Baranoff et al. modified one of the pyridyl rings to naphthyl and phenanthrene, and reported new cyclometallated Ir(III) complexes as sensitizers for DSSCs, which also reached efficiency as high as 2.5%. Yuan et al. reported a series of bis-cyclometalated Ir(III) complexes containing benzothiazole moiety and the highest efficiency they got is 1.39%.  

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On the other hand, charged Ir(III) complexes can also be applicable in the biochemical field. Jiang et al.\textsuperscript{[18]} showed special interest on zwitterionic Ir(III) complexes, especially on the amphiphilicity of hydrophilic carboxyl groups substituted on the dipyridyl ligand, which leads to differences in lipophilicity, the encapsulation, and release of these complexes, making amphiphilicity the key point in the molecular designing for cell imaging: the hydrophilic part and lipophilic part are needed for the solubility in aqueous solution and the cell permeation, respectively. The compounds were investigated as luminescent dyes for both living and fixed KB cells imaging in aqueous solution. In 2011, Li et al.\textsuperscript{[19]} reported an ultrasensitive biosensor employing a novel electrochemiluminescent (ECL) labeling reagent cyclometalated Ir complex containing carboxyl groups substituted bipyridine ligands, which were applied in cancer cell detection successfully.

Therefore, charged Ir(III) complexes containing carboxyl groups substituted bipyridine ligands are chosen to be synthesized and investigated. All the ligands are characterized by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy. The complexes were only investigated by \textsuperscript{1}H NMR, infrared spectroscopy and mass spectrometry because of poor solubility. The photochemical properties of these ligands and complexes were investigated by both UV/Vis absorption and photoluminescence spectroscopy at different temperatures. Some of the complexes were applied for fabrication of DSSC devices.
2.2 Synthesis of Ligands

Scheme 2.1 delivers a synthetic route of ligand L₁. First 2-bromo-9,9-diethylfluorene was prepared by reacting 2-bromofluorene and bromoethane under a strongly alkaline condition, and subsequent Stille coupling with 2-tributylstannyl pyridine to afford L₁.

Scheme 2.1: Synthetic route of ligand L₁

Scheme 2.2 shows the synthetic route of ligands L₂ and L₃. 2-Bromo-9,9-diethylfluorene was prepared as described above and was further converted to 9,9-diethyl-fluorene-2-boronic acid after reacting with n-butyllithium and trimethyl borate. L₂ and L₃ were synthesized by Suzuki cross coupling of the
boronic acid and 2-chloropicoline or 2-chloro-5-trifluoromethylpyridine, respectively.

Scheme 2.2: Synthetic routes of ligands $L_2$ and $L_3$

Scheme 2.3 depicts the synthesis of $L_4$ by Suzuki cross coupling between 9,9-diethyl-fluorene-2-boronic acid and 1-chloroisquinoline.
Scheme 2.3: Synthetic route of ligand \( \text{L}_4 \)

Scheme 2.4 shows the synthetic route of \( \text{L}_5 \). Suzuki coupling of 2-bromo-9,9-diethylfluorene and thiophene-2-boronic acid gave 9,9-diethyl-2-thienyl-fluorene first. After bromination with NBS, 9,9-diethyl-2-thienyl-fluorene can further react with 2-tributylstannylpyridine by Stille coupling to produce \( \text{L}_5 \).

Scheme 2.4: Synthetic route of ligand \( \text{L}_5 \)
Triphenylamine was synthesized by Ullmann condensation of diphenylamine and 4-iodotoluene using 1,10-phenanthroline and copper(I) iodide as catalyst. 4-Bromotriphenylamine was obtained from bromination of triphenylamine by NBS, the brominated product was converted to cyclometalating ligand $L_6$ by Stille coupling with 2-(tributylstannyl)pyridine.

Scheme 2.5: Synthetic route of ligand $L_6$

Scheme 2.6 shows the synthetic route for cyclometalating ligand $L_6$. 1,4-Dibromobenzene was reacted with BuLi at -78 °C followed by addition of dimesitylborane fluoride to generate $(p$-bromophenyl)dimesitylborane, which further reacted with 2-tributylstannyl pyridine by Stille coupling to give $L_6$. 

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Scheme 2.6: Synthetic route of ligand L_7

Scheme 2.7 shows the synthetic route of cyclemetalated ligand L_8. 4-(Diphenylamino)benzaldehyde was synthesized from 4-bromotriphenylamine first, and then the product reacted with 2-aminothiophenol to afford L_8 after refluxing in water overnight.
Scheme 2.7: Synthetic route of ligand \textit{L}_8

2.3 Synthesis of Charged Iridium(III) Complexes

Schemes 2.8-2.10 summarize the synthetic strategies of heteroleptic Ir(III) complexes. The synthetic routes involve several steps. \(\text{IrCl}_3 \cdot n\text{H}_2\text{O}\) was reacted with an excess of the corresponding cyclometalating ligands first, to generate a chloride-bridged iridium dimer after heating at 80-90°C under \(\text{N}_2\) for overnight. Then 4,4'-dimethyl-2,2'-bipyridine was oxidized by potassium permanganate under an acidic condition to form 4,4'-dicarboxyl-2,2'-bipyridine, followed by transforming the carboxylic acid groups to methyl esters after adding drops of concentrated sulfuric acid as catalyst in dry methanol. When the ester and Ir dimer were both well prepared, they were refluxed together in a 1:1 methanol /
dichloromethane (v/v) solution, and followed by addition of potassium hexafluorophosphate. The roughly purified heteroleptic charged Ir complex containing methyl ester groups on the bipyridyl ligand was further adjusted from alkaline to acidic, which allow the hygrolysis of the methyl ester to carboxylic acids and finally complexes 1 to 7 were generated.

Scheme 2.8: Synthetic route of Ir dimer
Scheme 2.9: Synthetic routes of charged Ir complexes 1 to 7
Complexes 8 and 9 were synthesized through a slightly different way. After the Ir dimers were generated, they reacted separately with 4,4'-dicarboxylic-2,2'-bipyridine under an alkaline condition in a mixture of dichloromethane and methanol, followed by adjusting the pH to around 5 with 0.5 M hydrochloric acid.

Scheme 2.10: Synthetic routes of charged Ir complexes 8 and 9

2.4 NMR Spectroscopic Characterization of Ligands and Ir(III) Complexes

$^1$H and $^{13}$C NMR spectroscopy was used to characterize the ligands. For most
of the Ir(III) complexes, only $^1$H NMR spectroscopy was performed since the Ir complexes have limited solubility in the deuterated solvents for $^{13}$C NMR measurements. The purity of the products were confirmed by comparing their proton NMR results with those of their corresponding ligands. Figure 2.1 shows the $^1$H NMR spectrum of ligand L7. The integration of aromatic proton is nineteen, with a very downfield shifted multiplet at 8.63 ppm assignable to the ortho-H on the pyridyl ring. For the $^1$H NMR spectrum of complex 7, the most downfield shifted signal is at 8.76 ppm and it was assigned to ortho-H on the bipyridyl ring, by using it as a standard for integration ($\delta = 8.76$, 2H), the number of aromatic protons of 7 can be counted as forty, which well matches with the theoretical number. Apart from those, as shown in Figure 2.3, strong singlets at 2.27, 1.74 ($\delta$ ppm) with the respective integration of twelve and twenty four are assigned to the methyl protons of the dimesityl groups, which also matches the structure of the complex. The presence of only one singlet for four or six methyl groups is contributed by the symmetry of the cyclometalated ligand. As a result, complex 7 can be confirmed as the desired product.
Figure 2.1: $^1$H NMR spectrum of L$_7$ in CDCl$_3$

Figure 2.2: $^1$H NMR spectrum of 7 in CDCl$_3$
Figure 2.3: $^1$H NMR spectrum of 6 in CDCl$_3$

Figure 2.4: $^1$H NMR spectrum of 1 in CDCl$_3$
Figure 2.5: $^1$H NMR spectrum of 2 in CDCl$_3$.

Figure 2.6: $^1$H NMR spectrum of 3 in CDCl$_3$.
Figure 2.7: $^1$H NMR spectrum of 4 in CDCl$_3$

Figure 2.8: $^1$H NMR spectrum of 5 in CDCl$_3$
Figure 2.9: $^1$H NMR spectrum of 7 in CDCl$_3$

Figure 2.10: $^1$H NMR spectrum of 8 in CDCl$_3$
2.5 Photophysical Properties of Ligands and Iridium(III) Complexes

The photophysical properties of all the ligands and the Ir(III) complexes were investigated by UV/vis absorption and PL emission spectroscopy in dilute dichloromethane solution. Relevant data are collected in Tables 2.1 and 2.2. The results demonstrate that the photophysical properties of these Ir(III) complexes are finely tuned by the modification of their ligands which are attached to the metal core. By comparison to those of their ligands, the absorption spectra of the metal complexes clearly can be divided into two regions, one appearing as intense bands mostly located in the ultraviolet region below 380 nm, which are originated from the ligand-based spin-allowed singlet $\pi-\pi^*$ transitions. For instance, as
demonstrated in Figure 2.12, strong absorption peaks around 320 nm can be found in the absorption spectra of both ligand L₂ and complex 2, and they shall be ligand-based transitions. The other region is a group of much weaker bands which are apart from these \( ^1(\pi-\pi^*) \) transition and extending into the visible region above 400 nm\(^{[7b]} \) They are \(^3\)MLCT band which benefit from spin mixing and heavy-atom effect of the metal centre\(^{[7b]} \) and suggest that a substantial mixing of ligand-based \(^3\pi-\pi^* \) states is accomplished.

![Normalized UV spectra of L₂ and 2 in CHCl₂ at 293 K](image)

**Figure 2.12:** Normalized UV spectra of L₂ and 2 in CHCl₂ at 293 K

In other words, intense bands could be observed in both spectra around 300 nm, which is due to spin-allowed intra-ligand-charge-transfer, and the weaker absorption band near 420 nm in complex 2 is due to the metal-to-ligand charge-transfer, in which intersystem crossing and spin-orbit coupling occurred, leading to red-shifted but much less intense absorption.
However, for complexes 6, 8 and 9, their UV spectra displayed in Figure 2.13 show totally different structures. Instead of a small shoulder band as in Figure 2.12, their latter absorption bands extended to the visible region exhibit remarkably high intensity, together with their weak PL emission, the theoretical study for this kind of compounds says that it is $^3$ILCT rather that $^3$MLCT that occurs during excitation and relaxation.$^{[17]}$ Since most of the electrons in the highest occupied molecular orbital (HOMO) are located on the conjugation around the nitrogen atoms while most of the electrons in the lowest unoccupied molecular orbital (LUMO) are located on the N^N ancillary ligand. In other words, electrons are transferred from the $\pi$ orbital of amino-centered C^N ligand to the $\pi^*$ orbital of the bipyridyl ligand, which provides possibilities to give organometallic complexes not only to have large absorptivity but also cover a wide range to the most useful solar spectrum.

![Normalized UV spectra of complexes 6, 8 and 9 in CH$_2$Cl$_2$ at 293 K](image)

Figure 2.13: Normalized UV spectra of complexes 6, 8 and 9 in CH$_2$Cl$_2$ at 293 K
Moreover, from Table 2.1 it can also be observed that by replacing the methyl group of $L_2$ to an electron-withdrawing group (EWG) CF$_3$ ($L_3$), a remarkable red shift of about 22 nm (from 358 nm to 380 nm) appeared. Although the published literature$^{[20]}$ reported that increasing the number of electron-withdrawing -COOH on the bipyridinyl ligand would result in a bathochromic shift of the emission maximum, according to the “energy gap law”$^{[21]}$ (see Figure 2.14), complex 3 with a strong electron-withdrawing CF$_3$ moiety exhibited a hypochromic shift of 54 nm (from 551 nm to 605 nm) as compared to complex 2, which showed an opposite trend for their ligands. This phenomenon can be explained by the published calculation.$^{[22]}$ For this kind of compounds, the HOMO is located on both the iridium(III) center and the phenyl groups of C$^\equiv$N ligands, while the LUMO maintains primarily on the N$^\equiv$N ligands. As a result when introducing strong electron-withdrawing groups (e.g. -COOH) on the bipyridine ligand, it would mostly affect the LUMO of the N$^\equiv$N ligand, which becomes a better acceptor. The stabilized LUMO would lead to a smaller energy gap and therefore a bathochromic shift was observed. Meanwhile when introducing an electron-withdrawing CF$_3$ group to the C$^\equiv$N ligands, it mostly affects to the HOMO of the compound, resulting in a wider band gap and a hypochromic shift was resulted.
Figure 2.14: Normalized PL spectra of complexes 2 and 3 in CH$_2$Cl$_2$ at 293 K

From Figure 2.2, it can be easily observed that the emission color of the materials can be tuned from orange red to deep red (from 551 to 666 nm) by simply changing their C$^\equiv$N ligands. As demonstrated in Figure 2.15, among complexes 2 and 5, the PL wavelength has a great bathochromic shift when installing a thiophene unit into the fluorene group. This may be explained by the fact that thiophene has strong electron donor properties and mostly contributes to the HOMO level. As mentioned above, theoretically the electrons in the HOMO are located on the Ir(III) center and the phenyl groups of C$^\equiv$N ligands, by enhancing the electron density, the HOMO is much more destabilized and the band gap between HOMO and LUMO becomes smaller, thus causing the emission wavelength of 5 to have a large red-shift. However, for complex 6, which contains
an electron-donating triphenylamine group, its photoluminescence achieves hypochromic shift. This may be attributed by the fact that the nitrogen atom in the triphenylamine moiety is not directly bonded to Ir atom, as a result the electron donating property is partly locked by the discontinued conjugation. Meanwhile, the conjugation length of triphenylamine is much shorter than that of fluorene group, as a result the emission wavelength of 6 is blue-shifted. This finding indicates that the energy gap between HOMO and LUMO energy level can be mostly affected by the properties of substituents on the conjugated rings directly coordinated to the metal atom.

Figure 2.15: Normalized PL spectra of complexes 2, 5 and 7 in CH₂Cl₂ at 293 K

According to the literature report,[22] because of the presence of an “empty” π orbital with strong π-accepting character, substantial electron density would be
drawn to the B(Mes)$_2$ moiety in the MLCT state while the MLCT processes in other complexes are more polarized towards the pyridyl moiety.\cite{23} Similar to the CF$_3$ group, B(Mes)$_2$ moiety will tend to destabilize the MLCT states strongly, in agreement with the more blue-shifted MLCT absorption bands.

However, due to the relative red color of this kind of complexes, the lifetime of these complexes are too short to be detected.

The PL quantum yields ($\Phi_P$) were measured in CH$_2$Cl$_2$ using $fac$-[Ir(ppy)$_3$] as standard reference ($\Phi_P = 0.40$, $\lambda_{ex} = 400$ nm, room temperature). The $\Phi_P$ of these emitters ranged from 0.14% to 62.9%. It is remarkable that complexes containing strong EWG exhibit significantly high quantum yields (3, 53.2%; 7, 69.2%) by introducing good electron-trapping abilities and EI/ET properties to these complexes.
Table 2.1: Photophysical data of ligands $L_1$ to $L_8$

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV absorption at 298 K$^{[a]}$</th>
<th>Emission at 298 K$^{[b]}$</th>
<th>Fluorescence quantum yields$^{[c]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{abs}}$ (nm)</td>
<td>$\lambda_{\text{em}}$ (nm)</td>
<td>$\Phi_F$ (%)</td>
</tr>
<tr>
<td>$L_1$</td>
<td>305 (4.2), 319 (4.3)</td>
<td>360</td>
<td>42.3</td>
</tr>
<tr>
<td>$L_2$</td>
<td>229 (1.0), 320 (1.5)</td>
<td>358</td>
<td>49.7</td>
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<tr>
<td>$L_3^{[24]}$</td>
<td>228 (1.2), 325 (3.5)</td>
<td>380</td>
<td>55.1</td>
</tr>
<tr>
<td>$L_4$</td>
<td>230 (2.0), 331 (2.3)</td>
<td>392</td>
<td>31.2</td>
</tr>
<tr>
<td>$L_5$</td>
<td>269 (0.6), 363 (3.0)</td>
<td>429</td>
<td>0.38</td>
</tr>
<tr>
<td>$L_6^{[25]}$</td>
<td>269 (0.6), 307 (1.7), 317 (1.7), 347 (2.5)</td>
<td>434</td>
<td>16.0</td>
</tr>
<tr>
<td>$L_7^{[26]}$</td>
<td>326 (2.6)</td>
<td>409</td>
<td>51.0</td>
</tr>
<tr>
<td>$L_8^{[27]}$</td>
<td>294 (3.0), 373 (4.1)</td>
<td>460</td>
<td>80.5</td>
</tr>
</tbody>
</table>

$^{[a]}$ Numbers in parentheses were extinction coefficients ($10^4$ M$^{-1}$ cm$^{-1}$), measured in CH$_2$Cl$_2$.

$^{[b]}$ Samples were excited at 290 nm in CH$_2$Cl$_2$.

$^{[c]}$ Fluorescence quantum yields ($\Phi_F$) were measured in CH$_2$Cl$_2$ using anthracene ($\Phi_F = 0.27$, $\lambda_{\text{ex}} = 290$ nm) as reference.
Table 2.2: Photophysical data of complexes 1 to 9

<table>
<thead>
<tr>
<th>Complex</th>
<th>UV absorption at 298 K&lt;sup&gt;[a]&lt;/sup&gt;</th>
<th>Emission at 298 K&lt;sup&gt;[b][c]&lt;/sup&gt;</th>
<th>Emission at 77 K&lt;sup&gt;[d]&lt;/sup&gt;</th>
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<td>2</td>
<td>296 (3.2), 324 (3.7), 422</td>
<td>605</td>
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<td>324 (2.0), 352 (2.1), 458</td>
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<td>4</td>
<td>302 (3.2), 375 (2.3), 459</td>
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<td>330 (0.8), 379 (0.8), 438 (0.5)</td>
<td>666, 724 (sh)</td>
<td>0.14, 716 (sh), 732 (sh)</td>
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<td>6</td>
<td>263 (5.0), 307 (4.2), 388 (3.6)</td>
<td>604</td>
<td>1.54</td>
</tr>
<tr>
<td>7</td>
<td>259 (4.4), 327 (3.7), 438 (0.2)</td>
<td>558</td>
<td>69.2</td>
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<tr>
<td>8</td>
<td>272 (5.5), 443 (5.9)</td>
<td>609</td>
<td>-</td>
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<tr>
<td>9</td>
<td>257 (4.9), 309 (4.0), 389 (3.5), 422 (3.1)</td>
<td>606</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>[a]</sup> Numbers in parentheses were extinction coefficients (10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) measured in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>[b]</sup> Samples were excited by 400 nm in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>[c]</sup> Phosphorescence quantum yields (Φ<sub>P</sub>) were measured in CH<sub>2</sub>Cl<sub>2</sub> using fac-[Ir(ppy)<sub>3</sub>] (Φ<sub>P</sub> = 0.40, λ<sub>ex</sub> = 400 nm) as reference.

<sup>[d]</sup> Excited by 350 nm in CH<sub>2</sub>Cl<sub>2</sub>, sh means shoulder peak.
2.6 Electrochemical Properties

The electrochemical properties of the heteroleptic iridium(III) ions were determined by cyclic voltammetry (CV). The measurements were taken in an acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate and a glassy carbon as the working electrode. Thin films of these complexes were produced by solution evaporation on the working electrode. There are two other electrodes involved as well, one is Ag/Ag⁺ reference electrode and the other is Pt-wire counter electrode. The CV procedures were performed under an N₂ atmosphere and the scan rate is 50 mV/s. The experimental and calculated results are presented in Table 2.3 including onset oxidation (E_{ox}) potentials, onset reduction (E_{red}) potentials, calculated highest occupied molecular orbital (HOMO) energy levels, and that of lowest unoccupied molecular orbital (LUMO).

It has been well accepted that for most of the Ir(III) complexes, the energy gap can be finely tuned by varying and adjusting the ligand properties, and the HOMO and LUMO levels of Ir(C^N)₃ or Ir(C^N)₂(acac) complexes are mainly located on the iridium metal centered d orbitals and part of the ligand π-orbitals. However, according to the literature data, for this kind of heteroleptic Ir(III) complexes mentioned in this chapter, the LUMO is usually located on the strong electron-withdrawing N^N ligand while the HOMO level still depends on the chemical nature of the C^N ligands. In this case,
theoretically, by attaching electron-withdrawing groups, either substituted on the pyridyl ring or the phenyl part of the C^N ligand, the HOMO should both be beneficially stabilized, and the energy gap will increase. In addition, it is believed that for most of the Ir(III) complexes, the oxidation process involves a Ir(III)/Ir(IV) transformation.\textsuperscript{[29]} In other words, during oxidation, one electron is removed from the metal center. By taking this into consideration, the introduction of EWGs will obviously make a lower HOMO energy level since they lead to much lowered electron density around the metal center. In contrast, similarly to those complexes mentioned in the literature,\textsuperscript{[17, 18]} the LUMO is mainly located on the N^N ligand and the reduction process involves addition of one electron of the LUMO, which may also be slightly influenced by the electron density of the metal center.

The experimental CV plots for complexes 1-9 are displayed in Figure 2.16-2.20, their results are summarized in Table 2.3, in which the HOMO energy levels ranged from \(-5.62\) to \(-5.24\) eV, while those of LUMOs ranged from \(-3.00\) to \(-2.88\) eV, and the energy gaps are from 2.28 to 2.75 eV.

For complexes 1-3, their HOMO and LUMO energy values are \((-5.44, -2.93)\), \((-5.45, -2.97)\) and \((-5.62, -3.00)\) eV respectively. It is obvious that the HOMO of complex 3 achieves the largest value which is almost 0.2 eV bigger than those of complexes 1 and 2. This well matched the prediction above that by adding EWG
group (i.e. CF$_3$) to the pyridyl ring, the HOMO should be substantially stabilized. Similarly, complex 7 containing a strongly electron-withdrawing dimesitylboron moiety has a stabilized HOMO as low as -5.63 eV, and correspondingly the energy gaps for both 3 and 7 have been enlarged. Complex 4 has a bigger conjugation length introduced by isoquinoline moiety at C^N ligand, therefore its HOMO is stabilized. Complex 5 has a strongly electron-donating thienyl ring involved in the C^N ligands and has a HOMO level as high as -5.29 eV. Notably for complexes 6, 8 and 9, all of their HOMO levels are also elevated to -5.24, -5.27 and -5.25 eV respectively, and it can be simply explained by the appearance of the electron-donating triphenylamine moieties in the C^N ligands as well, which greatly increase the electron density of the HOMOs and leads to a lower ionization potential. Therefore, the HOMOs of complexes 6, 8 and 9 are much destabilized to a higher energy level.

All of the LUMO energy levels of the complexes in this chapter are around -2.90 eV, which are relatively low and only have slight variances due to the attachment of especially strong electron-withdrawing N^N ancillary ligands. The LUMO level of complex 9 is a little bit higher than that of complex 6, since the only difference between them is the number of protons that are attached to the carboxylate groups. It may be explained by the fact that the addition of a proton to N^N ligand can make the LUMO more electron deficient to attract electron easier from the HOMO.
Figure 2.16: Cyclic voltammograms of complexes 1 and 2

Figure 2.17: Cyclic voltammograms of complexes 3 and 4

Figure 2.18: Cyclic voltammograms of complexes 5 and 6
Figure 2.19: Cyclic voltammograms of complexes 7 and 8

Figure 2.20: Cyclic voltammogram of complex 9
Table 2.3: Electrochemical properties of complexes 1 to 9

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox}}$ [V][a]</th>
<th>$E_{\text{red}}$ [V][a]</th>
<th>HOMO [eV][b]</th>
<th>LUMO [eV][c]</th>
<th>$E_g$ [eV][d]</th>
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<tbody>
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<td>-2.90</td>
<td>2.35</td>
</tr>
</tbody>
</table>

[a] 0.1 M [Bu$_4$N]PF$_6$ in THF, versus Fe/Fe$^+$ couple.

[b] HOMO = -(4.73 eV + $E_{\text{ox}}$) eV

[c] LUMO = -(4.73 eV + $E_{\text{red}}$) eV

[d] $E_g$ = LUMO – HOMO

2.7 DSSC Characterization

Based on the photophysical and electrochemical properties, complexes 6, 8 and 9, were chosen for DSSC fabrication and the performance data of the corresponding devices I, II and III are summarized in Table 2.4. Their IPCE curves, photocurrent-voltage ($J$-$V$) curves, IEIS Nyquist plots and the open-circuit voltage decay curves are shown in Figures 2.21-2.24, respectively.

The anode films consist of two layers, one is a transparent layer which is 12
μm thick and contains TiO$_2$ nanoparticle with 20 nm in diameter, the other is a scattering layer of 6 μm in thickness and contains TiO$_2$ nanoparticle with 200 nm in diameter. Those films were prepared through a doctor-blade technique, and a careful cleaning process was operated by soaking the transparent conducting glass (SnO$_2$:F, FTO glass, 15 Ω$^{-1}$) in ethanol, acetone and deionized water respectively and sonicated thoroughly for 20 min during each step. Then, the first layer was coated with a layer of 6 μm TiO$_2$ paste with 20 nm in diameter which was doctor-bladed onto the well cleaned FTO glass and allowed to relax for 3 min at room temperature, followed by heating for 6 min at 150 °C. The above procedure was repeated and the other half of 20 nm TiO$_2$ nanoparticles were bladed before the transparent layer was finally achieved with a desired film thickness of 12 μm. After that, the layer of 200 nm TiO$_2$ nanoparticles was applied on the surface of the first layer and the scattering layer was achieved when coating finished.

The electrodes consist of a three-dimensional TiO$_2$ nanoparticle-network which were generated by a series of heating process with air flow as follows: 275 °C for 5 min, 325 °C for 5 min, 375 °C for 5 min, and 480 °C for 30 min. After that, the resulting films were put into a 0.02 M TiF$_4$ aqueous solution and stayed at 70 °C for 45 min before being cleaned with deionized water. Then a further annealing process was performed at 450 °C for 30 min followed by a gradual cooling process. When the temperature was about 80 °C, the electrodes were soaked into a dye bath with 0.5 mM in concentration of an
acetonitrile/tert-butyl alcohol (volume ratio, 1:1) mixture in dark condition. After
18 h, the electrodes were taken out and rinsed by ethanol and acetonitrile. The
purified electrodes were dried in the air. The other kind of electrodes are platinum
counter electrodes. They were treated with sputtering method, staying at 15 mA
for 90 s with a power of 150 W.

The FTO glass was also pretreated. Two holes (0.75 mm in diameter) were
prepared for introducing the electrolyte. A sandwich-structured cell was
assembled with the dye-adsorbed TiO₂ and Pt-counter electrodes prepared above
and a parafilm was hot-melted and sealed at about 100 °C. The liquid electrolyte
is a mixture of acetonitrile/4-tert-butylpyridine (volume ratio, 1:1) containing 0.6
M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M lithium iodide, and
0.05 M iodine, which was added into the device cell through the prepared holes.
The cell fabrication was finished by sealing the holes and avoiding electrolyte
leakage.

The average effective area of all the TiO₂ electrodes was around 0.126 cm².
A semiconductor characterization system (Keithley 236) was used to measure the
current-voltage (J-V) characteristics of DSSC devices I, II and III under ambient
conditions, i.e. room temperature and air atmosphere, and the light power was set
at 100 mW/ cm² and supplied by a solar simulator (Newport) using an AM 1.5G
filter. The dc mode of Solar Cell QE/IPCE Measurement System (Zolix Solar Cell
Scan 100) was used to record the IPCEs of DSSCs. The DSSC electrochemical properties were characterized by CHI 660D and electrochemical impedance spectroscopy (EIS) was measured under dark conditions and the frequency ranged over 0.1−105 Hz together with an 10 mV ac amplitude. Z-View software (v2.1b, Scribner Associates, Inc.) was used to calculate the parameters. The cell was illuminated for 20 second under a steady voltage, followed by 80 second without illumination to obtain the open-circuit voltage decay curve.

Device II achieved the highest efficiency of 1.50%, followed by device III at 0.75% and device I at 0.40%. Compared with the other DSSC devices, these results are relatively poor and this may be caused by the narrow absorption band coverage at the visual region. However, when comparing with Ir(III) based DSSC devices, these results are still reasonable.[17] Although most of the Ir(III) complexes have strong MLCT character, there exists an important problem in that it is very difficult to further red shift their absorption to the visual zone. As mentioned above, the phenylamine-containing ligands make this kind of heteroleptic complexes to achieve excellent ILCT properties and largely improve their UV absorptivity. And as for complex 8, the benzothiazole moiety contributes a lot to the conjugation length and further improves the stability of the complex relative to those phenylpyridine-based complexes 6 and 9.[29] The better absorption properties greatly increase the $J_{sc}$ value of device II, which is almost twice as large as that of device III and third times as large as that of device I.
Complex 6 has one more terminal carboxyl unit than complex 9, theoretically it should have better performance since more anchoring groups lead to tighter dye adsorption towards ITO glass. However, the results below are completely in contrast to the hypothesis. This may be caused by repulsion between positive charged metal core and ITO surface.

Table 2.4 Detailed photovoltaic data of DSSCs I, II and III based on 6, 8 and 9

<table>
<thead>
<tr>
<th>Devices</th>
<th>Samples</th>
<th>PCE (%)</th>
<th>( V_{OC} ) (V)</th>
<th>( J_{SC} ) (mA/cm(^2))</th>
<th>Fill Factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6</td>
<td>0.40</td>
<td>0.564</td>
<td>1.13</td>
<td>62.9</td>
</tr>
<tr>
<td>II</td>
<td>8</td>
<td>1.50</td>
<td>0.644</td>
<td>3.29</td>
<td>70.9</td>
</tr>
<tr>
<td>III</td>
<td>9</td>
<td>0.75</td>
<td>0.606</td>
<td>1.77</td>
<td>69.5</td>
</tr>
</tbody>
</table>

Figure 2.21: Incident photon-to-current efficiency (IPCE) curves of DSSCs based on complexes 6, 8 and 9

Figure 2.22: Photocurrent–voltage (J–V) plots of devices based on complexes 6, 8 and 9
2.8 Concluding Remarks

In this chapter, a group of Ir(C^N)_2(N^N) (C^N: substituted phenylpyridine or phenylbenzothiazole ligands, N^N: -COOH substituted bipyridyl ligands) complexes were synthesized and well studied. Their photophysical and electrochemical properties were determined by UV/vis, PL and CV characterization, and complexes 6, 8 and 9 were further applied in DSSC fabrication. From the results, it can be summarized that all of the complexes in this chapter exhibit significant bathochromic shifts in both UV absorption (232 to 443 nm) and PL emission (551 to 666 nm) spectra, mostly caused by the introduction of strong electron-withdrawing N^N ligand. Their HOMO energy levels ranged from -5.62 to -5.24 eV, LUMOs from -3.00 to -2.88 eV, and the energy gaps from 2.28 to 2.75 eV. The energy gap can be adjusted by varying the
ligand field properties, i.e. the introduction of EWG to the C\N ligand will decrease the HOMO level to give a larger gap, and vice versa. Complexes 6, 8 and 9 have intense absorption bands in the visible region with quite low PL intensity and are suitable candidates for DSSC application with EQE 0.40%, 1.50% and 0.75%, respectively.
References:


Chapter 3

Synthesis, Photoluminescence and Electroluminescence Properties of Iridium(III) Phosphorescent Emitters Containing 2-substituted Carbazolyl Moiety

3.1 Introduction

Many efforts have been made in the field of organic light-emitting diodes (OLEDs) in the past decades; these are motivated by their potential applications in display technology and lighting applications.\(^1\) For instance, OLED materials are considered to be used in new flexible monitors for portable electronic equipments, which may replace the traditional liquid-crystal displays (LCDs). The best OLEDs may contain sophisticated multilayer structures, low-work-function cathodes but should achieve high efficiencies and low operating voltages. However, the traditional fabrication technique, vacuum sublimation, is a way suffering from the difficulty of molecular design and waste of materials, since all the materials need to be sublimatable and compatible with the hydrophobic matrices used.\(^2\)

Recently, much attention has been drawn on the development of electrophosphorescent OLEDs with the usage of organometallic complexes as dopants.\(^3, 13\) Among those, Ir(III) complexes containing cyclometalated C^N ligands (C^N) are attracting extensive attention.\(^13\) These Ir(III) complexes
usually have large spin-orbit coupling constants and can overcome the spin-forbidden rule by the formation of triplet metal-to ligand charge transfer (³MLCT) states. Therefore, highly efficient electroluminescence (EL) can be achieved since the phosphorescence may also be encountered.¹³ Moreover, as shown in the literature report,⁴, ⁵ the excited state behavior of iridium(III) complexes can be simply modified by adjusting the ligand properties, generating a phosphor with specific photophysical and electrochemical behaviors.¹³ These may be achieved by changing the degree of conjugation,⁶ symmetry or electronegativity of the ligands.⁷, ¹³ Among which, the ligand electron affinities always have a significant influence on the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).⁷c

Pyridinyl moiety are commonly used as the N part of the C^N ligand, and many Ir(III) complexes containing substituted 2-phenylpyridinyl ligands have been reported. It has been found that the emission color and efficiency can be finely tuned by adjusting the position and property of the ligand substituents.³d, ⁴a, d, ⁸–₁₀, ¹³.

Carbazole derivatives have been widely used as dopants or host materials in OLED fabrication, since they have good hole injection/hole transport (HI/HT) properties.¹² Meanwhile, carbazolyl bearing Ir(III) complexes have also been studied as emission layer (EML) dopants, since the carbazolyl moiety in the C
part of the ligands can elevate the HOMO level.[11, 13] Wong et al. reported a series of carboxyl-containing Ir(III) complexes, which display remarkable OLED performance.[5, 13] Among which, the 2-substituted-carboxyl derivatives exhibit further bathochromic shift than those substituted at 3 position,[13] and provides possible strategy for the development of deep red OLEDs.

In this chapter, [2-(N-arylcarboxyl)]pyridinyl ligand are examined in the ligands of the Ir(III)-based phosphors. Substituents with different electron affinity were attached at pyridinyl ring positions, the photophysical and electrochemical properties of the corresponding metal complexes were characterized and OLED fabrications were performed as well.

3.2 Synthesis of Ligands

Scheme 3.1 describes the synthetic route for L₉ and L₁₀. Phenylboronic acid was reacted with 2,5-dibromonitrobenzene under an alkaline condition using Pd(PPh₃)₄ as catalyst, to generate 4-bromo-2-nitrobiphenyl. After reduction with triethyl phosphite, 2-bromocarbazole was obtained after ring closing. 2-Bromo-N-tolylcarbazole was obtained by the Ullmann condensation of the 2-bromocarbazole with 4-iodotoluene in the presence of CuI, KOH and 1,10-phenanthroline in p-xylene. After that, 2-bromo-N-tolylcarbazole was converted to 9-tolylcarbazole-2-boronic acid before it further underwent Suzuki
coupling with 2-chloropicoline or 2-trifluoromethylpyridine to generate \( \mathbf{L}_9 \) and \( \mathbf{L}_{10} \), respectively.

Scheme 3.1: Synthetic routes of ligands \( \mathbf{L}_9 \) and \( \mathbf{L}_{10} \)

Scheme 3.2 shows the synthetic route of \( \mathbf{L}_{11} \), which is directly generated by Stille coupling of 2-bromo-N-tolylcarbazole and 2-(tributylstannyl)pyridine using \( \text{Pd(PPH}_3\text{)}_4 \) as catalyst in toluene.
Scheme 3.2: Synthetic route of ligand L₁₁

Scheme 3.3 depicts the synthetic route of L₁₂, which is directly synthesized from Suzuki coupling of N-tolylcarbazole-2-boronic acid and 2-chloroisouquinoline under alkaline condition with the help of Pd(PPh₃)₄.

Scheme 3.3: Synthetic route of ligand L₁₂

Scheme 3.4 shows the synthetic route of L₁₃, which is quite similar to L₁₂. 2-Bromocarbazole was reacted with iodobenzene to generate 2-bromo-N-phenylcarbazole. Then it was converted to N-phenylcarbazole-2-boronic acid before it further underwent Suzuki coupling.
with 2-chloroisouquinoline under alkaline condition by using Pd(PPh$_3$)$_4$ as catalyst.

![Scheme 3.4: Synthetic route of ligand L$_{13}$]

As described in Scheme 3.5, the synthetic route for L$_{14}$ is similar to that of L$_{13}$. Tolylboronic acid and 2,5-dibromonitrobenzene underwent Suzuki coupling reaction to generate 4-bromo-2-nitrotolylphenyl first. Then the nitrophenyl was reduced by triethyl phosphite at 90 °C to form 2-bromo-7-methylcarbazole. After that, 2-bromo-N-phenylcarbazole was made by the Ullmann condensation, followed by conversion to its corresponding boronic acid for further reaction with tributyltinpyridine by Stille coupling to generate L$_{14}$. 

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3.3 Synthesize of Heteroleptic Iridium(III) Complexes

Scheme 3.6 shows the synthetic route of the heteroleptic Ir(III) complexes.\textsuperscript{[20]}

First IrCl$_3$$\cdot$nH$_2$O reacted with an excess of the corresponding carbazolyl based ligands at 80-90\(^\circ\)C overnight to generate a chloride-bridged iridium dimer. Then acetylacetone (Hacac) was added in and the Ir(III) complexes were generated after the mixture was heated at 100 \(^\circ\)C overnight with the presence of sodium carbonate.
Scheme 3.6: Synthetic routes of complexes 10-15
3.4 NMR Characterization of Ligands and Iridium(III) Complexes

$^1$H and $^{13}$C NMR spectroscopy was performed to characterize the products. As demonstrated in Figures 3.1-3.3, several spectroscopic techniques are commonly used together to determine the structure of a particular compound. Figure 3.1 shows $^1$H NMR spectrum of $L_{10}$. The number of integrated aromatic protons is fifteen, among which the ortho proton on the pyridyl ring can be found in very downfield as a multiplet at around 8.91 ($\delta$ ppm), and the methyl group substituted on the para position of phenyl ring appears as a strong singlet at 2.50 (3H, $\delta$ ppm). The observed spectral features agree with the structure of $L_{10}$. As for its corresponding complex 11, the most downfield signal should also arise from the ortho proton on the pyridyl ring, thus its integration can be standardized ($\delta =$ 8.91, 2H), and the proton number of each peak can be calculated. As shown in Figure 3.2, the aromatic and aliphatic protons are found to be twenty-four and twelve, respectively. Apart from those, $^{13}$C NMR spectrum was also applied to ascertain the total number of chemically inequivalent carbon atoms. In Figure 3.3, there are a total of twenty-six $\delta$C signals, which corresponds to twenty-one carbon signals and together with those of the coupling with fluorine atoms. This number is smaller because carbon atoms sharing symmetry have the same $^{13}$C NMR value since the tolyl ring at 9-position of carbazole group enjoys a rotational symmetry. In summary, complex 11 is the desired compound. Similar methods were used to confirm the structure of the remaining complexes.
Figure 3.1: $^1$H NMR spectrum of L$_{10}$ in CDCl$_3$

Figure 3.2: $^1$H NMR spectrum of 11 in CDCl$_3$
Figure 3.3: $^{13}$C NMR spectrum of 11 in CDCl$_3$

Figure 3.4: $^1$H NMR spectrum of 10 in CDCl$_3$
Figure 3.5: $^{13}$C NMR spectrum of 10 in CDCl$_3$

Figure 3.6: $^1$H NMR spectrum of 12 in CDCl$_3$
Figure 3.7: $^{13}$C NMR spectrum of 12 in CDCl$_3$

Figure 3.8: $^1$H NMR spectrum of 13 in CDCl$_3$
Figure 3.9: $^{13}$C NMR spectrum of 13 in CDCl$_3$

Figure 3.10: $^1$H NMR spectrum of 14 in CDCl$_3$
Figure 3.11: $^1$H NMR spectrum of 14 in CDCl$_3$

Figure 3.12: $^1$H NMR spectrum of 15 in CDCl$_3$
3.5 Photophysical Properties of Ligands and Iridium(III) Complexes

Before device fabrication, all of the synthesized compounds were applied for UV/vis and PL characterization to determine their photophysical properties. All measurements for ligands were taken in CH$_2$Cl$_2$ at 293 K and the results are summarized in Table 3.1. The data demonstrate that both absorption and emission wavelengths of these ligands have obvious bathochromic shifts compared to those of [3-(N-phenylcarbazolyl)]pyridine ligands in the literature.$^{[5,13]}$ Meanwhile, by replacing the methyl unit in $\mathbf{L}_9$ to an electron withdrawing group (EWG) CF$_3$ in $\mathbf{L}_{10}$, a remarkable bathochromic shift of about 32 nm (from 399 nm to 431 nm)
appears. According to the literature data, it is because that CF$_3$ group enlarges the electron affinity of LUMO which is located at the pyridyl ring.$^{[5, 13]}$ However, there is no significant difference in the emission peaks between L$_{12}$ and L$_{13}$, indicating that the addition of methyl group either on the phenyl ring at 9 position or on the pyridyl ring on the 2 position has little effect on the energy gap of the compounds. From the PL data, it can also be summarized that most of the ligands except L$_{12}$ and L$_{13}$ emit in the blue region under ultraviolet irradiation in dichloromethane solutions at room temperature.

![Normalized PL spectra of ligands L$_9$ and L$_{10}$ in CH$_2$Cl$_2$ at 293 K](image)

Figure 3.14: Normalized PL spectra of ligands L$_9$ and L$_{10}$ in CH$_2$Cl$_2$ at 293 K

The data collected in Table 3.2 shows the absorption and photoluminescence data of complexes 1 to 5. The absorption spectra of these complexes can be obviously divided into two regions. By comparison to the absorption spectra of
their corresponding ligands, the first region contains intense bands below 370 nm can be assigned as the ligand-based spin-allowed singlet \(^1(\pi-\pi^*)\) transitions. For instance, the first set of spectral bands of complex 11 are located at \(\lambda_{\text{max}}\) of 286, 316 and 548 nm while those of its corresponding ligand L\(_{10}\) are at around 300 nm, confirming that they are ligand-based transitions. Apart from these \(^1(\pi-\pi^*)\) transitions, there are also another region of weaker bands at above 500 nm, extending into the visible region. According to the literature report, they are arise from to the spin forbidden triplet metal-to-ligand charge transfer (\(^3\)MLCT) states, which are formed because of the heavy-atom effect induced by the metal core.\(^{[2]}\)

The existence of the second region absorption suggests that there are substantial metal-ligand orbital mixing to release the spin forbidden triplet transitions.

Highly-intense phosphorescence was observed for all the Ir(III) complexes 10-15 in CH\(_2\)Cl\(_2\), from the lowest-energy \(^3\)MLCT transition.

All of the Ir(III) complexes except 13 and 14 were excited by light at 400 nm, and 13 and 14 were excited at 450 nm. Strong photoluminescence was observed for all of them, and the emission color was varied according to each ligand attached.
Figure 3.15: Normalized UV and PL spectra of complex 11 and L_{10} in CH_{2}Cl_{2} at 293 K

Figure 3.16 shows UV/vis and PL spectra of complexes 10, 11, 12 and 14. When comparing the emission wavelength of 10 (\lambda_{em} = 593 nm) to that of 11 (\lambda_{em} = 638 nm), a significant bathochromic shift (30 nm) appears and it is simply achieved by changing the substituent from methyl (CH_{3}) to trifluoromethyl (CF_{3}) on the pyridyl ring. Since the LUMO of this kind of complexes are mainly located at the pyridyl region,^{13} the bathochromic shift can be explained by the fact that the LUMO becomes more electron deficient to a higher energy level when a weak electron donor (CH_{3}) is attached, and as a result the energy gap is slightly increased;^{15} however, the LUMO becomes more electron affinity when bulky EWG (CF_{3}) is attached, therefore the LUMO of complex 11 is more electron-withdrawing to a lower energy level, and the energy gap becomes much
smaller. These results also well meet the fact that the energy gap between HOMO and LUMO can be mostly affected by adjusting the properties of the substituent on the conjugated rings which directly chelated with the metal core.\textsuperscript{13}

From Table 3.2, when comparing 11 to 13, after replacing the substituent from pyridyl to isoquinoline, which attaches to 2-position of the carbazole core, a substantially large red shift (103 nm) can be observed. This is attributed by the enlarged π-conjugation system introduced by isoquinoline moiety.

However, as shown in Table 3.2, when comparing 13 to 14, it can be found that the PL wavelength is almost independent of the 9-position substituent of the phenyl ring (13: $\lambda_{\text{em}} = 695$ nm; 14: $\lambda_{\text{em}} = 691$ nm). It is because the substitution on that position is hardly involved in the conjugation length, in other words, the electron delocalization is blocked by the nitrogen atom of carbazolyl ring. This is another evidence that the energy gap is mainly affected by the modification of the properties of substituent which directly chelated to the iridium atom and much involved the conjugation.\textsuperscript{13}
Figure 3.16: Normalized PL spectra of complexes 10, 11, 12 and 14 in CHCl$_2$ at 293 K

Moreover, broad and featureless phosphorescence structure can be observed from $^3$MLCT state, while vibronic progression appears in those from the ligand-centered $^3\pi-\pi^*$ excited states.

In general, the emission wavelength of all these complexes displayed significant bathochromic shift as compared to those containing 3-substituted carbazole as ligands, and the reasons are different from those discussed above in which the emission wavelength can be tuned by varying the electronic properties of the substituent on the cyclometalated ligands.$^{[16]}$ It is because the carbon atoms at 2-/7- and 3-/6-positions of carbazole molecules have different electronic density. The 3-/6-position is activated by the nitrogen atom and becomes more
electron-rich than those of the 2-/7-site, thus the energy gap of carbazole-containing complexes can also be tuned by changing the location of substituent, either at 3-/6- or 2-/7-position. While chelating with metal ion, the more electron rich 3-substituted ligand pushes up the energy level of metal d orbital, raising a higher energy HOMO than that of a 2-substituted complex. As a result, remarkable bathochromic shift in wavelength for complexes 10 to 15 can be observed.\textsuperscript{[17]}

![Normalized PL spectra of complex 10 in CH₂Cl₂ at 298 K and 77 K](image_url)

**Figure 3.17: Normalized PL spectra of complex 10 in CH₂Cl₂ at 298 K and 77 K**

All the complexes are intensely luminescent in the glass matrices at 77 K and undergo notable rigidochromic blue shifts. These phenomena are mainly induced
by the solvent reorganization in a rigid-fluid solution formed at 77 K which stabilize the charge-transfer states prior to emission.\textsuperscript{[18]} Hence, phosphorescence at 77 K occurs at higher energy. Due to the same reason, the vibration of PL structure appears more clearly. As shown in Figure 3.17, the emission wavelength of complex 10 at 77 K has a blue shift of 12 nm than that at 298 K, and the shape of spectrum at 77 K is obviously more structured.

The quantum yields ($\Phi_P$) of complexes 10, 11, 12 and 15 were measured in dilute CH$_2$Cl$_2$ solutions at 293 K, by using $fac$-[Ir(ppy)$_3$] as standard ($\Phi_P = 0.40$), and those of complexes 13 and 14 were measured in the same condition but by using rhodamine B as standard ($\Phi_P = 0.50$). The $\Phi$ values lie between 4.3 $\%$ and 5.5$\%$ for complexes 10, 11, 12 and 15, which are within the normal range of orange-red phosphors while those of complexes 13 and 14 are only 0.45 and 0.60 respectively, since they are deep red emitters. In this work, the room-temperature lifetimes are too short to be detected. As reported,\textsuperscript{[19]} the phosphorescence lifetime is one of the key factors that causes triplet–triplet annihilation, especially for Ir complexes in the OLED operation. Such short lifetimes of all six complexes can increase spin-state mixing and reduce the chance of device efficiency decay.
Table 3.1: Photophysical data of ligands L₉ to L₁₄

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV absorption at 298 K</th>
<th>Emission at 298 K</th>
<th>Fluorescence quantum yields</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λₘₐₓ (nm)[a]</td>
<td>λₑₘ (nm)[b]</td>
<td>Φₔ (%)[c]</td>
</tr>
<tr>
<td>L₉</td>
<td>230 (2.5), 258 (0.7), 323 (0.4)</td>
<td>399</td>
<td>49.9</td>
</tr>
<tr>
<td>L₁₀</td>
<td>228 (1.5), 230 (2.0), 317 (1.2)</td>
<td>431</td>
<td>25.6</td>
</tr>
<tr>
<td>L₁₁</td>
<td>243 (1.9), 293 (2.0), 330 (1.4)</td>
<td>384</td>
<td>48.8</td>
</tr>
<tr>
<td>L₁₂</td>
<td>229 (2.2), 301 (0.7), 329 (0.6)</td>
<td>448</td>
<td>2.8</td>
</tr>
<tr>
<td>L₁₃</td>
<td>230 (3.4), 302 (1.3), 330 (1.2)</td>
<td>450</td>
<td>2.5</td>
</tr>
<tr>
<td>L₁₄</td>
<td>256 (2.3), 319 (1.7)</td>
<td>401</td>
<td>50.0</td>
</tr>
</tbody>
</table>

[a] Numbers in parentheses are extinction coefficients \((10^4 \text{ M}^{-1} \text{ cm}^{-1})\) measured in CH₂Cl₂.

[b] Excited at 290 nm in CH₂Cl₂.

[c] Fluorescence quantum yields \((Φ_F)\) were measured using anthracene (Φₐ = 0.27, λₑₓ = 290 nm), quinine sulfate (Φₐ = 0.48, λₑₓ = 313 nm; Φₐ = 0.56; Φₐ = 0.55, λₑₓ = 350 nm) as references.
Table 3.2: Photophysical data of the complexes 10 to 15

<table>
<thead>
<tr>
<th>Complex</th>
<th>UV absorption at 298 K</th>
<th>Emission at 298 K[^b][^c]</th>
<th>Emission at 77 K[^e]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ (nm)^[a]</td>
<td>λ (nm)</td>
<td>Φₚ (%)</td>
</tr>
<tr>
<td>10</td>
<td>287 (5.4), 341 (4.8), 501 (0.3)</td>
<td>582</td>
<td>4.6</td>
</tr>
<tr>
<td>11</td>
<td>286 (5.0), 316 (4.7), 548 (0.2)</td>
<td>638</td>
<td>4.3</td>
</tr>
<tr>
<td>12</td>
<td>288 (5.9), 342 (4.6), 511 (0.4)</td>
<td>592</td>
<td>5.5</td>
</tr>
<tr>
<td>13</td>
<td>231(12.5), 295 (7.1), 375 (5.5), 579 (0.4)</td>
<td>695</td>
<td>0.45</td>
</tr>
<tr>
<td>14</td>
<td>232 (13.7), 295 (8.0), 374 (6.4), 535 (0.6)</td>
<td>691</td>
<td>0.60</td>
</tr>
<tr>
<td>15</td>
<td>287 (5.5), 343 (4.8), 513 (0.4)</td>
<td>595</td>
<td>4.9</td>
</tr>
</tbody>
</table>

[^a]: Numbers in parentheses are extinction coefficients (10⁴ M⁻¹ cm⁻¹) measured in CH₂Cl₂.

[^b]: Excited at 400 nm in CH₂Cl₂.

[^c]: Phosphorescence quantum yields (Φₚ) were measured by using fac-[Ir(ppy)₃] (Φₚ = 0.40, λₑₓ = 400 nm) as reference.

[^d]: Phosphorescence quantum yield (Φₚ) were measured by using Rhodamine B (Φₚ = 0.50, λₑₓ = 500 nm) as reference.

[^e]: Excited at 350 nm in CH₂Cl₂.
3.6 Electrochemical Properties

The electrochemical behavior of these 2-substituted carbazole based iridium(III) complexes were investigated by cyclic voltammetry (CV) with measurements of air-dried thin films on a glassy carbon working electrode respectively in 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution. The other two electrodes consist of one Ag/Ag⁺ reference electrode and one Pt-wire counter electrode. The measurements were performed under N₂ with a scan rate of 50 mV/s. The performance results are summarized in Table 3.3 including onset oxidation (E_{ox}) and reduction (E_{red}) potentials estimated versus Ag/Ag⁺ reference as well as calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels.

As mentioned above, the energy gap of iridium(III) complexes can be finely adjusted by varying the substituents on the ligands.[20] And it is also generally accepted that the oxidation electrochemical behavior of Ir(III) complexes mainly focused on the metal center and the HOMO mostly attributes to metal d orbitals with part of ligand π-orbital.[21] The HOMO levels of these complexes are relatively low which can be explained by the fact that the acac component has a stronger ligand-field strength and stabilize the HOMO level.[22] The LUMO of phenylpyridine based Ir(III) complexes usually attributes to the N-part of the cyclometalated C^N ligands.[21] As mentioned above, electron-withdrawing
substituents on the pyridyl ring can substantially stabilize the LUMO energy level, while electron-donating units can play an opposite role. The previous research also demonstrated that the chemical nature of the 9-aryl ring of carbazole has little effect on the frontier orbital energy levels,\textsuperscript{[23(a)]} while the para position of 2-substituted pyridyl ring is much more sensitive and can easily affect the photophysical and electrochemical properties of the complexes.\textsuperscript{[23(b)]} Some of the reported iridium complexes show obviously reversible oxidation process because of the metal-focused Ir\textsuperscript{III}/Ir\textsuperscript{IV} oxidation couple.\textsuperscript{[24]} However for these 2-substituted carbazole based complexes, the oxidation process is irreversible. This may be explained by the fact that the dimerization reactions occurred among the radical cations formed during the oxidation scan since the relatively labile 3- and 6-positions of carbazoles are not substituted.\textsuperscript{[25]}

Thus, when comparing complexes 10 to 15, the HOMO levels ranged from -4.95 V to -4.83 V, while the LUMO levels varied from -2.15 V to -2.67 V, and the experimental results are consistent with the theoretical prediction above. As mentioned above, the LUMO of this kind of cyclometalated Ir(III) complexes is mainly located on the pyridyl ring\textsuperscript{[21]}, when comparing complexes 11 to 12, by attaching an electron-withdrawing CF\textsubscript{3} group to the N part of ligand, the LUMO of 11 becomes more electron-deficient and much easier to attract electrons from the HOMO. In other words, the LUMO energy of complex 11 is improved to a much higher level than that of 12, from -4.95 to -4.84 eV. Meanwhile, since the
HOMO is mainly located on the phenyl ring and part of the metal core, by attaching EWG to the pyridyl ring, the electrons density is drawn away from phenyl ring even at ground state. Thus the HOMO level of complex 11 is stabilized and becomes higher than that of complex 12, from 0.22 to 0.11 eV. When comparing complexes 10 to 12, by introduction of methyl moiety on the pyridyl ring, the LUMO electron density is slightly increased and as a result their energy levels are correspondingly adjusted to -4.88 and -2.29 eV. When comparing complexes 13 and 14 to complex 12, the former LUMO energy levels are obviously much higher than the latter one, this may be explained by the fact that the isoquinoline unit has a larger conjugation length than the pyridyl ring. As a result, the LUMO levels of complexes 13 and 14 are stabilized to -2.06 and -2.09 eV while that of complex 12 is -4.84 eV. However, the HOMO and LUMO energy levels of complexes 13 and 14 only have slight differences, indicating that the substituent at 9-aryl ring of carbazole can only weakly affect the frontier orbital energy levels, since the conjugation is blocked. When the 6-position of the carbazole is substituted by a methyl group as in complex 15, the electron density of HOMO and LUMO is weakly elevated and they have a 0.02 eV higher and 0.03 eV lower than those of complex 12, respectively.
Figure 3.18: Cyclic voltammograms of complexes 10 and 11

Figure 3.19: Cyclic voltammograms of complexes 12 and 13

Figure 3.20: Cyclic voltammograms of complexes 14 and 15
Table 3.3: Electrochemical properties of complexes 10 to 15

<table>
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<tr>
<th>Compound</th>
<th>$E_{\text{ox}}$ [V]$^a$</th>
<th>$E_{\text{red}}$ [V]$^a$</th>
<th>HOMO [eV]$^b$</th>
<th>LUMO [eV]$^c$</th>
<th>$E_g$ [eV]$^d$</th>
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<td>-2.44</td>
<td>-4.82</td>
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$^a$ 0.1 M [Bu$_4$N]PF$_6$ in ACN

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

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

$^d$ $E_g = \text{LUMO} - \text{HOMO}$

3.7 Electrophosphorescent OLED Characterization

Complexes 1 to 5 were applied for the OLED fabrication. Devices I, II, III, IV and V were fabricated by using complexes 1, 2, 3, 4 and 5, respectively. They all demonstrated good electrophosphorescent properties. The result data were collected in Table 3.4 at different doping concentrations. Vacuum deposition were applied as the fabrication method since all of the complexes are sufficiently stable to sublimation.

The OLEDs were fabricated with a multilayer architecture (Figure 8). 4,4’-N,N’-Dicarbazolebiphenyl (CBP) was chosen as the material for the host
layer since the PL spectrum of CBP can overlap well with the UV-vis absorption of all of the complexes, making Förster energy transfer efficiently to the guest molecules. 4, 4’-Bis [N-(1-naphthyl-1)-N-phenyl-amino]-biphenyl (NPB) was used in the hole transport layer (HTL), LiF was doped in the electron-injection layer (EIL), and 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) was acted as both hole blocking (HBL) and electron transporting layer (ETL). TPBi was chosen since it can present better electron mobility and help the excitons combination within the emissive zone efficiently\textsuperscript{[20]}

The concentration dependence experiments were carried out for each of the complexes in a range of 3-12 wt.-\%, with thickness of each layer fixed to optimize the device efficiency. For devices I and II, there was no CBP emission peak even at high current density of all doping ratios, indicating that CBP is a suitable host which completely transferred its excitation energy to the doped complexes. However, the emission of NPB (\(\sim 450 \text{ nm}\))\textsuperscript{[26]} can be observed in the EL spectra of devices II and IV at relatively low doping concentrations. This indicates that the energy transfer may not be complete in these OLEDs.

As described in Table 3.4, different dopant concentrations are used to determine the optimum weight percentages for devices to achieve the highest EL efficiencies. The OLEDs showed remarkable performance. The devices I to V generate strong EL peaks from orange to deep red between 573 and 688 nm with
low turn-on voltages ($V_{\text{turn-on}}$) at 1 cd m$^{-2}$ of 3.6-6.3 V and Commission Internationale de L'Eclairage (CIE) color coordinates of (0.59, 0.41), (0.68, 0.32), (0.60, 0.40), (0.64, 0.36) and (0.74, 0.27), respectively. The EL spectra resemble their corresponding PL spectra, confirming that the EL and PL both arise from the same excited state. Meanwhile, no evidence could be found towards metal-complex aggregation. Generally, the device brightness slightly decreased as the dopant concentration increased at a given current density. Device I at 12 wt.-% gave a maximum $\eta_{\text{ext}}$ of 17.33%, $\eta_L$ of 33.61 cd A$^{-1}$, and $\eta_p$ of 35.27 lm W$^{-1}$ at 0.53 mA cm$^{-2}$. Its luminance reached as high as 31854 cd m$^{-2}$ at 15.0-15.2 V. However, the efficiencies obtained a decay with the increase of driving voltage and current density. For device II, the maximum $\eta_{\text{ext}}$ is 6.45% with a luminance efficiency of 3.55 cd A$^{-1}$, at 9 wt.-% doping ratio and a practical current density of 3.54 mA cm$^{-2}$. The quantum efficiency and luminance efficiency gradually dropped to 4.54% and 2.33 cd A$^{-1}$ at a higher current density of 100 mA cm$^{-2}$. This kind of decrease can be explained by a triplet–triplet annihilation effect.[21]

For device III, the $\eta_{\text{ext}}$ got a maximum at 9.22% at 6 wt.-% doping ratio, when the luminance efficiency was 20.91 cd A$^{-1}$ and the practical current density reached 0.31 mA cm$^{-2}$. At a higher current density of 100 mA cm$^{-2}$, the quantum efficiency and luminance efficiency also gradually dropped to 4.41% and 9.06 cd A$^{-1}$, respectively. For device IV, the $\eta_{\text{ext}}$ got a maximum of 5.62 % at 12 wt.-% doping when the luminance efficiency was 2.91 cd A$^{-1}$ and the practical current
density was 0.033 mA cm\(^{-2}\). And the quantum efficiency and luminance efficiency gradually drop to 1.84\% and 1.10 cd A\(^{-1}\) as well at a higher current density of 100 mA cm\(^{-2}\). For device V, the highest \(\eta_{\text{ext}}\) reached 8.59\% with a luminance efficiency of 0.53 cd A\(^{-1}\), 12 wt.-\% doping ratio and a practical current density of 0.45 mA cm\(^{-2}\). Meanwhile, at a higher current density of 100 mA cm\(^{-2}\), the quantum and luminance efficiencies also gradually drop to 3.91\% and 0.96 cd A\(^{-1}\), respectively.

Figure 3.21: The general configuration for I to IV and the molecular structures of the relevant compounds in these devices
Figure 3.22: Luminance (■), power (●) and external quantum yield (% , ▲) efficiencies as a function of current density of OLED devices II and III using (a) 9 wt.-% of 2 and (b) 6 wt.-% of 3

Figure 3.23: The current-voltage-luminance (J-V-L) curves for (a) II at 9 wt.-% dopant concentration and (b) III at 6 wt.-% dopant concentration
Figure 3.24: The electroluminescence curves for (a) I at 6 wt.-% dopant concentration and (b) III at 12 wt.-% dopant concentration
Table 3.4: Performance of Ir-doped electrophorescent OLED I to IV

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<th>Device</th>
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<th>L [cd m$^{-2}$]</th>
<th>$\eta_{\text{ext}}$ [%]</th>
<th>$\eta_L$ [cd A$^{-1}$]</th>
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[a] Values collected at 20 mA cm<sup>-2</sup>.

[b] Values collected at 100 mA cm<sup>-2</sup>.

[c] Maximum L values of the device. Values in parentheses are the voltages at which the maximum were obtained, respectively.

[d] CIE coordinates [x, y] in parentheses.
3.8 Concluding Remarks

In this chapter, a series of Ir(III) complexes based on C^N ligands derived from 2-substituted carbazoles were synthesized, their photophysical and electrochemical properties were fully characterized by UV-PL and CV measurements respectively. Some of the complexes were further studied for OLED device fabrication. Generally, all of the complexes demonstrate bathochromic shift from those 3-substituted carbazole-based complexes. For complexes 10-12, which only have differences on the substituent of the para position of pyridyl ring, their UV-PL and CV results are varied correspondingly to the electron affinity of the substituent. A stronger EWG group leads to much more stable HOMO but higher LUMO level, thus a narrower band gap and red-shifted emission can be observed for complex 11 and further confirmed by its OLED results. For complexes 13 and 14, their LUMO are stabilized by the longer conjugation length introduced by isoquinoline moiety, and thus they have narrower band gap together with deep red color in both PL and EL emission. OLED devices I to V fabricated by using complexes 10 to 14 as emitters showed remarkable efficiencies, indicating that those orange-red to deep-red phosphors are suitable candidates for further luminescence applications.
References:


Chapter 4

Tetraphenylethylene Based Platinum(II) Acetylide Complexes: Synthesis, Characterization and Aggregation Induced Emission (AIE) Study

4.1 Introduction

As typical aggregation induced emission (AIE) active materials, tetraphenylethene (TPE) together with its derivatives have received much attention in the past decades. They can be easily prepared and functionalized, and thus they are regarded as promising candidates for many different applications.

AIE describes the phenomenon that at an aggregation state, non-radiative aggregation-caused quenching (ACQ) pathway, such as π-π stacking process, is prevented and thus the emission intensity is largely increased. ACQ is a spontaneously process, which was noticed half a century ago. This process is regarded as one of the major limitations for high efficiency light emitting electronics development. Therefore, in the past decades, many approaches have been reported to deal with the above problem; however, none of them was proved to a very effective solution, since it is extremely difficult to interrupt naturally
Hence, as an exception against ACQ, AIE draws considerable interest ever since it was firstly reported in 2001.\textsuperscript{[3]} An AIE active material or compound have to fulfill a basic requirement that it has no or only weak light emission in dilute solution but exhibits strong or much enhanced luminescence in aggregation state.\textsuperscript{[1]}

Nowadays, many scientists are still working on the detailed theoretical study of the existing AIE luminogens and trying to design new kinds of AIE derivatives.\textsuperscript{[1-4]}

Among which, the mechanisms of organic AIE materials, including TPE derivatives, have been fully studied and well developed by Tang's group.\textsuperscript{[1]} After elimination of possible conformation changes including planarization-enlarged delocalization, intramolecular charge transfer or J-aggregation, they found that AIE is produced by a restriction of intramolecular rotation (RIR).\textsuperscript{[1, 5]} In solution, rotations only consume a small amount of energy and is affordable by the energy released through excited state relaxation, as a result a non-radiative channel is open and hence hardly any or only small amount of photons are obtained, leading to a non-emissive solution phase; however in the aggregation state, there is far less freedom for molecules to rotate, which restricts the intramolecular motivations and blocks the non-radiative decay. Therefore, the more energy of
excitons can be released as photons and enhanced luminescence can be observed.\textsuperscript{[5]}

TPE is one of the firstly mentioned AIE active materials. Although it was synthesized more than a hundred years ago,\textsuperscript{[6]} it was not until Prof. Tang's group discovered and further developed its adequate AIE properties that TPE started to draw very large attention.\textsuperscript{[5]} TPE derivatives have been applied to many different kinds of applications such as organic light-emitting devices (OLEDs),\textsuperscript{[4]} fluorescent probes,\textsuperscript{[7]} and organic vapor explosive detectors.\textsuperscript{[8]}

Since TPE is regarded as a typical AIE material, it is a perfect example to demonstrate the detailed AIE mechanism.\textsuperscript{[1]} In solution state, the four phenyl rings rotate along the single bond linking to the central ethylenyl unit and consume most of the exciton relaxation energy; while in aggregation states, such rotations are blocked and saved energy is allowed for light emission.\textsuperscript{[5]} Apart from saving energy from rotation, it is also reported that in a TPE crystalline lattice, phenyl rings are all twisted out of plane to a propeller-like conformation, and this can prevent the formation of non-radiative recombination, i.e., $\pi-\pi$ stacking.\textsuperscript{[4]} Moreover, hydrogen bonds are also observed between two adjacent TPE molecules. It is found that phenyl protons of one TPE molecule can form weak bonds with the phenyl $\pi$ electrons of its adjacent neighbor, which further block the molecular conformations and stiffened to save energy for photon generation.\textsuperscript{[4]}
Thanks to all of the above interactions, TPE molecules are facilitated to be highly emissive in aggregation state.

Meanwhile, TPE is also chosen as a building block for further AIE material development.\textsuperscript{[9]} It is found that an ACQ molecule can be flipped to an AIE luminophore by simply adding TPE moiety.\textsuperscript{[10]} Successful examples are a series of planar molecules such as naphthalene, anthracene, phenanthracene, pyrene, triphenylamine, and carbazole.\textsuperscript{[11]}

In addition, recent study also discovered that AIE behaviors are maintained in a group of TPE-acetylide based monomers and polymers, extending the AIE exploration to aryleneethynlenes.\textsuperscript{[9]}

However, the extending AIE exploration towards heavy metal systems are not completed yet. Therefore, in this chapter, TPE moiety was introduced to tertiary phosphine substituted Pt(II) acetylide compounds and their AIE behaviors were carefully studied.

Pt(II) acetylides were firstly reported by Chatt and Shaw in 1959,\textsuperscript{[12]} and the number of them was further expanded ever since Sonogashira coupling was invented in 1975.\textsuperscript{[13]} Nowadays, Pt(II) acetylides have drawn great attention because of their relatively superior absorption properties,\textsuperscript{[14]} transparency,\textsuperscript{[15]} and electrical conductivities\textsuperscript{[16]}. Based on these, they have been applied for various
optical usages such as bulk heterojunction (BHJ) solar cells,\textsuperscript{[17]} dye-sensitized solar cells (DSSCs),\textsuperscript{[18]} optical power limiting (OPL)\textsuperscript{[19]} materials. Although there are some reported Pt(II) acetylide complexes which give considerable triplet emissions at room temperature,\textsuperscript{[20]} for most of the cases, phosphorescence can only be partially or even hardly detected under ambient conditions, since their excited states show strong ligand characters and the electron transitions are substantially prevented by the spin-forbidden law.\textsuperscript{[21]} Therefore, they are considerable candidates for AIE study.

4.2 Synthesis of Ligands

Scheme 4.1 shows the synthetic route of \( \text{L}_{15} \). BuLi was added dropwise into a diphenylmethane solution in THF at 0 °C first to remove one proton from the methylene group, followed by addition of 4-bromobenzophenone THF solution in THF. Then an alcohol product was generated which further condensed to trimethyl[(4-(1,2,2-triphenylvinyl)phenyl)ethynyl]silane (TPE-Br) by elimination of water. After that, acetylene group was attached through Sonogashira coupling of the synthesized TPE-Br with trimethylsilylacetylene. And finally \( \text{L}_{15} \) was synthesized after elimination of trimethylsilyl group under alkaline condition.
Scheme 4.1 Synthetic route of ligand $L_{15}$

Scheme 4.2 shows the synthetic route of $L_{16}$. 4-Bromotriphenylamine was produced as the procedure mentioned above. It underwent Sonogashira coupling reaction with trimethylsilylacetylene first followed by a deprotection reaction under potassium carbonate to give target $L_{16}$. 
Scheme 4.2: Synthetic route of ligand \( L_{16} \)

Scheme 4.3 depicts the synthetic route of \( L_{17} \). 2,5-Difluorophenyl bromide was firstly reacted with trimethylsilylacetylene through Sonogashira coupling, and the desired ligand was synthesized after elimination of TMS group in alkaline condition.
4.3 Synthesis of Pt(II) Acetylide Complexes

Scheme 4.4 shows the synthetic route of precursor trans-[Pt(PEt₃)PhCl]. cis-Pt(PEt₃)₂Cl₂ was generated first by reacting of PEt₃ and K₂PtCl₄ in a water-ethanol mixture, the cis-Pt(PEt₃)₂Cl₂ was reacted with freshly prepared phenyllithium in dry toluene to afford Pt(PEt₃)₂Ph₂. After that cis-[Pt(PEt₃)PhCl] was prepared by the addition of HCl ether solution and stirred overnight at room temperature. And the final product trans-[Pt(PEt₃)PhCl] was produced after refluxing in dry hexane under a catalytic amount of PEt₃.

![Scheme 4.4: Synthetic route of trans-[Pt(PEt₃)PhCl]](image)

Scheme 4.5 depicts the preparation of trans-[Pt(PBu₃)₂Cl₂]. Cis-[Pt(PBu₃)₂Cl₂] was formed first after K₂PtCl₄ and tributylphospine stirred viscously in a mixture of water and ethanol for two days. Then it was transformed
to \textit{trans-[Pt(PBu$_3$)$_2$Cl$_2$]} by keeping it at 230 °C for three hours.

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\text{K}_2\text{PtCl}_4 \xrightarrow{\text{H}_2\text{O}:\text{EtOH} = 2:1 \atop \text{r.t., 2 d}} \text{Pt} \xrightarrow{\text{Pt} \cdot \text{P}^\text{Bu}_3} \xrightarrow{200 \; \text{°C} \atop \text{3 h}} \text{Pt} \cdot \text{Pt} \cdot \text{P}^\text{Bu}_3 \xrightarrow{\text{Cl} \cdot \text{Cl} \cdot \text{P}^\text{Bu}_3} \text{P}^\text{Bu}_3 \cdot \text{P}^\text{Bu}_3 \cdot \text{P}^\text{Bu}_3 \cdot \text{P}^\text{Bu}_3}
\end{tikzpicture}
\end{center}

Scheme 4.5: Synthetic route of \textit{trans-[Pt(PBu$_3$)$_2$Cl$_2$]}

Scheme 4.6 demonstrates the synthetic route of complex 16. It was simply generated by coupling ligand \textit{L$_{15}$} with \textit{trans-[Pt(PBu$_3$)$_2$Cl$_2$]} in weak base solution with a catalytic amount of copper(I) iodide.

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\text{Pt} \xrightarrow{\text{Pt} \cdot \text{P}^\text{Bu}_3} \xrightarrow{\text{Cl} \cdot \text{Cl} \cdot \text{P}^\text{Bu}_3} \xrightarrow{\text{CuI} \atop \text{r.t., overnight}} \text{P}^\text{Bu}_3 \cdot \text{P}^\text{Bu}_3 \cdot \text{P}^\text{Bu}_3 \cdot \text{P}^\text{Bu}_3}
\end{tikzpicture}
\end{center}

Scheme 4.6 Synthetic route of complex 16

Scheme 4.7 shows the synthetic route of complex 17. \textit{L$_{15}$} and \textit{L$_{16}$} were added dropwise into a \textit{trans-[Pt(PBu$_3$)$_2$Cl$_2$]} solution dropwise containing CuI catalyst
under a weakly alkaline condition. After stirring at room temperature for three hours, the unsymmetrical product complex 17 can be generated.

\[
\begin{align*}
&\begin{array}{c}
\text{N-} \quad \text{C} \quad \text{C} \\
\text{C} \quad \text{C} \quad \text{C}
\end{array} \\
&\begin{array}{c}
\text{P}^3\text{Bu}_3 \\
\text{Cl-Pt-Cl} \\
\text{P}^3\text{Bu}_3
\end{array}
\end{align*}
\]

Scheme 4.7: Synthetic route of complex 17

Scheme 4.8 shows the synthetic route of complex 18. The acetylene proton of \( L_{17} \) was taken off by butyllithium first, then it was reacted with \( \text{trans-[Pt(PBu}_3\text{)_2Cl}_2] \) at the same condition as described above to get a monochloride Pt complex first and then after further reaction with \( L_{18} \), the desired complex 18 was generated.
Scheme 4.8: Synthetic route of complex 18

Scheme 4.9 shows the synthetic route of complex 19. It was synthesized by the CuI-catalyzed reaction of L_{15} and trans-[Pt(PEt_3)PhCl] with in a mixture of triethylamine and dichloromethane.

Scheme 4.9: Synthetic route of complex 19
4.4 NMR Spectroscopic Characterization

The products were characterized by $^1$H, $^{13}$C and $^{31}$P NMR spectroscopy. Their results are displayed in Figures 4.1-4.12. The number of aromatic protons integrated from the $^1$H spectrum matches with that of the compound involved. All of the $^1$H NMR spectra show intense butyl group patterns in the aliphatic region for complexes 16-18, and ethyl group signals for complex 19. All of the $^{31}$P spectra only contain one peak with satellites which resulted from the coupling with Pt atom.

Figure 4.1: $^1$H NMR spectrum of 16 in CDCl$_3$
Figure 4.2: $^{13}$C NMR spectrum of 16 in CDCl$_3$

Figure 4.3: $^{31}$P NMR spectrum of 16 in CDCl$_3$
Figure 4.4: ¹H NMR spectrum of 17 in CDCl₃

Figure 4.5: ¹³C NMR spectrum of 17 in CDCl₃
Figure 4.6: $^{31}$P NMR spectrum of 17 in CDCl$_3$

Figure 4.7: $^1$H NMR spectrum of 18 in CDCl$_3$
Figure 4.8: $^{13}$C NMR spectrum of 18 in CDCl$_3$

Figure 4.9: $^{31}$P NMR spectrum of 18 in CDCl$_3$
Figure 4.10: $^1$H NMR spectrum of 19 in CDCl$_3$

Figure 4.11: $^{13}$C NMR spectrum of 19 in CDCl$_3$
4.5 Photophysical Properties of Ligands and Pt(II) Complexes

The photophysical properties of acetylide ligands and their corresponding Pt(II) complexes were characterized by UV/vis absorption and PL emission spectroscopy in dilute CH$_2$Cl$_2$ solutions. The measurements for ligands were taken under ambient conditions while the PL of complexes at 77 K were measured in frozen CH$_2$Cl$_2$. The lifetimes of all of the ligands and complexes were also measured in CH$_2$Cl$_2$ solution and the relevant data are summarized in Tables 4.1 and 4.2.

Figure 4.13 contains the UV-PL spectra of ligands $L_{15}$-$L_{17}$. It shows that they
follow the behaviors of most of the acetylide compounds. It is widely accepted that the intense bands at the latter pattern (281-367 nm) arise from the $\pi$ to $\pi^*$ transition of -C≡C- bonds[22] and it is obvious that the more electron withdrawing ligand $L_{17}$ shows a large blue shift relative to the others. This may be caused by the fact that the electron deficiency at aromatic side stabilizes the HOMO level, thus increasing the energy gap.

The UV absorption spectra of complexes 16-19 are displayed in Figure 4.14, from which similar patterns can be observed as compared to their corresponding ligands. The dominant intense bands appear at the latter region, from 343 to 358 nm. It indicates that the transitions during excitation are largely affected by the $\pi-\pi^*$ orbital of the triple bonds as well for all of those complexes. Meanwhile,
their maximum absorption wavelengths shifted to much lowered field than those of the corresponding ligands by comparing the collected data of Tables 4.1 and 4.2. This proves that the metal-to-ligand charge transfers are still substantially involved for the complexes in the excited state. By comparing complexes 19 to 16, a red shift of 15 nm (343 to 358 nm) can be observed and this may be caused by the shortening of conjugation length of complex 16 since it only has an acetylide ligand on one side arm. Complex 17 also shows a slight red shift of 9 nm relative to complex 16 and may be induced by the stronger electron withdrawing property from one ligand $L_{17}$, which draws the electron density away from the triple bond and may stabilize the LUMO level.$^{[22]}$

![Normalized UV spectra of complexes 16-19 in CH$_2$Cl$_2$ at 293 K](image)

**Figure 4.14:** Normalized UV spectra of complexes 16-19 in CH$_2$Cl$_2$ at 293 K

**Figure 4.15** demonstrates the PL spectra of complexes 16 and 18 at different
temperatures. The 77K PL spectrum of complex 16 shows a similar structure but much narrower coverage than that taken at room temperature, while complex 18 not only has a narrower width but also eliminates a former band at low temperature measurement. However, all the short lifetime results demonstrate that they are spin-allowed singlet emissions and thus the enhancement of intensity may be caused by the restriction of rotations other than the appearance of spin forbidden phosphorescent at low temperature.

Figure 4.15: Normalized PL spectra of complexes 16-19 in CH₂Cl₂ at 293 K
Table 4.1: Photophysical data of ligands L\textsubscript{15} to L\textsubscript{17}

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV absorption at 298 K\textsuperscript{[a]}</th>
<th>Emission at 298 K\textsuperscript{[b]}</th>
<th>Fluorescence quantum yields\textsuperscript{[c]}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{abs}}$ (nm)</td>
<td>$\lambda_{\text{em}}$ (nm)</td>
<td>$\Phi_F$ (%)</td>
</tr>
<tr>
<td>L\textsubscript{15}</td>
<td>316 (4.3)</td>
<td>372 (0.72)</td>
<td>1.16</td>
</tr>
<tr>
<td>L\textsubscript{16}\textsuperscript{[25]}</td>
<td>327 (11.5)</td>
<td>405 (1.20)</td>
<td>18.3</td>
</tr>
<tr>
<td>L\textsubscript{17}\textsuperscript{[26]}</td>
<td>276 (5.6), 281 (5.0)</td>
<td>304 (0.74)</td>
<td>31.9</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} In CH\textsubscript{2}Cl\textsubscript{2} at 298 K, extinction coefficients (10\textsuperscript{3} M\textsuperscript{-1} cm\textsuperscript{-1}) are shown in parentheses.

\textsuperscript{[b]} Excited by 340 nm in CH\textsubscript{2}Cl\textsubscript{2}. Lifetime (ns) data obtained by 337 nm nitrogen laser in CH\textsubscript{2}Cl\textsubscript{2} are shown in parentheses.

\textsuperscript{[c]} Fluorescence quantum yields ($\Phi_F$) relative to anthracene ($\Phi_t = 0.27$, $\lambda_{\text{ex}} = 290$ nm), quinine sulfate ($\Phi_t = 0.48$, $\lambda_{\text{ex}} = 313$ nm; $\Phi_t = 0.56$, $\lambda_{\text{ex}} = 350$ nm, 0.55).

\textsuperscript{[d]} Excited by 340 nm in CH\textsubscript{2}Cl\textsubscript{2}, sh means shoulder peak.
Table 4.2: Photophysical data of complexes 15 to 18

<table>
<thead>
<tr>
<th>Complex</th>
<th>UV absorption at 298 K[^{[a]}]</th>
<th>Emission at 298 K[^{[b][c]}]</th>
<th>Emission at 77 K[^{[d]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>PL $\lambda_{\text{em}}$ (nm)</td>
<td>PL $\lambda_{\text{em}}$ (nm)</td>
</tr>
<tr>
<td></td>
<td>($\varepsilon$, $10^3$M$^{-1}$cm$^{-1}$)</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>16</td>
<td>292 (1.6), 358 (32.4)</td>
<td>421 (0.87), 470</td>
<td>415 (6.22), 459 (5.51)</td>
</tr>
<tr>
<td>17</td>
<td>293 (4.3), 361 (69.0)</td>
<td>396 (1.21), 466</td>
<td>390, 454 (4.15)</td>
</tr>
<tr>
<td>18</td>
<td>292 (0.5), 349 (1.2)</td>
<td>399 (1.44), 468</td>
<td>396, 452 (38.74)</td>
</tr>
<tr>
<td>19</td>
<td>294 (0.8), 343 (1.3)</td>
<td>399 (1.62), 465</td>
<td>457 (6.37)</td>
</tr>
</tbody>
</table>

\[^{[a]}\] In CH$_2$Cl$_2$ at 298 K, extinction coefficients ($10^3$M$^{-1}$cm$^{-1}$) are shown in parentheses.

\[^{[b]}\] Excited by 340 nm in CH$_2$Cl$_2$. Lifetime (ns) data obtained by 337 nm nitrogen laser in CH$_2$Cl$_2$ are shown in parentheses.

\[^{[c]}\] Quantum yields $\Phi$ relative to Ir(ppy)$_3$ ($\Phi = 0.40$) at 298 K, $\lambda_{\text{ex}} = 400$ nm.

\[^{[d]}\] Excited by 340 nm in CH$_2$Cl$_2$. Lifetime ($\mu$s) data obtained by 337 nm nitrogen laser are shown in parentheses.

4.5 Electrochemical Properties

The electrochemical properties of these TPE containing Pt acetylides complexes were measured by cyclic voltammetry (CV) method of air-dried thin films on a glassy carbon working electrode respectively in 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution. The other two electrodes consist of one Ag/Ag$^+$ reference electrode and one Pt-wire counter electrode. The experiments were performed under N$_2$ with a scan rate of 50 mV/s.
The performance results are summarized in Table 4.3 including onset oxidation ($E_{\text{ox}}$) and reduction ($E_{\text{red}}$) potentials estimated versus Ag/Ag$^+$ reference as well as calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. As mentioned above, although for most of the cases the ligand based $\pi-\pi^*$ transitions are largely involved, the energy levels of HOMO and LUMO as well as their differences still significantly vary among different ligands attached.$^{[22]}$ The HOMOs ranged from -5.42 to -5.21 eV while the LUMOs have a region from -2.50 to -2.16 eV, and the energy gaps varied from 2.91 to 3.21 eV.

Table 4.3: Electrochemical properties of complexes 16-19

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox}}$ [V]$^{[a]}$</th>
<th>$E_{\text{red}}$ [V]$^{[a]}$</th>
<th>HOMO [eV]$^{[b]}$</th>
<th>LUMO [eV]$^{[c]}$</th>
<th>$E_g$ [eV]$^{[d]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.64</td>
<td>-2.57</td>
<td>-5.37</td>
<td>-2.16</td>
<td>3.21</td>
</tr>
<tr>
<td>17</td>
<td>0.68</td>
<td>-2.23</td>
<td>-5.41</td>
<td>-2.50</td>
<td>2.91</td>
</tr>
<tr>
<td>18</td>
<td>0.69</td>
<td>-2.44</td>
<td>-5.42</td>
<td>-2.29</td>
<td>3.13</td>
</tr>
<tr>
<td>19</td>
<td>0.48</td>
<td>-2.46</td>
<td>-5.21</td>
<td>-2.27</td>
<td>2.94</td>
</tr>
</tbody>
</table>

[a] 0.1 M [Bu$_4$N]$^+$PF$_6$ in ACN

[b] HOMO = -(4.73 eV + $E_{\text{ox}}$) eV

[c] LUMO = -(4.73 eV + $E_{\text{red}}$) eV

[d] $E_g$ = LUMO – HOMO
4.6 AIE Results

All of the complexes were studied for AIE by measuring their PL emission spectra in a series of water/THF mixtures. The resulting spectra are depicted in Figures 4.16-4.19.

As demonstrated in Figures 4.16, complex 16 showed straightforward AIE behaviors. Similar to those published organic TPE acetylide materials,[9] the emission intensity is enhanced along with the increase of the water fraction in the aqueous mixtures; the emission remains weak for mixtures with low water content (≤50%). The mixture started to exhibit a significant emission enhancement at 60% water content, and the emission intensity reached a maximum at 99% water content. The total increase between the strongest and the weakest PL intensity is almost 17 fold.

![Figure 4.16: (a) PL spectra of 16 in THF/water mixtures. Solution concentration: 10 mM; excitation wavelength: 350 nm.](a)
Figure 4.16: (b) $I/I_0$ plot versus the composition of the mixtures. Solution concentration: 10 mM; excitation wavelength: 350 nm.

Figure 4.17 has the PL spectra and $I/I_0$ plot of complex 17. It is obvious that the PL intensities are quite low for all of the mixtures but there are still abundant varieties among each peak. The emissions were weak under 50% water fraction but started to increase at 60% water content and becomes steady with water content of 70-90%. The maximum intensity was achieved at 99% water content and the largest $I/I_0$ value is 280-fold large.
Figure 4.17: (a) PL spectra of 17 in THF/water train. (b) $I/I_0$ plot versus the composition of the mixtures. Solution concentration: 10 mM; excitation wavelength: 350 nm.
Figure 4.18 shows the PL spectra and $I/I_0$ plot of complex 18. It has similar behaviors as those of complex 17. The general PL intensities of complex 17 are quite low but still vary slightly. There are hardly any luminescence below 50% water fraction while the emission starts to appear at 60% and got maximum at 99%. Also, there is an obvious decrease at 80% water content as well. The largest $I/I_0$ value is more than 24-fold.

Figure 4.18: (a) PL spectra of 18 in THF/water train. Solution concentration: 10 mM; excitation wavelength: 350 nm.
Complex 19 is another AIE active material. There is hardly any luminescence that can be detected within low water concentration mixtures (≤60%, v/v). The emission starts to appear at 70% water fraction and gets a maximum at 99%. The maximum $I/I_0$ value is more than 64-fold.
Figure 4.19: (a) PL spectra of 19 in THF/water train. (b) I/I₀ plot versus the composition of the mixtures. Solution concentration: 10 mM; excitation wavelength: 350 nm.
As mentioned in the literature,[9] this kind of AIE behaviors can be simply explained by the restriction of rotations around TPE core at aggregate states. In a good organic solvent (THF), where molecules are well dissolved and have much freedom to rotate, the excited state energy can be easily consumed by the intra-molecular rotations (IMR). However in a poor solvent (water), the compounds are precipitated out and form aggregates since they do not have enough solubility. However, the phenyl groups of TPE moiety can form propeller shaped structure rather than planar and therefore greatly reduce the chance of π-π stacking (typical ACQ process). Through the above process the nonradiative relaxation channel of excited molecules in good solvents can be blocked while the radiative pathway is still maintained, and largely encourages the luminescence decay in aggregation states.[9, 23]

However, by attaching different ligands to the Pt core, the photophysical properties among the AIE mixture chain are substantially affected, which indicates that there are still MLCT characters in this kind of complexes.[9, 23]
4.7 Concluding Remarks

To conclude, four Pt acetylides complexes with the involvement of TPE in the ligand systems are successfully designed, synthesized and characterized. They all show very weak luminescence in organic solvents but achieve much enhanced emission intensity at aggregates states, especially for complexes 16 and 19. The optical absorption and emission properties are investigated for all of the above complexes. Their UV absorption spectra have strong ligand based π to π* transition characters and the major peaks appear at the latter pattern at around 350 nm. Their PL peaks at 77 K are only slightly blue shifted from those taken at ambient conditions and together with the short lifetimes it can be confirmed that these complexes are fluorescent materials. In addition, their HOMO and LUMO energy levels can be greatly affected by the electron affinities of the ligand system, which provide a way for further design of highly tunable AIE active organometallic compounds.
References:


Chapter 5

Cyclometalated Iridium(III) and Platinum(II) Complexes: Synthesis, Characterization and AIE study

5.1 Introduction

Cyclometalated Ir(III) and Pt(II) complexes have received widespread interest in the past decades\cite{1} because of their excellent metal-ligand orbital mixing and charge transfer characters.\cite{2} A variety of research have been devoted to tuning their photophysical and electrochemical properties\cite{3} as well as exploring their potential applications in optoelectrical and biochemical fields such as organic light-emitting devices (OLEDs),\cite{4} dye-sensitized solar cells (DSSCs),\cite{5} and chemo-/biosensors or bio-labeling materials.\cite{6}

However, one large limitation of this kind of complexes is that many of them suffer from inevitable aggregation caused quenching (ACQ) process in the solid state,\cite{7} which significantly affects the application performance and could possibly lower the efficiency or sensitivity as well. To overcome this, many efforts have been made on the design and synthesis of aggregation induced emission (AIE) organometallic Ir(III) and Pt(II) materials.\cite{8}

As published and fully supported by Tang’s group,\cite{7} for pure organic system,
AIE phenomenon mainly caused by the restriction of intramolecular rotations (RIR) process in the aggregation states. In this chapter, to identify whether this theory could be applied for organometallic compounds, a typical AIE active tetraphenylethylene (TPE) unit is linked with a pyridyl ring to form a C^N ligand, and further chelated with Ir(III) or Pt(II) to generate cyclometalated complexes, respectively.

It is widely accepted that the chemical nature is much more complicated in heavy metal complexes than that of pure organic materials. As a result, the principles of AIE behaviors in organometallic complexes are still controversial and much less predictable. As for the recently published AIE Ir(III) or Pt(II) complexes from different groups, the emission mechanism in the solid states always involves several others rather than RIR process,

For instance, the existence of a triplet metal-metal-ligand charge-transfer (3MMLCT) states, also, many planar Pt(II) complexes are reported to have large bathochromic shift after aggregation because of excimer formation, and for molecules owning donor-acceptor (D-A) character, their intermolecular interactions also make remarkable influence emissions in the solid states.

To have a closer look at the excited state behavior among aggregated heavy metal complexes, two simple cyclometalated Pt(II) complexes are also designed. Both of them have D-A conformation but the conjugation of complex 23 is
blocked by the methylene unit between carbazyl and phenylpyridyl groups.

Herein, in complex 23, the intramolecular charge transfer can be mostly neglected and intermolecular interactions become the major explanation for chromatic change during aggregation. The photophysical properties including AIE behaviors and intramolecular charge transfer influence of these complexes were fully investigated.

As for AIE active Ir(III) complexes, most of the published work are focused on the modification of hetero-ligands such as O^O or N^N ligands rather than C^N ligands.\textsuperscript{[8, 9]} This may be caused by the fact that the octahedral conformation of is much larger in space and makes both intra- and inter-molecular interactions more complicated than those of pure organic compounds or even Pt(II) complexes.\textsuperscript{[8, 9]} Therefore even slight modification of the excitation participated hetero-ligands (such as O^O ligands or N^N ligands) may largely affect the intramolecular rotations, meanwhile the influences of C^N ligand is not yet negligible.\textsuperscript{[8a, 9b, 12c]}

According to the literature report, the band gap and location of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) determines most of the luminescence characters of heavy metal compounds,\textsuperscript{[14]} in other words, lots of the published Ir(III) complexes are focused on tuning photophysical and electrochemical properties by affecting HOMO and
LUMO energy levels through adjusting C^N ligands,\cite{14}

Surprisingly, there are not much research based on tuning C^N ligand field for the development of AIE Ir(III) complexes. Recently Su's group published a series of heteroleptic Ir(III) ions based on attaching triphenylamine (TPA) units on their N^N ligands,\cite{8b, 14c, 15} and strong ^3ILCT characters at excited-state contribute to remarkable AIE behavior. To date, a heteroleptic Ir(III) complex is designed for further study, in which the carbazolyl unit is incorporated into C^N ligand and N^N ligand contains strong electron withdrawing carboxyl groups to generate ILCT characters.

5.2 Synthesis of Ligands

Scheme 5.1 shows the synthetic route of L_{18}. TPE-Br was synthesized using the same procedure as mentioned in Chapter 4. It was then reacted with 2-(tributylstannyl)pyridine through Stille coupling and generated L_{18} after refluxing in toluene with catalyst tetrakis(triphenylphosphine)palladium overnight.
Scheme 5.1: Synthetic route of ligand L₁₈

Scheme 5.2 describes the synthetic route of ligand L₁₉. The Ullmann condensation of carbazole and 1-bromo-4-iodobenzene in a strong alkaline condition with 1, 10-phenanthroline and catalytic amount copper(I) iodide gave 1-bromo-4-iodobenzene. Then, the latter was reacted with 2-(tributylstannyl)pyridine by Stille coupling to produce L₁₉.

Scheme 5.2: Synthetic route of ligand L₁₉

Scheme 5.3 shows the synthetic route of ligand L₂₀. A dry DMF solution of carbazole was dropped onto sodium hydride suspended in a DMF solution at 0 °C and the mixture was stirred for half an hour before
1-bromo-4-(bromomethyl)benzene was added. The N-H proton of carbazole was removed by sodium hydride and subsequently alkylated by 1-bromo-4-(bromomethyl)benzene at room temperature. And ligand L20 was afforded by Stille coupling of the product bromide and tributylstannly pyridine.

![Scheme 5.3: Synthetic route of ligand L20](image)

5.3 Synthesis of Cyclometalated Ir(III) and Pt(II) Complexes

Scheme 5.4 summarizes the synthetic route of heteroleptic Ir(III) complex 20. As mentioned in Chapter 3, two steps were involved in this strategy.\(^{[20]}\) Firstly, IrCl3·3H2O was reacted with an excess of L18 at 80 °C to produce a chloride-bridged iridium dimer. Secondly, acetylacetone anion (acac) were derived by deprotonation of acetylacetone (Hacac) at alkaline condition and the
dimer was cleaved to the monomeric state by replacing the bridging chlorides to acac.

Scheme 5.4: Synthetic route of complex 20

Scheme 5.5 summarize the synthetic route of homoleptic Ir(III) complex 21. 

L_{18} was reacted with Ir(acac)$_3$ in ethylene glycerol and complex 21 was generated after the reaction mixture was refluxed at 200 °C overnight.
Scheme 5.5: Synthetic route of complex 21

Scheme 5.6 describes the synthesis of cyclometalated Pt(II) complexes 22, 23, and 24, a chloride-bridged platinum dimer was formed first by reacting the ligands and K$_2$PtCl$_4$ respectively in a water and 2-ethoxylethanol mixture at 80 °C for overnight. Then it was reacted with acetylacetone (Hacac) and an excess of sodium carbonate in 2-ethoxylethanol at 80 °C overnight. After that Hacac was deprotonated by alkaline condition and the chloride-bridge was cleaved by the newly formed cation acac to generate complexes 22, 23, and 24.
Scheme 5.6: Synthetic route of complexes 22 to 24
5.4 NMR Spectroscopic Characterization of Ligands and Ir(III) Complexes

Complexes 20-25 were characterized by $^1$H and $^{13}$C NMR spectra. Their results are displayed in Figures 5.7-5.16. For complexes 20-22, the integration of aromatic protons to consistent with the structure of the ligand L$_{18}$, while those of complexes 23 and 24 are related to their ligand L$_{19}$ and L$_{20}$ respectively. The most downfield signals of $^1$H spectra, of around 8.0 ppm for complex 20, 8.8 ppm of complexes 21 and 22, 9.0 ppm of complexes 23 and 24, correspond to the protons adjacent to the nitrogen atoms in pyridyl rings. For acac substituted complexes, each of them has significant proton peaks at around 5.30 ppm and 1.80 ppm, which are relative to the proton on the acac core and the methyl ones attached to it. All of the integration of carbon peaks match the corresponding carbon count while those within symmetry share the same chemical shift values.
Figure 5.1: $^1$H NMR Spectrum of 20 in CDCl$_3$

Figure 5.2: $^{13}$C NMR Spectrum of 20 in CDCl$_3$
Figure 5.3: $^1$H NMR Spectrum of 21 in CDCl$_3$

Figure 5.4: $^{13}$C NMR Spectrum of 21 in CDCl$_3$
Figure 5.5: $^1$H NMR Spectrum of 22 in CDCl$_3$

Figure 5.6: $^{13}$C NMR Spectrum of 22 in CDCl$_3$
Figure 5.7: $^1$H NMR Spectrum of 23 in CDCl$_3$

Figure 5.8: $^{13}$C NMR Spectrum of 23 in CDCl$_3$
Figure 5.9: $^1$H NMR Spectrum of 24 in CDCl$_3$

Figure 5.10: $^{13}$C NMR Spectrum of 24 in CDCl$_3$
5.5 Photophysical Properties of Ligands, Ir(III) and Pt(II) complexes

The photophysical properties of all ligands, Ir(III) and Pt(II) complexes were investigated by UV/vis absorption and PL emission spectroscopy in dilute dichloromethane solution. Relevant data are presented in Tables 5.1 and 5.2. The results show that all of the metal complexes have efficient MLCT characters.

The normalized UV absorption spectra of all the complexes are displayed in Figure 5.11. They show that the absorption peaks can be divided into two regions. The first ones below 340 nm are intense, which are regarded as spin-allowed ligand based singlet π-π* transitions; while the latter ones are much weaker and extended to the visible range, which are regarded as the results of MLCT transitions.\textsuperscript{[16]}

![Normalized UV absorption spectra](image)

Figure 5.11: Normalized UV absorption spectra of 20-24 in CH\textsubscript{2}Cl\textsubscript{2} at 293 K
We can have a clearer view as demonstrated in Figures 5.20 and 5.21, when we compare the UV spectra of complexes and their corresponding ligands at a same time.

As shown in Figure 5.12, $L_{18}$ has a dominant absorption peak at 322 nm, while complexes 20-22 also have an intense band at 341, 342 and 329 nm, respectively. These peaks are considered to be ligand based $^1\pi-\pi^*$ transitions, and together with another absorption region which are significantly red shifted to the visible region (468 and 465 nm) and have much lowered extinction coefficient after chelation to the metal core. These data indicate that there are abundant spin mixing of $^1$MLCT states, spin forbidden $^3$MLCT states and ligand based $^3\pi-\pi^*$ states.\cite{17}

![Normalized UV absorption spectra of complexes 20-22 and ligand $L_{18}$ in CH$_2$Cl$_2$ at 293 K](image)

Figure 5.12: Normalized UV absorption spectra of complexes 20-22 and ligand $L_{18}$ in CH$_2$Cl$_2$ at 293 K
As for Pt(II) complexes, their UV behaviors are slightly different. As shown in Figure 5.13. When comparing the UV spectra of complex 24 with its corresponding ligand L20, both of them have intense bands below 330 nm and another band at around 340 nm, where as complex 24 has peaks at 291, 328 and 344 nm and the ligand L20 has peaks at 292, 327, 341 nm. These are known as spin allowed ligand based $^1\pi-\pi^*$ transitions and the relatively weak bands are regarded to arise from at the carbazolyl moiety.\textsuperscript{[19]} However, when comparing with Ir(III) complexes,\textsuperscript{[19]} the second band extended to the visible region is much closer to those resulting from $^1\pi-\pi^*$ transitions (405 nm). It is commonly accepted that this is because the strong C\textsuperscript{\equiv}N ligand field pushes the metal based d-d transition to a higher energy level, and thus the second band is assigned from mixed singlet and triplet states among $^1$MLCT, $^3$MLCT and a certain amount of $^3\pi-\pi^*$ transitions.\textsuperscript{[20]}

However, when comparing the UV absorption properties for complexes 23 and 24, as shown in Figure 5.11, it is obvious that the second band of complex 23 with MLCT characters is more dominant while the band at around 340 nm is weaker than that of complex 22. This may be caused by the cooperation among carbazolyl and phenylpyridyl moieties in complex 22 which contributes to the MLCT process and thus make the complex to have more MLCT properties.\textsuperscript{[1b]} However in complex 23, the conjugation between carbazolyl and phenylpyridyl moieties are blocked by the methylene group in the middle, and therefore it shows
weaker MLCT but more intense carbazolyl based band than those of complex 22.

![Normalized UV absorption Spectra of complexes 24 and ligand L20 in CH2Cl2 at 293 K](image)

**Figure 5.13:** Normalized UV absorption Spectra of complexes 24 and ligand L20 in CH2Cl2 at 293 K

As for photoluminescence properties, complexes 20-22 show very weak PL band at both ambient and low temperature conditions.

When comparing the PL spectra of complexes 23 and 24, as demonstrated in Figure 5.14, both of them have more than 70 nm red shift than their corresponding ligands, and their long lifetime at both room temperature (0.37, 0.45μs) and low temperature (14.7, 16.3 μs), suggest that they are strong blue phosphorescent emitters. Both of the spectra have vibrational structures, and this can be explained by the fact that they are originated from a significant amount of mixing among MLCT and ligand based \( \pi-\pi^* \) transitions.\(^{20-21}\) According to the literature for this
kind of ppy based Pt(II) cyclometalated complexes,[22-23] the LUMOs are mainly located at the pyridyl ring while the HOMOs are mostly located at the phenyl ring and part of the Pt core. Therefore for complex 23, by introduction of a carbazolyl moiety within the conjugation length, it can act as a strong donor and increase the electron density and thus destabilize the HOMO; in other words, the HOMO becomes more electron rich and favors to donate one electron out. As a result the band gap between HOMO and LUMO is smaller. However, in complex 24, the conjugation is totally blocked by the aliphatic methylene group in the middle, since the carbazolyl moiety cannot contribute electron density to the HOMO level and therefore red shift of 7 nm can be observed for both peaks when comparing complex 23 to complex 24.

Figure 5.14: Normalized PL spectra of complexes 23 and 24 in CH₂Cl₂ at 293 K
To have a closer look into the intermolecular interactions of complexes 23 and 24, their solvatochromic effects were studied and the results are displayed in Figures 5.23 and 5.24, and the relevant data are collected in table 5.3. The polarity index of hexane, dichloromethane, tetrahydrofuran (THF) and methanol (MeOH) are 0.0, 3.1, 4.0 and 5.1, respectively.

Figure 5.15 contains the PL spectra of complex 23, which were measured in dilute solutions (10 μM) in different solvents. It is quite obvious that the emission wavelengths do not change much among hexane, dichloromethane, tetrahydrofuran and methanol for complex 23, so as to their vibrational fine structures. These results suggest that the emission property of complex 23 is hardly affected by intramolecular charge transfer.
The PL spectra of complex 24 were also measured in a series of solvents at dilute concentration (10 μM). However, the PL spectrum in methanol was not recorded because of the poor solubility of complex 24. Figure 5.16 shows similar results for complex 23. The emission peaks and vibrational structures of dichloromethane and tetrahydrofuran solutions are almost identical, while the results in hexane afforded similar emission peaks but larger density distributed at the lower PL pattern. These results suggest that the intramolecular charge transfer can also be neglected for complex 24.

Figure 5.16: Normalized PL spectra of complex 24 in a series of solvents at 293 K. Solution concentration: 10 μM; excitation wavelength: 400 nm
Table 5.1: Photophysical data of ligands $L_{18}$ to $L_{20}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV absorption at 298 K$^a$</th>
<th>Emission at 298 K$^b$</th>
<th>Fluorescence quantum yields$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{abs}}$ (nm)</td>
<td>$\lambda_{\text{em}}$ (nm)</td>
<td>$\Phi_L$ (%)</td>
</tr>
<tr>
<td>$L_{18}$</td>
<td>294 (7.45), 322 (8.64)</td>
<td>425 (3.82)</td>
<td>0.19</td>
</tr>
<tr>
<td>$L_{19}^{[15]}$</td>
<td>243 (3.91), 283 (1.39)</td>
<td>410 (4.90)</td>
<td>59.6</td>
</tr>
<tr>
<td></td>
<td>293 (1.82) 318 (1.37)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L_{20}$</td>
<td>282 (8.89), 292 (9.60)</td>
<td>348 (3.45), 363</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>327 (1.39), 341 (1.65)</td>
<td>(3.78)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In CH$_2$Cl$_2$ at 298 K, extinction coefficients ($10^4$ M$^{-1}$ cm$^{-1}$) are shown in parentheses.

$^b$ Excited by 340 nm in CH$_2$Cl$_2$. Lifetime (ns) data obtained by 337 nm nitrogen laser in CH$_2$Cl$_2$ are shown in parentheses.

$^c$ Quantum yields $\Phi_L$ relative to quinine sulphatethe at 298 K. $\lambda_{ex} = 313, 334, 365$ nm with $\Phi = 48, 56, and 55\%$ respectively.

$^d$ Excited by 340 nm in CH$_2$Cl$_2$. sh means shoulder peak.
<table>
<thead>
<tr>
<th>Complex</th>
<th>UV absorption at 298 K&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Emission at 298 K&lt;sup&gt;b&lt;/sup&gt;[&lt;sup&gt;c&lt;/sup&gt;][&lt;sup&gt;e&lt;/sup&gt;]</th>
<th>Emission at 77 K&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\lambda_{\text{max}}) (nm)</td>
<td>PL (\lambda_{\text{em}}) (nm)</td>
<td>(\Phi_P) (%)</td>
</tr>
<tr>
<td>20&lt;sup&gt;e&lt;/sup&gt;</td>
<td>250 (58.2), 341 (39.7), 468 (2.75)</td>
<td>451</td>
<td>0.027</td>
</tr>
<tr>
<td>21&lt;sup&gt;e&lt;/sup&gt;</td>
<td>247 (62.7), 344 (41.2), 465 (2.81)</td>
<td>449</td>
<td>0.031</td>
</tr>
<tr>
<td>22&lt;sup&gt;e&lt;/sup&gt;</td>
<td>252 (23.3), 329 (12.0), 414 (3.42)</td>
<td>452</td>
<td>0.018</td>
</tr>
<tr>
<td>23</td>
<td>259 (45.8), 281 (29.1), 328 (13.0), 342 (9.70), 400 (2.75)</td>
<td>499, 534 (0.37)</td>
<td>22.4</td>
</tr>
<tr>
<td>24</td>
<td>291 (28.6), 328 (20.2), 344 (21.4), 405 (6.87)</td>
<td>486, 520 (0.45)</td>
<td>47.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> In CH\(_2\)Cl\(_2\) at 298 K, extinction coefficients \((10^3 \text{ M}^{-1} \text{ cm}^{-1})\) are shown in parentheses.

<sup>b</sup> Excited by 340 nm in CH\(_2\)Cl\(_2\). Lifetime (\(\mu\text{s}\)) data obtained by 337 nm nitrogen laser in CH\(_2\)Cl\(_2\) are shown in parentheses.

<sup>c</sup> Phosphorescence quantum yields \((\Phi_P)\) relative to \(\text{fac-[Ir(ppy)}_3\text{]}\) \((\Phi_P = 0.40)\) at 298 K, \(\lambda_{\text{ex}} = 400 \text{ nm}\).

<sup>d</sup> Excited by 340 nm in CH\(_2\)Cl\(_2\), sh means shoulder peak.

<sup>e</sup> The PL intensity are too low to generate lifetime data.
Table 5.3: Solvent effect results of complexes 23 and 24

<table>
<thead>
<tr>
<th>Complex</th>
<th>Emission at 298 K&lt;sup&gt;[a][b]&lt;/sup&gt; λ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hexane</td>
</tr>
<tr>
<td>23</td>
<td>503, 537</td>
</tr>
<tr>
<td>24</td>
<td>490, 526</td>
</tr>
</tbody>
</table>

[a] Excited by 400 nm in hexane, dichloromethane, THF and methanol. Excited by 450 nm in ethyl acetate.

[b] Solution concentration: 10 μM.

[b] Data cannot be generated due to poor solubility.

5.6 Electrochemical Properties

The electrochemical properties of complexes 20-24 were determined by cyclic voltammetry (CV). The glassy carbon working and Pt wire counter electrodes were placed inside 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution, and Ag/Ag⁺ electrode was used as a reference. The data were collected by detecting the air-dried thin films on the working electrode under N₂ with a scan rate of 50 mV/s. The redox results are displayed in Table 5.4.

For both iridium and platinum complexes in this chapter containing the C^N type ligands, it has been found that the HOMOs generally involve phenyl, and/or acac π-orbitals and metal d-orbitals while the LUMOs are mostly located at the pyridyl ring.<sup>[4, 25, 26]</sup> As a result, the LUMO levels of complexes 20 and 21 are
quite similar (-2.47 to -2.41 eV) since they are chelated by a same ligand. Meanwhile they also show reversible oxidation waves which are caused by the Ir(III)/Ir(IV) oxidation couple.\textsuperscript{[25]} On the contrary, cyclometalated Pt(II) complexes show irreversible redox process since they have open coordination sites on Pt core which can be nucleophilic attacked by solvent molecules and allow the ligand to undergo rearrangement. For complex 23, the diphenylamine exerts a strong electron donation effect to the HOMO and destabilizes the HOMO level (-5.05 eV) and but lowers the LUMO level (-2.84 eV). However for complex 24 the conjugation is blocked by the methylene unit and therefore the diphenylamine cannot directly affect the electron affinity of ppy unit, in other words, the energy gap between HOMO and LUMO energy level is larger than that of complex 23 (2.60 to 2.21 eV). And this result is also supported by the photophysical data.

\textbf{Figure 5.17:} Electrochemical properties of complexes 20 and 22
Table 5.4: Electrochemical properties of complexes 20 to 24

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox}}$ [V][a]</th>
<th>$E_{\text{red}}$ [V][a]</th>
<th>HOMO [eV][b]</th>
<th>LUMO [eV][c]</th>
<th>$E_g$ [eV][d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.34</td>
<td>-2.26</td>
<td>-5.07</td>
<td>-2.47</td>
<td>2.60</td>
</tr>
<tr>
<td>21</td>
<td>0.46</td>
<td>-2.32</td>
<td>-5.19</td>
<td>-2.41</td>
<td>2.78</td>
</tr>
<tr>
<td>22</td>
<td>0.73</td>
<td>-2.15</td>
<td>-5.46</td>
<td>-2.58</td>
<td>2.88</td>
</tr>
<tr>
<td>23</td>
<td>0.32</td>
<td>-1.89</td>
<td>-5.05</td>
<td>-2.84</td>
<td>2.21</td>
</tr>
<tr>
<td>24</td>
<td>0.41</td>
<td>-2.19</td>
<td>-5.14</td>
<td>-2.54</td>
<td>2.60</td>
</tr>
</tbody>
</table>

[a] 0.1 M [Bu$_4$N]PF$_6$ in ACN

[b] HOMO = - (4.73 eV + $E_{\text{ox}}$) eV

[c] LUMO = - (4.73 eV + $E_{\text{red}}$) eV

[d] $E_g$ = LUMO – HOMO

5.7 AIE Results of Complexes 20, 21 and 22

The AIE analysis for complexes 20, 21 and 22 were generated by measuring their PL intensity at certain wavelength among a series of water/THF matrices. The resulting spectra are displayed in Figures 5.24-5.27. Although their ligand $L_{18}$ shows very good AIE property, both iridium and platinum cyclometalated complexes 20, 21 and 22 give very poor AIE results.

As demonstrated in Figure 5.18, the AIE analysis of ligand $L_{18}$ showed positive results. The ligand is hardly emissive in pure organic solvent, and starts to afford an obvious emission enhancement at 80% water content, while its PL
intensity is elevated along with the addition of water fraction after that till getting a maximum at 99%. The total increase between the strongest and the weakest PL intensity is almost 466-fold.

Figure 5.18: (a) Emission spectra of $L_{18}$ in THF/water mixtures. (b) $I/I_0$ plot of emission spectra of $L_{18}$ in THF/water mixtures. $I_0$ = PL intensity in pure THF solution. All data collected at 490 nm. Solution concentration: 10 mM; excitation wavelength: 326 nm.
Figure 5.19 displays the AIE analysis of complex 20, from which we can observe that the PL intensity keeps low throughout the whole H$_2$O/THF matrix and therefore it can be concluded that complex 20 is not AIE active.

Figure 5.19: (a) Emission spectra of complex 20 in THF/water mixtures. (b) $I/I_0$ plot of emission spectra of L$_{18}$ in THF/water mixtures. $I_0 =$ PL intensity in pure THF solution. All data collected at 485 nm. Solution concentration: 10 $\text{M}$; excitation wavelength: 345 nm.
Complex 21 shows similar results as complex 20. It is hardly emissive among all kinds of H₂O/THF mixture and thus can be confirmed as not a suitable candidate for AIE active materials.

Figure 5.20: (a) Emission spectra of complex 21 in THF/water mixtures. Solution concentration: 10 □M; excitation wavelength: 350 nm. (b) I/I₀ plot of emission spectra of complex 21 in THF/water mixtures. I₀ = PL intensity in pure THF solution. Data collected at 447 nm. Solution concentration: 10 □M; excitation wavelength: 400 nm.
As demonstrated in Figure 5.21, the Pt complex 22 also affords very poor results for AIE study. It is not regarded as a suitable candidate for AIE active materials as well.

Figure 5.21: (a) Emission spectra of complex 22 in THF/water mixtures. (b) I/I₀ plot of emission spectra of complex 21 in THF/water mixtures. I₀ = PL intensity in pure THF solution. Data collected at 484 nm. Solution concentration: 10 □M; excitation wavelength: 336 nm.
5.8 AIE Results of Complexes 23 and 24

Although it is simple to observe that complexes 20 to 22 are not AIE active, the reasons behind are much difficult to determine since they have relatively complicated orbital distribution and structure conformation. Thus, instead of simply linking organic AIE active moiety to the metal core, we decided to introduce RIR properties to organometallic complexes with most simple structures. Platinum complexes were chosen because they have square planar conformation which are easier to study as well as to predict. Surprisingly, they show remarkable AIE results.

Figure 5.22 demonstrates the AIE analysis of complex 23. Complex 23 was derived based on the concept of adding a rotatable functional group to [Pt(ppy)acac] core. It is well known that [Pt(ppy)acac] is an outstanding triplet emitter,\[^4\] so that it can neglect the possibility of non-emission even after movement restriction. Meanwhile, carbazolyl unit also has a planar conformation and the single bond between it and ppy makes sure that it can rotate freely. In addition, the carbazolyl moiety has a comparable size to ppy unit, therefore the rotation of it can have remarkable influences on the whole complex. Theoretically, complex 23 fulfills the requirements of "rotation" in a good solvent system, possible "restriction" at aggregation states, and potential "emission" without mechanical energy lost.
From Figure 5.22, it can be observed that there are mainly three emission peaks (490, 525, 600 nm) appearing during the AIE analysis. The first two peaks show significant increase in PL intensity with water concentration enlarged from 40% to 80%. And the largest folds between the strongest and the weakest PL intensity are 5 and 8 folds, respectively. After that when the water content continued to go up, the first two peaks began to fade out till they totally disappeared. And the third peak came out at very high water concentration (90%) and maintained its intensity. As mentioned above, the vibrational structures of the first two peaks can be traced to a abundant mixing among MLCT and ligand based $3\pi-\pi^*$ transitions.\(^{[20-21]}\) Moreover, the solvent effect study has shown that complex 23 does not have intramolecular charge transfer character, indicating that the latten peak is induced by intermolecular interactions.
Figure 5.22: (a) Emission spectra of complex 23 in THF/water mixtures. (b) I/I₀ plot of emission spectra of complex 23 in THF/water mixtures. I₀ = PL intensity in pure THF solution. Data collected at 495 nm for water fractions 0-60%, and at 487, 496, 486, 486 nm for 70%-100% respectively. Solution concentration: 10 mM; excitation wavelength: 400 nm.
Figure 5.22: (c) $I/I_0$ plot of emission spectra of complex 23 in THF/water mixtures. $I_0 = \text{PL intensity in pure THF solution}$. Data collected at 530 nm for water fractions 0-60%, and at 524, 531, 526, 525 nm for 70%-100% respectively. (d) $I/I_0$ plot of emission spectra of complex 23 in THF/water mixtures. $I_0 = \text{PL intensity in pure THF solution}$. All data collected at 600 nm. Solution concentration: 10 $\text{M}$; excitation wavelength: 400 nm.
Figure 5.23 demonstrates the results of AIE study of complex 24. By introducing methylene moiety to interrupt the conjugation, interesting data were collected apart from the enlarged band gap and blue shifted wavelength. Similar to complex 23, complex 24 also shows three peaks (484, 519, 580 nm) throughout the whole analysis train. The intensity increase of the first two peaks is much more gradual than those of complex 23, and the folds between the strongest and the weakest PL intensity are only around 2 and 3 respectively. This indicates that the lack of participation in HOMO and LUMO of the whole complex has much less influences on the AIE results. Also, the presence of third peak appearing at high water content (>80%) helps to confirm that it is originated from intermolecular interaction since intramolecular charge transfer is blocked in complex 24. At the same time, it can also be summarized that the AIE effect of first peaks for complex 23 is originated from RIR process.
Figure 5.23: (a) Emission spectra of complex 24 in THF/water mixtures. b) $I/I_0$ plot of emission spectra of complex 24 in THF/water mixtures. $I_0 =$ PL intensity in pure THF solution. Data collected at 484 nm. Solution concentration: 10 μM; excitation wavelength: 400 nm.
Figure 5.23: (c) $I/I_0$ plot of emission spectra of complex 24 in THF/water mixtures.

$I_0$ = PL intensity in pure THF solution. Data collected at 519 nm. (d) $I/I_0$ plot of emission spectra of complex 24 in THF/water mixtures.

$I_0$ = PL intensity in pure THF solution. Data collected at 577 nm for water fractions 0-70% and 90%, and at 572, 596 nm for 80% and 100% respectively. Solution concentration: 10 $\text{M}$; excitation wavelength: 400 nm.
5.9 Concluding Remarks

To conclude, two Ir(III) and three Pt(II) cyclometalated complexes were designed and synthesized in this chapter. They have been fully characterized and their photophysical, electrochemical properties and AIE analysis were also studied. Unfortunately by just involving TPE containing L_{18} to chelate with metals cannot afford suitable AIE active candidates for further development. Therefore, two cyclometalated Pt(II) complexes 23 and 24 with simple structures were designed for a better understanding of the metal containing AIE molecules. Surprisingly they both display interesting AIE properties, whereas complex 23 demonstrates both RIR and intermolecular interactions the mechanism in the same water tetrahydrofuran matrix. This suggests a possible way to further design AIE active Ir complexes. For example, Car-Ir as shown below may also contain interesting AIE effects since its LUMO is located at the N^N ligand while the HOMOs are mostly likely located around the carbazolyl moiety.\(^{[8b, 14c, 15]}\) To further confirm the origin of AIE behavior, tert-butyl group may be introduced as shown in tBu-Ir to increase the RIR process.\(^{[8b, 14c, 15]}\)
References:


2001, 20, 4476.


Chapter 6

Platinum(II) Acetylide Complexes: Synthesis, Characterization and Time Resolved Infrared (TRIR) Study

6.1 Introduction

As another triplet emitting complexes showing typical heavy metal effect,\(^1\) Pt(II) acetylides have been explored and have been approved to be suitable candidate of organic light emitting diodes (OLED),\(^2\) optical power limiting (OPL) materials,\(^3\) two-photon chromophores,\(^4\) bulk heterojunction (BHJ) solar cells,\(^5\) and dye-sensitized solar cells (DSSCs).\(^6\)

This kind of complexes contain extraordinary photophysical and electrochemical properties mostly caused by the efficient metal-ligand orbital coupling, through which the intersystem crossing (ISC) process is significantly accelerated and therefore the limitation of spin-forbidden character is greatly relieved while triplet transition is largely encouraged.\(^1\)

One remarkable result of highly efficient ISC is abundantly increased emission yields since it involves both fluorescence and phosphorescence. Therefore, some research of Pt(II) acetylides has been directly applied on
electroluminescence and triplet exiton formations.\textsuperscript{[7]} Meanwhile, the intramolecular charge transfer (ICT) character arising from the pπ-dπ orbital mixing allows Pt(II) acetylides to cover relatively broad absorption spectrum, and together with that their band gap can be finely tuned by adjusting ligand field properties even to the visual region, Pt(II) acetylides and polyynes have been regarded as suitable candidates for BHJ and DSSC solar cells as well.\textsuperscript{[5, 6, 8]}

Under pulsed laser irradiation, the rapid ISC process of Pt(II) acetylides also leads to large nonlinear absorption with respect to the rate of singlet-triplet population,\textsuperscript{[1e, 9]} i.e. the transmission decreases as the input light intensity increases.\textsuperscript{[10]} The most accepted mechanisms for this behavior include reverse saturable absorption (RSA),\textsuperscript{[11]} excited state absorption (ESA) and two-photon absorption (TPA).\textsuperscript{[12]} RSA involves the accumulation of long-lived triplet states during laser excitation,\textsuperscript{[11]} while ESA relates to the absorption of excited state,\textsuperscript{[12]} and most of the TPA behavior is caused by large dipole change after excitation.\textsuperscript{[1e]} Moreover, Pt(II) acetylides not only show significant nonlinear absorption property in a wide range, but also have good transparency in the visible region. And this makes them good candidates for OPL applications.\textsuperscript{[3, 11a]}

As for two-photon absorption materials,\textsuperscript{[4]} they have large potential in the application of biosensing and imaging using since it is effective to prevent the damage of higher-energy photons exposure.\textsuperscript{[1e]} It has been found that the
two-photon properties are greatly influenced by the molecular dipole distribution and a significant polarization change during excitation leads to an obvious enhancement in two-photon cross section.\textsuperscript{[1c, 13]} There are many published Pt acetylides processing two-photon absorption in the literature, with modifications on the ligand electron density or conjugation length.\textsuperscript{[14]} They attract large interest since their properties can also be well adjusted by modifying interaction between the metal core and the organic ligands, and the alkynyl units also display good rigidity and linearity in geometry.\textsuperscript{[15]}

Obviously, most of those phenomena have strong relationship with the region and behavior of the excited states of Pt(II) acetylides, and it has been well accepted that the detail study of intramolecular energy transfer during excitation or relaxation is very important for further structure-property exploration and development.\textsuperscript{[16]}

So far, there are mainly two kinds of methods which are commonly used to study the configuration of compound's excited states - experimental measurements and computational calculations. They usually can complimentarily support each other and generate more credible results through comparison.\textsuperscript{[16]}

Among which, time resolved infrared spectroscopy (TRIR) is an outstanding measurement for detailed study of the excited state and electron or energy transitions within Pt(II) acetylide complexes upon excitation.\textsuperscript{[19]} Since Pt(II)
acetylides have a -C≡C- bond, which is highly specific in infrared spectrum, and the MLCT character makes the excited state lifetime long enough to be well recognized.\[^{19}\] Furthermore, the electron density change around the active bonds can provide significant signals in TRIR spectra.\[^{20}\] Therefore, the excited state behavior especially energy redistribution could be reflected through -C≡C-stretches of Pt(II) acetylide complexes and it has been successfully involved in the previous studies.\[^{19, 21}\]

In 2003, Emmert et al. firstly studied the excited state behaviors of a very primary complex [Pt(P(nBu)_3)_2(ethynylbenzene)_2] by TRIR spectroscopy.\[^{19}\] They found that the symmetry of this complex changed from D_{2h} to C_{2v} under laser irradiation, indicating that only one side of the acetylenic ligands was involved during excitation, and it was suggested that this change was caused by a deformation along antisymmetric b_{3u} coordinate.\[^{19}\] Later on in 2005, Batista et al. also further complementarily supported these results by computational calculations.\[^{7b, 22}\] Meanwhile, they also confirmed that the HOMO of this complex mainly consists of ligand conjugated π orbital and part of metal d orbital, while LUMO is mostly located at the ligand based π* orbital. And since it is antibonding in character, the vibration wavelength at excited state is within the region of typical double bond and triple bond.\[^{19, 22}\]

However, the research of Emmert and Batista are mostly focused on
symmetric Pt(II) acetylides with ligands of neutral electronegativity. As mentioned above, complexes with donor and/or accepter acetylenic ligands are drawing larger attention recently because of their potentially multifunctional nature.\textsuperscript{[2-5]} Surprisingly, there is seldom TRIR research on this kind of complexes. In 2009, Zhou et al. reported a group of Pt(II) acetylide complexes with ligands largely varied in electron affinity. And it shows interesting results on their excited states distributions, among them, complex \textbf{FPtF} delivers a similar property as [Pt(P(\textsuperscript{n}Bu)\textsubscript{3})\textsubscript{2}(ethynylbenzene)\textsubscript{2}] while complex \textbf{NFPtNF} has remarkable ligand to metal charge transfer (LMCT) character and ligand π orbital significantly contributes to the complex LUMOs.\textsuperscript{[3]}

\textbf{FPtF}

\textbf{NFPtNF}
Hence, a series of Pt(II) complexes with acetylenic ligands of different electron affinities were designed, synthesized and characterized. And some of them were employed for TRIR spectroscopy study to predict information on their excited state behaviors to have a better look especially of excited state electron redistribution.

6.2 Synthesis of Ligands

All of the ligands were synthesized by Sonogashira coupling reaction from their bromide precursors. The synthesis of 2-bromo-9,9-diethylfluorene, and 2-bromo-5-(9,9-diethyl-9H-fluoren-2-yl)thiophene were described in chapter 2, and those of ligands \( L_{16} \) and \( L_{17} \) were already discussed in chapter 4.

Scheme 6.1 shows the synthetic route for \( L_{22}\text{-Br} \). 2-Bromo-9,9-diethylfluorene was reacted with periodic acid and iodine at 50 °C overnight in a mixture of acetic acid and concentrated sulfuric acid to generate 2-bromo-9,9-diethyl-7-iodo-9H-fluorene first. Then it underwent Ullmann condensation with diphenylamine under a strong basic condition and the precursor of ligand \( L_{22} \). \( L_{22}\text{-Br} \) was obtained after 3 days of reflux in p-xylene.
As demonstrated in scheme 6.3, ligands $L_{21}$-$L_{23}$ were synthesized through similar routes. The bromide ligand precursors, $L$-$Br$ underwent Sonogashira reaction, it was stirred in a mixture of NEt$_3$ and CH$_2$Cl$_2$ at 0 $^\circ$C for half an hour with excessive PPh$_3$ and a catalytic amount Pd(OAc)$_2$ and CuI to allow the formation of Pd(II) catalyst. Then trimethylsilylacetylene was added into the reaction mixture and cooled in an ice bath for another 30 min. After that the temperature was raised to 50 $^\circ$C. And the TMS acetylide moiety was composed to provide intermediate $L$-$TMS$ after refluxing overnight. And $L_{21}$-$L_{23}$ were generated after the deprotection of $L$-$TMS$ was by elimination of TMS unit through alkaline condition.
Scheme 6.2: Synthetic Route of ligand L<sub>21</sub>-L<sub>23</sub>
6.3 Synthesis of Pt(II) Acetylide Complexes

The Pt(II) complexes studied in this work were synthesized by similar procedures as described in chapter 4. Scheme 6.3 shows the synthesis of the symmetric complex 25. It was prepared through a dehydrohalogenation reaction between \( L_{23} \) and \( \text{trans-}[\text{Pt}(\text{PBu}_3)_2\text{Cl}_2] \) with the presence of catalytic amount CuI in the mixture of CH\(_2\)Cl\(_2\) and NEt\(_3\).

Scheme 6.3: Synthetic route of complex 25

Scheme 6.4 demonstrates the synthetic routes of complexes 26-28. An intermediate Pt(II) chloride \( \text{F-Pt-Cl} \) was prepared as described in chapter 4. In a mixture of CH\(_2\)Cl\(_2\) and NEt\(_3\), it underwent dehydrohalogenation reactions with ligands \( L_{16}, L_{21} \) and \( L_{22} \) respectively and complexes 26-28 were generated after
the reaction mixture was stirred in room temperature overnight.

Scheme 6.4: Synthetic routes of complexes 26-28

Scheme 6.5 shows the synthetic routes of complexes 29-32. The platinum
Intermediate PhPt−Cl was prepared as mentioned in chapter 4. It reacted with ligands L_{21}-L_{23} in CH_{2}Cl_{2} and NEt_{3} mixed solutions. Dehydrohalogenation took place with the presence of CuI to afford complexes 29-32.

Scheme 6.5: Synthetic routes of complexes 29-32
6.4 NMR Spectroscopic Characterization of Ligands and Pt(II) Complexes

All of the synthesized air-stable ligands and the corresponding Pt(II) acetylides were characterized by NMR spectroscopic techniques including $^1$H, $^{13}$C and $^{31}$P NMR spectroscopy. For ligands $L_{21}$-$L_{23}$, they all show well defined the spectral features in $^1$H NMR spectra, which are characterized by downfield peaks of aromatic protons, the sharp peak of terminal acetylenic proton (C≡C-H) located at around 3.5 ppm and upfield signals of aliphatic protons (ethyl groups). As for the Pt(II) acetylides, it is quite obvious that the terminal acetylenic proton signals were absent after the linkage with the Pt center and the patterns of butyl or ethyl peaks appeared at upfield spectra while the integration of aromatic protons remains the same as those of the ligands. The $^{13}$C NMR spectra of Pt(II) acetylides also displayed the corresponding signals into the aromatic (i.e. 120–170 ppm) and aliphatic regions (i.e. 80–110 ppm). All of the $^{31}$P NMR spectra of these complexes only show one main signal with two satellites coupled with the platinum atom and the $^1J_{P\cdot Pt}$ values are within the typical range to confirm that the complexes are consistent with a trans geometry.\textsuperscript{[17]}
Figure 6.1: $^1$H NMR spectrum of 25 in CDCl$_3$

Figure 6.2: $^{13}$C NMR spectrum of 25 in CDCl$_3$
Figure 6.3: $^{31}$P NMR spectrum of 25 in CDCl$_3$

Figure 6.4: $^1$H NMR spectrum of 26 in CDCl$_3$
Figure 6.5: $^{13}$C NMR spectrum of 26 in CDCl$_3$

Figure 6.6: $^{31}$P NMR spectrum of 26 in CDCl$_3$
Figure 6.7: $^1$H NMR spectrum of 27 in CDCl$_3$

Figure 6.8: $^{13}$C NMR spectrum of 27 in CDCl$_3$
Figure 6.9: $^{31}$P NMR spectrum of 27 in CDCl$_3$

Figure 6.10: $^1$H NMR spectrum of 28 in CDCl$_3$
Figure 6.11: $^{13}$C NMR spectrum of 28 in CDCl$_3$

Figure 6.12: $^{31}$P NMR spectrum of 28 in CDCl$_3$
Figure 6.13: $^1$H NMR spectrum of 29 in CDCl$_3$

Figure 6.14: $^{13}$C NMR spectrum of 29 in CDCl$_3$
Figure 6.15: $^{31}$P NMR spectrum of 29 in CDCl$_3$

Figure 6.16: $^1$H NMR spectrum of 30 in CDCl$_3$
Figure 6.17: $^{13}\text{C}$ NMR spectrum of 30 in CDCl$_3$

Figure 6.18: $^{31}\text{P}$ NMR spectrum of 30 in CDCl$_3$
Figure 6.19: $^1$H NMR spectrum of 31 in CDCl$_3$

Figure 6.20: $^{13}$C NMR spectrum of 31 in CDCl$_3$
Figure 6.21: $^{31}$P NMR spectrum of 31 in CDCl$_3$

Figure 6.22: $^1$H NMR spectrum of 32 in CDCl$_3$
Figure 6.23: ¹³C NMR spectrum of 32 in CDCl₃

Figure 6.24: ³¹P NMR spectrum of 32 in CDCl₃
6.5 Photophysical Properties of Ligands and Pt(II) Complexes

The photophysical properties of all the synthesized ligands and Pt acetylides were characterized by UV-vis absorption and PL emission spectroscopy. Their results are summarized in Tables 6.1 and 6.2 respectively.

As mentioned in chapter 4, all of the ligands show dominant absorption peaks at around 330 nm, and it is widely accepted that they reflect the $\pi$ to $\pi^*$ transition which is mainly located around the carbon-carbon triple bonds. Unlike cyclometalated Pt(II) acac complexes which exhibit tail absorption bands extending to the visible region caused by the MLCT effect, the acetylide complexes 25-32 only show strong absorption characters similarly as their ligands from 343 to 399 nm.\(^{[17]}\) These bands with large extinction coefficients are also irradiated from the $\pi$ to $\pi^*$ transition of their ethynylene units and apart from that the bathochromic shifts apparently indicate the existence of $d\pi-p\pi$ coupling during excitation.\(^{[3, 18]}\)

Meanwhile, the physical properties of the complexes can also be influenced by the ligand properties since the HOMO and LUMO mostly involve ligand-centered $p\pi$ delocalization mixing with part of metal-centered $d\pi$ orbital.\(^{[3, 7a]}\) Therefore the band gap of symmetric Pt(II) complexes can be well adjusted by modifying the electronegativity and conjugation length of ligand system.
For complexes without thienyl moieties, the PL spectra can be clearly divided into two parts. The first bands (<420 nm) can be assigned as singlet fluorescence since they have extremely short lifetimes (<2.5 ns). The latter bands show large Stokes shift (>100 nm) and should be phosphorescence since they afford long lifetime (in the microsecond scale) in each case. Furthermore, at low temperature (77K), not only the PL spectra become more structured, the intensity of latter bands are largely improved as well, which also confirms the triplet character of these complexes.

![Figure 6.25: UV absorption and PL emission spectra of complex 27](image)

For complexes FPPtF and 29 with similar electron affinity, the PL wavelength of complex FPPtF shows a clear bathochromic shift than that of complex 29 (384 to 365 nm) at room temperature. According to the literature data, the majority of
both HOMO and LUMO of \textbf{FPtF} are located at the ligand-centered $\pi$ orbital while the Pt d orbital contributes only a very small amount.$^{[3]}$ Thus the above red shift can be explained by the fact that the extension of conjugation length stabilizes the LUMOs and as a result decreases the band gap.

However, as shown in Figure 6.26, when comparing complex \textbf{NFPtNF} to complex 30, their emission wavelengths at 293 K are almost the same (414 to 412 nm). It has been reported that the excited states of \textbf{NFPtNF} are mainly affected by ligand-to-metal charge transfer (LMCT) and the electron density is larger by the contribution of the other diphenylamino moiety which has a strong electron donating property but the spin orbital coupling become weaker.$^{[3]}$ Therefore, although the conjugation length of \textbf{NFPtNF} is extended, its band gap between HOMO and LUMO as compared to complex 30 changes much less than that of complex \textbf{FPtF} and complex 29.$^{[3, 24]}$

In contrast, when introducing electron withdrawing ligand $\text{L}_{17}$, the metal ligand coupling becomes stronger while the conjugation length gets shorter, as a result the emission wavelength of complex 27 also only has a small variation from complex \textbf{NFPtNF} (6 nm).$^{[3, 24]}$

Furthermore, the strength of spin-orbit coupling is mainly influenced by the metal's spin-orbit coupling constant and the ability of the ligand electrons penetrating into the metal ion.$^{[23]}$ And since the products in this chapter are all
Pt(II) complexes, the only effect is the ligand conjugation length. When it is considerably large, the singlet transition could mainly localize around the ligand side, encountering more $p\pi$ character, and reducing $d\pi$ coupling as well as triplet yield. Thus ligands with diphenylamino moiety demonstrate weak triplet bands at room temperature.

![Figure 6.26: UV-PL spectra of complexes 27, 30 and NFPtNF at 293 K](image)

Similarly, as demonstrated in Figure 6.27, there is a more obvious triplet emission band of complex 29 than that of complex FPtF, since the shortness of conjugation leads to better metal ligand orbital coupling, and as a result the triplet phosphorescence becomes more dominant.\textsuperscript{[24]}
Figure 6.27: UV-PL spectra of complexes 30 and NFpTNF

Table 6.1: photophysical data of cyclometalating ligands

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV absorption at 298 K</th>
<th>Emission at 298 K</th>
<th>Fluorescence quantum yields</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)$^a$</td>
<td>$\lambda_{\text{em}}$ (nm)$^b$</td>
<td>$\Phi_F$ (%)$^c$</td>
</tr>
<tr>
<td>L$_{21}$</td>
<td>316 (4.3)</td>
<td>343</td>
<td>65.3</td>
</tr>
<tr>
<td>L$_{22}$</td>
<td>327 (4.5)</td>
<td>390</td>
<td>77.4</td>
</tr>
<tr>
<td>L$_{23}$</td>
<td>325 (4.8)</td>
<td>393</td>
<td>2.43</td>
</tr>
</tbody>
</table>

[a] In CH$_2$Cl$_2$ at 298 K, extinction coefficients (10$^4$ M$^{-1}$ cm$^{-1}$) are shown in parentheses.

[b] Excited by 290 nm in CH$_2$Cl$_2$ at 298 K.

[c] Fluorescence quantum yields ($\Phi_F$) relative to anthracene ($\Phi_f = 0.27, \lambda_{\text{ex}} = 290$ nm), quinine sulfate ($\Phi_F = 0.48, \lambda_{\text{ex}} = 313$ nm; $\Phi_f = 0.56; \Phi_F = 0.55, \lambda_{\text{ex}} = 350$ nm)
Table 6.2: Photophysical data of complexes 25-32

<table>
<thead>
<tr>
<th>Complex</th>
<th>UV absorption at 298K</th>
<th>Emission at 298K&lt;sup&gt;[b]&lt;/sup&gt;</th>
<th>Emission at 77K&lt;sup&gt;[c]&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ (nm) &lt;sup&gt;[a]&lt;/sup&gt;</td>
<td>λ (nm)</td>
<td>Φ&lt;sub&gt;P&lt;/sub&gt; (%)</td>
</tr>
<tr>
<td>25</td>
<td>230 (2.9), 271 (1.3), 399 (5.7)</td>
<td>447 (1.20)</td>
<td>0.08</td>
</tr>
<tr>
<td>26</td>
<td>265 (2.5), 294 (2.7), 351 (5.6)</td>
<td>372 (1.29), 509, 552</td>
<td>0.21</td>
</tr>
<tr>
<td>27</td>
<td>263 (2.0), 297 (2.4), 356 (5.8)</td>
<td>408 (1.37), 528</td>
<td>0.32</td>
</tr>
<tr>
<td>28</td>
<td>264 (3.0), 289 (2.8), 354 (5.4)</td>
<td>393 (3.06), 483</td>
<td>0.07</td>
</tr>
<tr>
<td>29</td>
<td>231 (2.3), 304 (1.4), 346 (3.3)</td>
<td>365 (1.11), 504, 544</td>
<td>0.13</td>
</tr>
<tr>
<td>30</td>
<td>296 (1.3), 306 (2.4), 345 (3.5)</td>
<td>412 (2.81)</td>
<td>0.54</td>
</tr>
<tr>
<td>31</td>
<td>268 (1.4), 306 (2.1), 343 (3.1)</td>
<td>404 (2.30)</td>
<td>0.08</td>
</tr>
<tr>
<td>32</td>
<td>231 (3.9), 268 (1.5), 377 (5.2)</td>
<td>430 (1.72)</td>
<td>0.10</td>
</tr>
<tr>
<td>FPt&lt;sup&gt;[3]&lt;/sup&gt;F</td>
<td>270 (1.1), 300 (2.0), 357 (4.7)</td>
<td>384 (0.94), 506, 544</td>
<td>0.12</td>
</tr>
<tr>
<td>NFPt&lt;sup&gt;[3]&lt;/sup&gt;NF</td>
<td>265 (6.9), 305 (3.3), 385 (5.0)</td>
<td>414 (0.92), 531</td>
<td>0.85</td>
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</table>

[a] In CH₂Cl₂ at 298 K, extinction coefficients (10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) are shown in parentheses

[b] Excited by 313, 344, 364 nm respectively in CH₂Cl₂. Phosphorescence quantum yields (Φ<sub>P</sub>) relative to quinine sulfate (Φ<sub>F</sub> = 0.48, 0.56, 0.55 respectively) at 298 K, λ<sub>ex</sub> = 400 nm.

[c] Excited by 313, 344, 364+nm in CH₂Cl₂, sh means shoulder peak.
6.6 Electrochemical Properties

Cyclic voltammetry (CV) was utilized to determine the electrochemical properties of the Pt(II) acetyldies by placing air-dried thin films on a glassy carbon working electrode in 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution under N\textsubscript{2} with a scan rate of 50 mV/s. The other two electrodes including a reference, which consists of Ag/Ag\textsuperscript{+} and a Pt-wire which is used as counter electrode.

The CV data were recorded, calculated and summarized in Table 6.3. The onset oxidation (\(E_{\text{ox}}\)) and reduction (\(E_{\text{red}}\)) potentials are estimated versus Ag/Ag\textsuperscript{+} reference and the energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are calculated according to them. As mentioned above, although for most of the cases the ligand based \(\pi-\pi^*\) transitions are largely involved, the energy levels of HOMO and LUMO as well as their differences still significantly vary among different ligands attached.\textsuperscript{[22]} The HOMOs ranged from -5.45 to -5.05 eV while the LUMOs have a region from -2.0 to -1.83 eV, and the energy gaps varied from 2.86 to 3.23 eV.
Table 6.3.: Electrochemical properties of complexes 25-32

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox}}$ [V]$^\text{[a]}$</th>
<th>$E_{\text{red}}$ [V]$^\text{[a]}$</th>
<th>HOMO [eV]$^\text{[b]}$</th>
<th>LUMO [eV]$^\text{[c]}$</th>
<th>$E_g$ [eV]$^\text{[d]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.53</td>
<td>-2.33</td>
<td>-5.26</td>
<td>-2.40</td>
<td>2.86</td>
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<td>26</td>
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<td>-5.07</td>
<td>-1.98</td>
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</tr>
<tr>
<td>27</td>
<td>0.35</td>
<td>-2.81</td>
<td>-5.08</td>
<td>-1.92</td>
<td>3.16</td>
</tr>
<tr>
<td>28</td>
<td>0.31</td>
<td>-2.84</td>
<td>-5.04</td>
<td>-1.89</td>
<td>3.15</td>
</tr>
<tr>
<td>29</td>
<td>0.37</td>
<td>-2.9</td>
<td>-5.1</td>
<td>-1.83</td>
<td>3.27</td>
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<td>30</td>
<td>0.28</td>
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<td>-5.01</td>
<td>-2.02</td>
<td>2.99</td>
</tr>
<tr>
<td>31</td>
<td>0.33</td>
<td>-2.80</td>
<td>-5.06</td>
<td>-1.93</td>
<td>3.13</td>
</tr>
<tr>
<td>32</td>
<td>0.72</td>
<td>-2.44</td>
<td>-5.45</td>
<td>-2.29</td>
<td>3.16</td>
</tr>
<tr>
<td>FPtF$^\text{[3]}$</td>
<td>0.32</td>
<td>-2.83</td>
<td>-5.05</td>
<td>-1.90</td>
<td>3.15</td>
</tr>
<tr>
<td>NFPtNF$^\text{[3]}$</td>
<td>0.38</td>
<td>-2.75</td>
<td>-5.11</td>
<td>-1.98</td>
<td>3.13</td>
</tr>
</tbody>
</table>

[a] 0.1 M [Bu$_4$N]$^+$/PF$_6^-$ in ACN

[b] HOMO = -(4.73 eV + $E_{\text{ox}}$) eV

[c] LUMO = -(4.73 eV + $E_{\text{red}}$) eV

[d] $E_g = \text{LUMO} - \text{HOMO}$

6.7 Results of Time Resolved Infrared (TRIR) Spectroscopy

The laser system utilized a Ti:Sapphire oscillator and regenerative amplifier combination operating at 1 kHz. The fundamental laser beam passed either a DFG OPA to generate IR beam and further split to two parts with identical intensity by Ge beam splitter, one was used as probe while the other was a reference. Only the probe was overlapped with the pump beam while both of them were focused onto
the sample cell. A grating spectrometer (Triax 320) was used to record the data of both beams after passing through the sample. And the data were analyzed by separate HgCdTe array (32 elements) detectors which was cooled by liquid nitrogen. The signal of pump on/off conditions were measured by synchronizing the pump pulses through a chopper operating at 500 Hz. The reference signal is subtracted to generate the overall signal. Samples were dissolved in THF and with a concentration whose absorbance was approximately between 1.0-2.0 at maximum MLCT region. A Perkin Elmer rectangular semi-demountable cell was used to hold the samples which is in the middle of a 4 mm thick CaF$_2$ back window and 2 mm thick CaF$_2$ front window and with a 0.1 mm Teflon spacer in between. The absorption spectra were measured before and after TRIR exposure to ensure that decomposition did not occur during the whole experiment.

In the study of [Pt(P($^{n}$Bu)$_3$)$_2$(ethynylbenzene)$_2$], Emmert et. al suggested that for a Pt(II) acetylide complex, if the orbital symmetry remains at excited states, then a single $\nu$(C≡C)* absorption band should be observed at the region between ground state vibrations of $\nu$(C≡C) and $\nu$(C=C). On the contrary, if the symmetry gets destroyed at excited sates, i.e. only one side of ligands is substantially involved, then correspondingly, apart from the above mentioned largely shifted triplet signal, there should also be another absorption band which is a little bit shifted to the higher frequency than that of the ground state.$^{[19]}$ Since upon excitation the electron density of Pt $d\pi$ orbital is drew towards to only one of the
ligands which mostly involves in charge transfer, the bonds order of the other ligand left will be slightly increased as Pt d\textsubscript{xy} orbital has antibonding interaction with its C≡C p\textalpha orbital. Therefore the IR signal of uninvolved ν(C≡C) should be up shifted.

The experimental results of Emmert’s group successfully proved that the symmetry of [Pt(P\textsuperscript{6}Bu\textsubscript{3})\textsubscript{2}(ethynylbenzene)\textsubscript{2}] is reduced during excitation by showing two vibrational bands at both slightly higher shifted and much lowered shifted region.\textsuperscript{[19]} However, in 2003, the TRIR was taken in a microsecond time scale therefore Emmert’s result could not neglect the initial charge delocalization of triplet manifold.\textsuperscript{[19]} In 2009, by using femtosecond time-resolved transient absorption and fluorescence upconversion technique Ramakrishna et al. analyzed a group of Pt(II) acetylides and confirmed that the excitation mechanism involves an ultrafast ISC process (100 fs -2.5 ps) followed by a slower relaxation (4.1 ps -21 ps) of the triplet state.\textsuperscript{[27]}

To have a closer look at the ultra-fast behavior upon excitation, complexes 29, 30, FPtF and NFPtNF have been synthesized and subjected to fs-TRIR analysis. In ground state FTIR study, all of the complexes show typical ν(C≡C) bands near 2090 cm\textsuperscript{-1}. Upon excitation, it is quite obvious that there appear another group of transient bands which are shifted to much lower frequency (1854-1910 cm\textsuperscript{-1}). These kind of signals represent the electron transition from π to
\( \pi^* \) orbital in C≡C and sufficiently decrease the bond order by increasing antibonding character.

Figure 6.28: FTIR spectra of complexes 29 and 30

Figure 6.29: FTIR spectra of complexes FPtF and NFPtNF
The TRIR spectra for complexes 29 and \textbf{FPtF} are presented in Figures 6.6 and 6.7, and they obtain abundant similarities on $\nu$(C≡C) absorption bands at ground state (2095 cm$^{-1}$ and 2090 cm$^{-1}$) as displayed in Figures 6.4 and 6.5. After excitation, they all have new absorption bands appearing at much lower frequency (1895 cm$^{-1}$ and 1887 cm$^{-1}$). As mentioned above, the large shift $\Delta \nu$ (200 cm$^{-1}$, 203 cm$^{-1}$) to lower frequency is caused by the electron transition to antibonding $\pi^*$ orbital of ligand field, indicating that the electron transition mostly happens around ethylenyl bond. And according to the literature study of Ramakrishna et al.,\cite{27} their lifetime of $S_1$ state are 0.4 ps and 0.5 ps respectively and their vibrational cooling lifetime of $T_1$ state are 4 ps and 3 ps correspondingly.

These results agree with the theoretical expectation that complex 29 and \textbf{FPtF} may have similar behaviors at excited state since the electron/charge transfer of complex \textbf{FPtF} is mainly located at $\pi$ to $\pi^*$ orbital of the ethylenyl group in one side ligand.\cite{3} However, for \textbf{FPtF}, hardly any shifted signal around ground state absorption can be observed, this may be caused by the less involvement of metal core, since fluorenyl has a much larger conjugation than phenyl ring, hence allowing electrons delocalized further away from the Pt atom than the situation in \textit{trans}-PtCl$_2$((C≡CPh)$_2$),\cite{23} therefore the increase of bond order may be too small to detect or even covered by ground state bleaching.

The $S_1$ lifetime of \textbf{FPtF} is only 0.5 ps while that of the vibrational cooling of
$T_1$ transient band is 3 ps and a long lived transient band is still present after 2900 ps at nearly the same frequency (1895 cm$^{-1}$). These indicate that the $S_1$, $T_1$ and higher $T_n$ states of $\text{FptF}$ have very similar charge distribution and agree with the suggestion that LUMO mainly localized on the $C≡C\ pπ^*$ orbital. Since triplet states are normally transformed from the singlet states by ultrafast ISC process, thus the triplet state features can be reflected by LUMO patterns.$^{[26]}$

![Figure 6.30: $ν(C≡C)$ TRIR spectra of complex $\text{FptF}$ in THF at 293 K](image)

Figure 6.30: $ν(C≡C)$ TRIR spectra of complex $\text{FptF}$ in THF at 293 K
For complexes 30 and NFPtNF, although their ν(C≡C) absorption at ground state are quite similar (2097 cm\(^{-1}\) and 2095 cm\(^{-1}\)), as demonstrated in Figures 6.35 and 6.36, their TRIR spectra generate significantly different results. Upon excitation, \(T_1\) signal appears at 1854 cm\(^{-1}\) and 1910 cm\(^{-1}\); according to the literature study of Ramakrishna et al.,\(^{26}\) the lifetimes of \(S_1\) state are 0.4 ps and 0.5 ps, while the cooling vibrational lifetimes are 16 ps and 30 ps, respectively. The existence of significant Δν(C≡C) between ground and excited state, 243 cm\(^{-1}\) and 185 cm\(^{-1}\) respectively, indicates that the excitation is also largely located at \(\pi-\pi^*\) transitions of ethylenyl moiety, and the reduced bond order resulting in a vibration shifted to an intermediate frequency between that of typical double bond and triple bond stretch.\(^{19}\)
For NFPtNF, it shows interesting TRIR result which provides more signatures than that of the symmetry broken spectrum of trans-PtCl₂((C≡CPh)₂ in literature.[23] First of all there is no obvious new band formed in the higher shifted region than ground state ν(C≡C). Also, the initial S₁ shift is at 1955 cm⁻¹ and the transient T₁ band is vibrationally cooled at 1910 cm⁻¹ after ultrafast ISC process. The further shift between S₁ and T₁ states suggests that there may be a little bit greater π* contribution in triplet state.[26] Meanwhile, the ligand region also shows similar vibrations with a ultrafast S₁ band and a blue shifted long lasting T₁ signal (>2000 ps). According to the literature data,[3] DFT calculations support that ligand to metal charge transfer (LMCT) states significantly contributes to the excited behavior of NFPtNF,[3] and it is in agreement with the TRIR results that the excited states of complex NFPtNF is delocalized across the whole ligand.

However, no conclusion could be drawn on the symmetry broken mechanism of this complexes since only one ν(C≡C) with reduced bond order could be clearly observed after excitation. The explanation for higher shifted TRIR signal of trans-PtCl₂((C≡CPh)₂ at exited state is based on a 3ππ*/3MLCT mixed manifold,[26] where HOMO occupies a little bit dₓy orbital and is π-antibonded to C≡C bonding orbital; while LUMO has no electron density on the metal core.[26] In this case, upon excitation, the removal of electron density from dₓy orbital will slightly increase the bond order of the “not excited” ligand and as a result another slightly higher shifted stretch could be observed apart from the much lower shifted one.
However, NFPtNF shows remarkable LMCT characters.[3] According to the literature report,[3] the contribution of dπ to HOMO is much less than that of FPtF (4.1% to 9.8%), therefore there is a large possibility that the antibonding character between dxy and C≡C is much weaker so that the change in TRIR spectrum is too small to detect. Meanwhile, as demonstrates in Figure 6.37, DFT calculations generate that both ligands make contributions to the HOMO and LUMO of NFPtNF;[3] also, the metal π orbital occupies as much as 12.3% LUMO contribution as well.[3] These significant differences from \textit{trans}-PtCl$_2$(C≡CPh)$_2$ make the excited states behavior of NFPtNF more complicated, letting the possible existence of delocalized excited state extending to both ligands could not be neglected.

Figure 6.32 (a): $\nu$(C≡C) TRIR spectra of NFPtNF in THF at 293 K.
Figure 6.32 (b): Ligand vibration TRIR spectra of NFPtNF in THF at 293 K.

As demonstrated in Figure 6.36, the fs-TRIR result of complex 30 is even more interesting. It shows an obvious absorption band shifted slightly to the lower energy region than that of the ν(C≡C) absorption bands at ground state, and another one much more shifted to 1854 cm⁻¹. As complex 30 only contain one triple bond, it can be suggested that the excited state is not only focused on the C≡C π* but delocalized within the whole molecule. And the delocalization can be further confirmed by the strong intensity of transient ligand vibration together with the similar charge distribution among singlet and triplet states. This may be caused by the shortened conjugation length, which significantly strengthens the interaction between ligand and the metal core, and leads to much stronger spin orbital coupling. The enhancement of metal-ligand coupling could also be supported by the shorter lifetime of S₁ (0.7 ps) when comparing complex 30 to
complex NFPtNF (2 ps).

Figure 6.33: TRIR spectra of complex 30 in THF at room temperature: (a) ν(C≡C)

(b) Ligand vibrations
Table 6.4: TRIR summary of the complexes 29, 30, FPtF and NFPtNF

<table>
<thead>
<tr>
<th>Complex</th>
<th>$S_1$ [a] (ps)</th>
<th>$T_1$ [a] (ps)</th>
<th>$S_0$ [b] $\nu$ (cm$^{-1}$)</th>
<th>$T_1$ [b] $\nu$ (cm$^{-1}$)</th>
<th>$\Delta\nu$ [b] (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>0.4</td>
<td>4</td>
<td>2090</td>
<td>1887</td>
<td>203</td>
</tr>
<tr>
<td>30</td>
<td>0.7</td>
<td>16</td>
<td>2097</td>
<td>1854</td>
<td>243</td>
</tr>
<tr>
<td>FPtF</td>
<td>0.5</td>
<td>3</td>
<td>2095</td>
<td>1895</td>
<td>200</td>
</tr>
<tr>
<td>NFpTnF</td>
<td>2</td>
<td>30</td>
<td>2095</td>
<td>1910</td>
<td>185</td>
</tr>
</tbody>
</table>

[a] Lifetime of $S_1$; vibrational cooling lifetime of $T_1$

[b] $\nu$(C≡C) at ground state and excited state.

Figure 6.34:[3]: Contour plots of the LUMO (top) and HOMO (bottom) for FPtF and NFPtNF as determined from the DFT calculations.
6.8 Concluding Remarks and Future Works

In this chapter, a series of Pt(II) acetylide complexes were designed, synthesized and fully characterized. Their photophysical properties were measured by UV/vis absorption and PL emission spectroscopy, and the electrochemical properties were generated through CV analysis. The fs-TRIR were performed for complexes 29, 30, FPtF and NFPtNF to demonstrate the molecular dipole change during excitation. And it is suggested that for complexes 29 and FPtF, the excited states are mostly located at one side C≡C π* orbital, which is in coherent with the study of trans-PtCl₂(C≡CPPh)₂ in the literature.\[7b, 19\] The results for complexes 30 and NFPtNF are more complicated. It is suggested that instead of broken symmetry at the excited state, NFPtNF more likely has an excited state largely maintained symmetry and is supported by the literature DFT calculation.\[3\] The fs-TRIR spectrum of complex 30 demonstrates a significantly different situation from all of the other complexes since only little antibonding character is established during excitation. And we need further characterization such as XRD, DFT calculation or other transient spectroscopy to afford detail information on its conformation and distribution of excited states.
6.8 References


Chapter 7

Concluding Remarks and Future Work

Metal-organic compounds containing Ir(III) or Pt(II) have drawn great attention in the last decades, especially in the development of high efficiency light emitting and solar energy harvesting materials, since they provide very good metal-ligand orbital coupling characters with remarkable triplet emitting properties.

In this thesis, we synthesized several series of organometallic complexes: i) – COOH containing heteroleptic Ir(III) complexes that can be applied for dye sensitized solar cell (DSSC) fabrication; ii) Ir(III) complexes containing 2-substituted carbazolyl based ligand for organic light-emitting diode (OLED) application; iii) tetraphenylethylene (TPE) coordinated Pt(II) acetylides for aggregation induced emission (AIE) analysis; iv) Ir(III) and Pt(II) cyclometalated complexes for AIE analysis; v) ultrafast femtosecond time resolved infrared (fs-TRIR) study of symmetric and asymmetric Pt(II) acetylide complexes. The newly generated complexes have been subjected to $^1$H NMR / $^{13}$C NMR / $^{31}$P NMR / MS / IR / UV-vis / PL spectra respectively.
We found that by modifying the ligand fields, the heteroleptic complexes in chapter 2 can get PCE of 0.40-0.50 % and filled factors of 62.9-70.9%, which is respectable in iridium-based DSSC development. The results benefit from the strong ILCT characters which significantly shift the dominant absorption to the latter region. However, all of the UV/vis spectra of the tested complexes in chapter 2 still only cover a small part of the visible region; therefore we expect further device performance improvement through ligand modification to generate better solar spectral coverage. It is also quite obvious that the 2-substituted carbazolyl based ligand shifted the PL spectra of the cyclometalated Ir(III) complexes to lower energy region, with EL emission at 587-696 nm and $\eta_{ext}$ of 5.62-17.33%, providing suitable candidates for deep red emitter development. As for TPE containing Pt(II) acetylides, two of them show relatively good AIE behavior, while the others having ligand with electron donating or withdrawing character are not AIE active. As the mechanisms for this kind of AIE properties have not been well established yet, it is necessary to have a clearer look at the excited state electron/energy redistribution of this kind of complexes. It is quite surprising that all of the Ir(III) and Pt(II) cyclometalated complexes containing TPE ligands hardly show any AIE phenomenon. This indicates that the AIE mechanism for organometallic complexes may be much more complicated. Hence, we studied the AIE property of a published good emitter with very simple structure (complex 23) and it shows significantly enhanced emission at the
aggregate states. To have a better look, we further synthesized complex 24 with broken conjugation relative to complex 23, and the AIE analysis of complex 24 further confirmed that the enhanced emission of complex 23 comes from both restriction of rotation (RIR) and intermolecular interaction processes. This provides a fundamental clue for future development of organometallic AIE active materials. To have a better understanding of the excited state behavior of Pt(II) acetylides, in collaboration with Prof. Chisholm’s group, we studied the fs-TRIR spectra of some symmetric and mono-ligand Pt(II) acetylides based on reporting group, ν(C≡C) stretching mode. The results of these complexes show that only those with neutral fluorenyl moiety as ligand meet our expectation that the excitation transition is mainly localized on one of the ligands. However, the same conclusion could not be drawn for the other complex with strong LMCT character, and further investigations are required to determine the charge distribution at the excited state.

In the future work for the development of Ir(III) based DSSCs, complexes with strong ILCT characters may achieve advantages as their dominant absorption band lie in the lower energy region. Research may also be focused on the combination of TRIR technique and AIE active Pt(II) acetylides, since it can provide a clearer view regarding the electron density distribution of excited state, generating important information for possible energy loss pathway. Furthermore,
efforts could also be made on the AIE active cyclometalated metal complexes based on the intermolecular interactions rather than simple RIR process.
Chapter 8

Experimental Details

8.1 General Procedures

Most of the reactions were performed under a nitrogen atmosphere except for the synthesis of 2-bromo-9,9-diethylfluorene and the bromination reactions. For some reactions, solvents were carefully dried over sodium sticks and distilled before usage. Reagents or chemicals without stated were obtained from commercial sources and directly used without further purification. Separation of products was achieved by silica column chromatography or glass plates (20 cm x 20 cm) preparative thin-layer chromatography.

The mass spectra were recorded on Autoflex Bruker HR-MALDI-TOF (High resolution matrix-assisted laser desorption/ionization time-of-flight) spectrometer. Infrared (IR) data were obtained on a Nicolet Magna 550 Series II FTIR spectrometer. NMR spectra were measured in CDCl$_3$, DMSO-d$_6$ or MeOH-d$_4$ on a Varian Inova 400 MHz FT-NMR spectrometer; chemical shifts were quoted relative to the internal standard tetramethylsilane for $^1$H and $^{13}$C{1H} NMR data and the external reference 85% H$_3$PO$_4$ for $^{31}$P NMR data. The UV-absorption data were measured by a Hewlett Packard 8453 spectrometer and the photoluminescence spectra were measured in CH$_2$Cl$_2$ with a PTI Fluorescence
Master Series QM1 spectrophotometer. The lifetime was measured by recording the emission intensity of a PMT and a HP54522A 500 MHz oscilloscope after excited by a pulsed 355 nm line of a Q-switched Nd:YAG laser. The electrochemical properties were taken by CH Instrument CV 630C using a working electrode made of glassy carbon, a Ag/Ag⁺ reference electrode and a Pt wire as counter electrode within 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile solution and the experiments were performed in N₂ atmosphere and the scan rate is 50 mV/s.

8.2 Materials

Compounds bromoethane, 2-bromofluorene, 2,4-dibromonitrobenzene, iodotoluene, 4-iodo-toluene, butyllithium \([^\text{aBuLi}]\), 2-chloroisoquinoline, 2-chloro-5-trifluoromethylpyridine, 2-chloro-5-picoline, 1,4-dibromobenzene, trimethylborate, iridium(III) acetylacetone \([\text{Ir(acac)}_3]\) and iridium(III) chloride \((\text{IrCl}_3\cdot\text{nH}_2\text{O})\) as well as all the solvents in use were purchased from commercial sources and used without further purification unless otherwise specified. The compounds 2-bromo-9,9-diehtylfluorene,\(^{[1]}\) 2-bromo-9,9-diehyl-7-iodo-fluene,\(^{[1]}\) aryl boronic acid,\(^{[2]}\) aryl tributylstannane,\(^{[2]}\) diphenylbenzaldehyde,\(^{[3]}\) aryl trimethylsilane,\(^{[4]}\) \(\text{trans-[Pt(PEt}_3)_2\text{PhCl]}\),\(^{[5]}\) \(\text{trans-[Pt(PBu}_3)_2\text{Cl}_2}\),\(^{[4]}\) \(2-(4\text{-bromophenyl})\text{ethene-1,1,2-triyl}]\text{tribenzene}\),\(^{[6]}\) trimethyl{[4-
(1,2,2-triphenylvinyl)phenyl[ethynyl]silane,\(^6\)  \(\text{N-diphenyl-4} \)

-[(trimethylsilyl)ethyl]aniline,\(^5\)  \(9\)-(4-bromophenyl)carbazole,\(^7\)

9-(4-bromobenzyl)carbazole\(^8\)  \(7\)-bromo-9,9-diethyl-N,N-diphenylfluoren-2-amine,\(^4\) were prepared according to the literature methods.

### 8.3 Synthesis of the Key Compounds for Chapter 2

#### Synthesis of \(L_1\)

Pd(PPh\(_3\))\(_4\) (70 mg, 0.061 mmole) was added into a toluene (40 mL) mixture of 2-bromo-9,9-diethylfluorene (1.78 g, 5.91 mmole) and 2-tributylstannanyl-pyridine (2.14 g, 8.87 mmole). The reaction was heated to 110 °C for 2 days. Then it was extracted by ethyl acetate after cooling down. The organic layer was collected and dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure by rota-evaporation. The residue was purified by silica column chromatography by using hexane/ethyl acetate mixture as eluent. The product was a white solid (80%). \textit{Spectral data:} \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 8.71 (m, 1 H, Ar), 8.06 (m, 1H, Ar), 7.59 (m, 1H, Ar), 7.78-7.61 (m, 4H, Ar), 7.33-7.29 (m, 3H, Ar), 7.15-7.10 (m, 1H, Ar), 2.17-1.99 (m, 4H, CH\(_2\)), 0.35 (m, 6H, CH\(_3\)) (ppm); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 157.38, 150.20, 150.10, 149.30, 142.23, 140.71, 137.93, 136.36, 127.10, 126.63, 125.62, 122.66, 121.58, 121.02, 120.29, 119.71, 119.59 (Ar), 56.15 (quat. C), 32.68 (CH\(_2\)), 8.55 (CH\(_3\)) (ppm).
Synthesis of \textbf{L}_2

9,9-Diethylfluorene-2-boronic acid (1.07 g, 4.03 mmole) was dissolved in THF (40 mL) before \text{Pd(PPh}_3)_4 (70 mg, 0.061 mmole), 2-chloro-5-trimethylpyridine (0.171 g, 1.34 mmole), and 2 M aqueous K$_2$CO$_3$ (4 mL) were added. After heated to reflux for 2 days, the mixture was cooled down to room temperature and extracted with ethyl acetate. The organic layers were collected and dried over anhydrous sodium sulfate followed by concentration under reduced pressure. The residue was purified by silica column chromatography with hexane/ethyl acetate as eluting system. The product was a white solid (75\%). \textit{Spectral data:} $^1$H NMR (CDCl$_3$): $\delta$ 8.54-8.55 (s, 1H, Ar), 7.92-7.98 (m, 2H, Ar), 7.69-7.79 (m, 3H, Ar), 7.56-7.58 (m, 1H, Ar), 7.26-7.36 (m, 2H, Ar), 2.38 (s, 3H, CH$_3$), 2.16-2.06 (m, 4H, CH$_2$), 0.35-0.32 (m, 6H, CH$_3$) (ppm).

Synthesis of \textbf{L}_3

The compound was prepared following the similar procedures as described for \textbf{L}_2 except that 2-chloro-5-methylpyridine (0.241 g, 1.33 mmole) was used to react with 9,9-diethylfluorene-2-boronic acid (1.41 g, 5.32 mmole). The product was a white solid product (90\%). \textit{Spectral data:} $^1$H NMR (CDCl$_3$): $\delta$ 8.97 (m, 1H, Ar), 8.06 (m, 1H, Ar), 8.03-7.89 (m, 2H, Ar), 7.49-7.91 (m, 1H, Ar), 7.83-7.82 (m, 1H, Ar), 7.78-7.76 (m, 1H, Ar), 7.37-7.36 (m, 3H, Ar), 2.17-2.06 (m, 4H, CH$_2$)
(ppm); $^{13}$C NMR (CDCl$_3$): $\delta$ 151.78, 150.81, 148.23, 147.33, 140.64, 140.03, 136.70, 129.40, 126.47, 124.02, 123.94, 122.67, 121.40, 120.58, 119.71, 119.53, 110.00 (Ar), 56.43 (quat. C), 32.98 (CH$_2$), 8.90 (CH$_3$) (ppm).

**Synthesis of L$_4$**

The compound was prepared following a similar procedure as described for L$_2$ except that 2-chloro-5-methylpyridine (0.224 g, 1.37 mmole) was used to react with 9,9-diethylfluorene-2-boronic acid (1.46 g, 5.49 mmole). The product was a white solid product (83%). *Spectral data:* $^1$H NMR (CDCl$_3$): $\delta$ 8.66-8.64 (m, 1H, Ar), 8.14-8.12 (m, 1H, Ar), 7.91-7.86 (m, 2H, Ar), 7.81-7.78 (m, 1H, Ar), 7.72-7.66 (m, 4H, Ar), 7.57-7.53 (m, 1H, Ar), 7.40-7.35 (m, 3H, Ar) (ppm); $^{13}$C NMR (CDCl$_3$): $\delta$ 159.12, 147.67, 140.40, 139.01, 136.15, 134.96, 129.73, 129.58, 129.06, 128.22, 127.48, 126.59, 126.30, 126.11, 125.76, 124.94 122.61, 129.99, 117.17 (Ar), 57.02 (quat. C), 34.81 (CH$_2$), 8.37 (CH$_3$) (ppm).

**Synthesis of 9,9-diethyl-2-thienyl-fluorene**

The compound was prepared following the similar route as described for L$_2$ except that 2-bromo-9,9-diethylfluorene (1.00 g, 3.32 mmole) was used to react with thiophene-2-boronic acid (1.27 g, 9.95 mmole). The product was a white solid (73%). *Spectral data:* $^1$H NMR (CDCl$_3$): $\delta$ 7.68-7.65 (m, 2H, Ar), 7.60-7.56 (m, 2H, Ar), 7.35-7.27 (m, 4H, Ar), 7.23-7.22 (m, 1H, Ar), 7.07-7.04 (m, 1H, Ar),
2.08-1.99 (m, 4H, CH₂), 0.36-0.32 (m, 6H, CH₃) (ppm); $^{13}$C NMR (CDCl₃): $\delta$
150.79, 150.15, 145.26, 141.21, 141.14, 133.34, 128.16, 127.25, 127.03, 125.05, 124.57, 123.01, 122.97, 120.33, 120.17, 119.81 (Ar), 56.29 (quat. C), 32.90 (CH₂), 8.69 (CH₃) (ppm).

**Synthesis of 2-bromothienyl-9,9-diethyl-2-thienyl-fluorene**

N-Bromosuccinimide (NBS) (152 mg, 0.855 mmole) was added into a solution of 9,9-diethyl-2-thienyl-fluorene (248mg, 0.814 mmole) in 4:1 (v/v) chloroform and acetic acid mixture slowly. The reaction was stirred overnight in dark, followed by extraction with ethyl acetate and washed by brine for three times, dried over anhydrous Na₂SO₄, and purified by silica column chromatography with hexane as eluent (66%). *Spectral data:* $^1$H NMR (CDCl₃): $\delta$ 7.71-7.68 (m, 2H, Ar), 7.51-7.49 (m, 1H, Ar), 7.45 (m, 1H, Ar), 7.36-7.32 (m, 3H, Ar), 7.12-7.11 (m, 1H, Ar), 7.05-7.04 (m, 1H, Ar) (ppm); $^{13}$C NMR(CDCl₃): $\delta$ 150.81, 150.05, 146.63, 141.52, 140.83, 132.39, 130.82, 127.30, 126.95, 124.58, 122.92, 120.11, 119.89, 119.75, 119.66, 110.91 (Ar), 56.21 (quat. C), 32.75 (CH₂), 8.50 (CH₃) (ppm).
Synthesis of $L_5$

The compound was synthesized following a similar procedure as described for $L_1$, except that 2-bromothienyl-9,9-diethyl-2-thienyl-fluorene (1.5 g, 3.96 mmole) was used as the starting material. The product was a white solid (78%).

*Spectral data:* $^1$H NMR (CDCl$_3$): $\delta$ 8.60-8.58 (m, 1H, Ar), 7.73-7.66 (m, 6H, Ar), 7.58-7.57 (m, 1H, Ar), 7.40-7.39 (m, 1H, Ar), 7.37-7.31 (m, 3H, Ar), 7.19-7.14 (m, 1H, Ar), 2.09-2.03 (m, 4H, CH$_2$), 0.37-0.34 (m, 6H, CH$_3$) (ppm); $^{13}$C NMR (CDCl$_3$): $\delta$ 152.52, 150.72, 150.16, 149.62, 146.97, 143.37, 141.48, 140.96, 136.63, 132.95, 127.22, 126.92, 125.38, 124.56, 123.65, 122.92, 121.80, 120.20, 120.07, 119.74, 118.42 (Ar), 56.43 (quat. C), 32.98 (CH$_2$), 8.90 (CH$_3$) (ppm).

Synthesis of $(p$-bromophenyl)dimesitylborane

1,4-Dibromobenzene (1.76 g, 7.46 mmole) in dry diethyl ether was chilled at -78 °C in frozen acetone bath for 30 minutes, after that dimesitylboron fluoride (2.00 g 7.46 mmole) in dry ether was dropped in the mixture. The reaction was then slowly warmed up to room temperature and stirred overnight. The mixture was extracted by diethyl ether and washed by brine, dried over sodium carboxyl ate anhydrous and purified by column chromatography with hexane. The product was white solid (41%). *Spectral data:* $^1$H NMR: $\delta$ 7.49 (m, 2H, Ar), 7.37 (m, 2H, Ar), 6.82 (s, 4H, Ar), 2.30 (s, 6H, CH$_3$), 2.00 (s, 12H, CH$_3$) (ppm); $^{13}$C NMR: $\delta$
144.5, 141.3, 140.8, 138.9, 137.8, 131.3, 128.1, 127.3 (Ar), 23.4 (CH₃), 21.2 (CH₃) (ppm).

**Synthesis of L₆**

The compound was generated from a similar procedure as described for L₁, except that (p-bromophenyl)dimesitylboration (1.20 g, 2.95 mmole) was used as starting material. The product was white solid (65%). *Spectral data:* $^1$H NMR (CDCl₃): $\delta$ 8.72-8.70 (m, 1H, Ar), 7.97 (m, 2H, Ar), 7.78-7.76 (m, 2H, Ar), 7.64-7.62 (m, 2H, Ar), 7.27-7.24 (m, 1H, Ar), 6.84 (s, 4H, Ar), 2.32 (s, 6H, CH₃), 2.03 (s, 12H, CH₃) (ppm); $^{13}$C NMR (CDCl₃): $\delta$ 157.17, 149.76, 146.36, 142.31, 141.69, 140.85, 138.71, 136.78, 128.17, 126.39, 122.47, 121.02 (Ar), 23.45, 21.22 (CH₃) (ppm).

**Synthesis of L₇**

L₇ was prepared by a similar procedure as described for L₁, except that 4-bromotriphenylamine (3.14 g, 9.67 mmole) was used as starting material. The product was a pale yellow solid (59%). *Spectral data:* $^1$H NMR (CDCl₃): $\delta$ 8.64-8.63 (m, 1H, Ar), 7.88-7.84 (m, 2H, Ar), 7.72-7.65 (m, 2H, Ar), 7.29-7.23 (m, 4H, Ar), 7.18-7.12 (m, 7H, Ar), 7.06-7.02 (m, 2H, Ar) (ppm); $^{13}$C NMR
Synthesis of $L_8$

$L_8$ was prepared by reaction of 4-(diphenylamino)-benzaldehyde (3.00 g, 11.0 mmole) with 1.5 equivalent of 2- aminothiophenol (2.06 g, 16.5 mmole) in water (60 mL) and refluxed under nitrogen overnight. The resulting mixture was washed by brine and further purified by column chromatography using a mixture of hexane and CH$_2$Cl$_2$ as eluent (24%). $^1$H NMR (CDCl$_3$): $\delta$ 8.05-8.02 (m, 1H, Ar), 7.95-7.92 (m, 2H, Ar), 7.88-7.86 (m, 1H, Ar), 7.49-7.45 (m, 1H, Ar), 7.37-7.29 (m, 5H, Ar), 7.19-7.10 (m, 8H, Ar) (ppm); $^{13}$C NMR (CDCl$_3$): $\delta$ 168.28, 149.49, 147.08, 143.43, 129.41, 127.47, 127.03, 125.07, 123.67, 122.35, 117.79 (Ar) (ppm).

Synthesis of (2,2’-bipyridine)-4,4’,-dicarboxylate acid

4,4’-Dimethyl-2,2’-bipyridine (2.00 g, 10.9 mmole) in 50% H$_2$SO$_4$ was added in KMnO$_4$ (4.00 g, 25.3 mmole) and stirred for one hour in an ice bath. After the mixture was chilled on ice the other portion of KMnO$_4$ (4.00 g, 25.3 mmole) was added, then the mixture was slowly allowed to warm up to room temperature followed by reflux overnight. The mixture was adjusted to pH 8.
before filtering, and the brown residue was washed by aqueous NaOH (1 M, 10 mL). The collected colorless filtrate was further washed by chloroform before being acidified to pH 6. A white precipitate came out and was collected by filtration and washed with ethanol for three times. The product was a white solid (65%). Spectral data: $^1$H NMR (DMSO-d$_6$): $\delta$ 8.93-8.92 (m, 2H, Ar), 8.86-8.85 (m, 2H, Ar), 7.93-7.91 (m, 2H, Ar) (ppm).

**Synthesis of (2,2’-bipyridine)-4,4’-dimethylcarboxylate**

(2,2’-bipyridine)-4,4’-dicarboxylate acid (200 mg, 0.819 mmole) was added in 20 mL ethanol solution followed by several drops of concentrated H$_2$SO$_4$, and the mixture was refluxed overnight. Then the reaction was cooled by ice before aqueous K$_2$CO$_3$ was added in, a white participate formed and was collected by filtration, dried over vacuum. The product was a white solid (70%). Spectral data: $^1$H NMR (CDCl$_3$): $\delta$ 8.97 (m, 2H, Ar), 8.88-8.87 (m, 2H, Ar), 7.93-7.71 (m, 2H, Ar), 4.01 (s, 6H, CH$_3$) (ppm).

**Synthesis of charged Ir(III) complexes 1-7**

The complexes 1-7 were synthesized by a similar procedure. IrCl$_3\cdot$3H$_2$O and 2.5 equivalents of each corresponding ligand was reacted at 90°C in a mixture of 2-ethoxyethanol and water (3:1, v/v) overnight first. Then the Ir dimers were
collected by vacuum filtration and washed with two portions of hexane (2 mL) followed by one portion of cold ethanol (1 mL). The crude dimers were stayed under vacuum until dried thoroughly and were directly used for the next step. Each dimer and (2,2'-bipyridine)-4,4'-dimethylcarboxylate were dissolved in 1:1 (v/v) methanol/CH₂CH₂ solution and refluxed for 4 hours. Then KPF₆ was added and the reaction was stirred for another 4 hours before it was concentrated by rota-evaporation and purified through column chromatography using CH₂CH₂ and methanol mixture as eluent. Then each of the Ir precursors containing (2,2'-bipyridine)-4,4'-dimethylcarboxylate was dissolved in THF with several drops of aqueous NaOH (1 M), and the mixture was stirred overnight. After that the reaction was adjusted to approximately pH = 6, and the solvent was removed under reduced pressure rota-evaporation. The product was purified by column chromatography with CH₂CH₂ and methanol as eluent.

**Synthesis of charged Ir(III) complexes 8 and 9**

Ir dimers, (2,2'-bipyridine)-4,4',-dicarboxylate acid and an extensive amount of Na₂CO₃ were dissolved in a 1:1 (v/v) methanol/CH₂CH₃ mixture and refluxed overnight. After cooled down to room temperature, the solvent was removed under reduced pressure and the pH value of the mixture was carefully adjusted to 5 by adding 0.5 M hydrochloric acid. The product was collected by centrifugation
as a participate form and further purified by column chromatography with 
CH$_2$CH$_2$ and methanol as eluent.

The $^1$H NMR of complexes 1-7 were determined in DMSO-d$_6$ while those of 
complexes 8 and 9 were performed in MeOH-d$_4$. All of the $^{13}$C NMR could not be 
observed due to poor solubility.

1: An orange red powder (yield: 15%).

**Spectral data:** MS (MALDI-TOF) $m/z$: 1178.4 [M+H]$^+$. $^1$H NMR 
(DMSO-d$_6$): $\delta$ 8.83 (m, 2H, Ar), 8.40-8.38 (m, 2H, Ar), 8.04-8.01 (m, 2H, Ar), 
7.99-7.97 (m, 2H, Ar), 7.78-7.74 (m, 6H, Ar), 7.37-7.36 (m, 2H, Ar), 7.28-7.17 
(m, 10H, Ar), 2.17-1.92 (m, 8H, CH$_2$), 0.30-0.27 (m, 6H, CH$_3$), 0.12-0.08 (m, 6H, 
CH$_3$) (ppm).

2: A bright red powder (yield: 22%).

**Spectral data:** MS (MALDI-TOF) $m/z$: 1206.2 [M+H]$^+$. $^1$H NMR 
(DMSO-d$_6$): $\delta$ 8.83 (m, 2H, Ar), 8.66-8.64 (m, 2H, Ar), 8.42-8.39 (m, 2H, Ar), 
8.21 (m, 2H, Ar), 7.84-7.74 (m, 6H, Ar), 7.40-7.23 (m, 8H, Ar), 6.60 (m, 2H, Ar), 
2.18-1.91 (m, 8H, CH$_2$), 0.33-0.30 (m, 6H, CH$_3$), 0.06-0.03 (m, 6H, CH$_3$) (ppm).
3: An orange powder (yield: 17%).

*Spectral data: MS (MALDI-TOF) m/z: 1314.2 [M+H]⁺. ¹H NMR (DMSO-d$_6$): δ 8.78 (m, 2H, Ar), 8.30-8.26 (m, 2H, Ar), 7.96-7.84 (m, 2H, Ar), 7.82-7.72 (m, 2H, Ar), 7.52 (m, 2H, Ar), 7.36-7.34 (m, 2H, Ar), 7.27-7.20 (m, 6H, Ar), 6.58 (m, 2H, Ar), 2.18 (m, 6H, CH$_3$), 2.15-1.90 (m, 8H, CH$_2$), 0.31-0.27 (m, 6H, CH$_3$), 0.14-0.10 (m, 6H, CH$_3$) (ppm).

4: A deep red powder (yield: 19%).

*Spectral data: MS (MALDI-TOF) m/z: 1278.2 [M+H]⁺. ¹H NMR (DMSO-d$_6$): δ 8.98-8.96 (m, 2H, Ar), 8.83 (m, 2H, Ar), 8.31 (m, 2H, Ar), 8.17-8.15 (m, 2H, Ar), 7.99-7.93 (m, 5H, Ar), 7.66-7.62 (m, 7H, Ar), 7.52-7.50 (m, 2H, Ar), 7.41-7.39 (m, 2H, Ar), 7.28-7.24 (m, 2H, Ar), 7.16-7.12 (m, 2H, Ar), 6.88-6.86 (m, 2H, Ar), 6.58 (m, 2H, Ar), 2.14-1.99 (m, 8H, CH$_2$), 0.30-0.24 (m, 12H, CH$_3$) (ppm).

5: A deep red powder (yield: 22%).

*Spectral data: MS (MALDI-TOF) m/z: 1197.8 [M+H-PF$_6$]⁺. ¹H NMR (DMSO-d$_6$): δ 8.83 (m, 2H, Ar), 8.03-8.02 (m, 2H, Ar), 7.93-7.92 (m, 2H, Ar), 7.88-7.84 (m, 2H, Ar), 7.80-7.78 (m, 6H, Ar), 7.58-7.54 (m, 6H, Ar), 7.42-7.40
(m, 2H, Ar), 7.34-7.32 (m, 4H, Ar), 7.00-6.97 (m, 2H, Ar), 6.59 (m, 2H, Ar) 2.00 (m, 8H, CH₂), 0.25-0.15 (m, 12H, CH₃) (ppm).

6: A bright red powder (yield: 16%).

Spectral data: MS (MALDI-TOF) m/z: 991.2 [M+H-PF⁵-COOH]⁺. ¹H NMR (DMSO-d₆): δ 8.78 (m, 2H, Ar), 8.00-7.98 (m, 2H, Ar), 7.85-7.78 (m, 6H, Ar), 7.62-7.58 (m, 2H, Ar), 7.40-7.38 (m, 2H, Ar), 6.97-6.95 (m, 2H, Ar), 6.86-6.82 (m, 2H, Ar), 6.70 (m, 8H, Ar), 6.10 (m, 2H, Ar), 5.76 (m, 4H, Ar), 2.27, 1.74 (mes) (ppm).

7: A red powder (yield: 21%).

Spectral data: MS (MALDI-TOF) m/z: 1182.7 [M+H]⁺. ¹H NMR (DMSO-d₆): δ 8.76 (m, 2H, Ar), 7.96-7.90 (m, 4H, Ar), 7.79-7.77 (m, 2H, Ar), 7.69-7.67 (m, 2H, Ar), 7.51-7.47 (m, 2H, Ar), 7.27-7.21 (m, 10H, Ar), 7.05-7.02 (m, 4H, Ar), 6.96-6.94 (m, 6H, Ar), 6.69-6.66 (m, 2H, Ar), 6.53-6.50 (m, 2H, Ar), 5.79-5.78 (m, 2H, Ar) (ppm).

8: A red powder (yield: 21%).

Spectral data: MS (MALDI-TOF) m/z: 1191.6 [M+H]⁺. ¹H NMR (MeOH-d₄): δ 8.87(m, 2H, Ar), 8.20-8.19 (m, 2H, Ar), 7.89-7.87 (m, 2H, Ar), 7.62-7.60 (m,
2H, Ar), 7.47-7.45 (m, 2H, Ar), 7.14-7.10 (m, 2H, Ar), 6.98-6.94 (m, 8H, Ar), 6.89-6.85 (m, 6H, Ar), 6.79-6.76 (m, 8H, Ar), 6.55-6.52 (m, 2H, Ar), 5.91-5.88 (m, 2H, Ar), 5.75-5.74 (m, 2H, Ar) (ppm).

**9:** A red powder (yield: 21%).

*Spectral data:* MS (MALDI-TOF) m/z: 1079.6 [M+H]+. ¹H NMR (MeOH-d₄): δ 8.95 (m, 2H, Ar), 8.11-8.09 (m, 2H, Ar), 7.86-7.84 (m, 2H, Ar), 7.53-7.51 (m, 2H, Ar), 7.44-7.41 (m, 2H, Ar), 7.35-7.31 (m, 2H, Ar), 7.18-7.17 (m, 2H, Ar), 7.11-7.01 (m, 8H, Ar), 6.94-6.90 (m, 4H, Ar), 6.85-6.82 (m, 8H, Ar), 6.55-6.50 (m, 4H, Ar), 5.79-5.78 (m, 2H, Ar) (ppm).

### 8.4 Synthesis of the Key Compounds for Chapter 3

**Synthesis of 4-bromo-2-nitrobiphenyl**

Phenylboronic acid (1.50 g, 12.3 mmol), 2,5-dibromonitrobenzene (3.45 g, 12.3 mmol) and Pd(PPh₃)₄ (1.42 g, 1.42 mmol) were dissolved in a mixture of toluene (250 mL) and 2 M Na₂CO₃ (12 mL). The mixture was heated at 90 °C for 5 h, followed by dilution with deionized H₂O after cooled down to room temperature. The organic phase was extracted by diethyl ether and washed by brine. The combined extracts were dried over Na₂SO₄ anhydrous and concentrated under reduced pressure rota-evaporation to give a dark brown liquid. The product
was purified by chromatography by using a mixture of hexane and CH₂Cl₂ as eluent. The mixture was used in the next step without further purification (70%).

*Spectral data:* ¹H NMR (CDCl₃): δ 8.00 (m, 1H, Ar), 7.75 (m, 1H, Ar), 7.45-7.41 (m, 3H, Ar), 7.33 (m, 1H, Ar), 7.31-7.27 (m, 2H, Ar) (ppm); ¹³C NMR (CDCl₃): δ 136.5, 135.6, 135.5, 133.5, 131.8, 129.5, 129.1, 128.8, 128.0, 127.3, 124.2, 121.6 (Ar) (ppm).

**Synthesis of 2-bromocarbazole**

4-Bromo-2-nitrobiphenyl (1.50 g, 5.42 mmol) and P(OEt)₃ (4.80 g, 37.9 mmol) were heated to reflux for 10 h. The excess P(OEt)₃ was distilled away under vacuum. The residue was then diluted with a 1:1 mixture of MeOH and deionized H₂O and the precipitates were collected through filtration and washed several times with a 1:1 mixture of MeOH/H₂O and hexane. The product was further purified by column chromatography using hexane as eluent and it was a white solid (38%). *Spectral data:* ¹H NMR (CDCl₃): δ 11.40 (s, 1H, NH), 8.15-8.11 (m, 2H, Ar), 7.68 (m, 1H, Ar), 7.54-7.19 (m, 4H, Ar) (ppm); ¹³C NMR (CDCl₃): δ 140.6, 139.9, 126.1, 121.9, 121.8, 121.6, 121.3, 120.3, 119.1, 118.2, 113.5, 111.2 (Ar) (ppm).

**Synthesis of 2-bromo-N-phenylcarbazole**
The compound was generated through Ullmann condensation. 2-Bromocarbazole (2.50 g, 10.2 mmol) reacted with iodobenzene (3.12 g, 15.3 mmol) in the presence of CuI (1.35 g, 7.14 mmol), KOH (4.00 g, 71.4 mmol) and 1,10-phenanthroline (1.42 g, 7.14 mmol) in p-xylene (50 mL). The mixture was refluxed at 140 °C for two days. The cooled mixture was extracted with CH₂Cl₂ and washed with water and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the product was purified by silica column chromatography using hexane as eluent to give a pure white solid (90%). Spectral data: ¹H NMR (CDCl₃): δ 8.10-8.08 (m, 1H, Ar), 7.98-7.96 (m, 1H, Ar), 7.63-7.59 (m, 2H, Ar), 7.53-7.48 (m, 4H, Ar), 7.42-7.35 (m, 3H, Ar), 7.30-7.27 (m, 1H, Ar) (ppm); ¹³C NMR (CDCl₃): δ 141.68, 141.08, 137.03, 130.05, 127.91, 127.11, 126.34, 123.05, 122.71, 122.25, 121.44, 120.36, 120.26, 119.50, 112.78, 109.95 (Ar) (ppm).

**Synthesis of 2-bromo-N-tolylcarbazole**

This compound can be produced by using similar procedure as described for 2-bromo-N-phenylcarbazole, except for using 4-iodotoluene to undergo Ullmann condensation with 2-bromocarbazole. Spectral data: ¹H NMR (CDCl₃): δ 7.99-7.97 (m, 2H, Ar), 7.85-7.83 (m, 2H, Ar), 7.48 (m, 2H, Ar), 7.35-7.28 (m, 6H, Ar), 7.22-7.18 (m, 2H, Ar), 7.05-7.03 (m, 1H, Ar), 6.87-6.85 (m, 1H, Ar), 2.36 (s, 3H, CH₃) (ppm); ¹³C NMR (CDCl₃): δ 155.54, 142.00, 141.40, 137.96, 134.50, 134.50, 134.50.
Synthesis of 2,6-dimethyl-9-phenylcarbazole

This compound was synthesized by a similar procedure as of 2-bromo-N-phenylcarbazole by using p-tolylboronic acid as the starting material.  
*Spectral data:* $^1$H NMR (CDCl$_3$): $\delta$ 7.99-7.97 (m, 2H, Ar), 7.85-7.83 (m, 2H, Ar), 7.48 (m, 2H, Ar), 7.35-7.28 (m, 6H, Ar), 7.22-7.18 (m, 2H, Ar), 7.05-7.03 (m, 1H, Ar), 6.87-6.85 (m, 1H, Ar), 2.36 (s, 3H, CH$_3$) (ppm); $^{13}$C NMR (CDCl$_3$): $\delta$ 155.54, 142.00, 141.40, 137.96, 134.50, 132.58, 130.84, 130.40, 127.06, 126.53, 123.13, 122.85, 122.39, 121.66, 120.49, 119.74, 118.83, 113.00, 110.17 (Ar), 21.45 (CH$_3$) (ppm).

Synthesis of L$_9$

This compound was prepared by a similar procedure as described for L$_2$, except that 9-tolyl-carbazole-2-boronic acid (1.851 g, 6.45 mmole) and 2-chloropicoline (0.527 g, 3.22 mmole) were used as the starting materials, giving the product as pale-brown crystals (64%).  
*Spectral data:* $^1$H NMR (CDCl$_3$): $\delta$ 8.52 (m, 1H, Ar), 8.23-8.17 (m, 2H, Ar), 8.03 (m, 1H, Ar), 7.90-7.88 (m, 1H, Ar), 7.70-7.68 (m, 1H, Ar), 7.55-7.53 (m, 1H, Ar), 7.50-7.48 (m, 2H, Ar), 7.45-7.39
(m, 4H, Ar), 7.32-7.29 (m, 1H, Ar), 2.50 (s, 3H, CH₃), 2.37 (s, 3H, CH₃) (ppm);

$^{13}$C NMR (CDCl₃): δ 155.49, 149.96, 141.86, 141.61, 137.47, 137.33, 134.88, 131.34, 130.58, 127.18, 126.70, 126.10, 123.63, 122.96, 120.55, 120.47, 120.45, 119.89, 118.84, 109.90, 108.14 (Ar), 21.28 (CH₃), 18.19 (CH₃) (ppm).

By using similar synthetic strategy, L₁₀, L₁₂ and L₁₃ could be generated.

**Synthesis of L₁₀ (52%)**

*Spectral data: *$^1$H NMR (CDCl₃): δ 8.92-8.91 (m, 1H, Ar), 8.24-8.22 (m, 2H, Ar), 8.18-8.16, (m, 1H, Ar), 8.08 (m, 2H, Ar), 7.95-7.87 (m, 1H, Ar), 7.48-7.38 (m, 6H, Ar), 7.33-7.29 (m, 1H, Ar), 2.41 (s, 3H, CH₃) (ppm); $^{13}$C NMR (CDCl₃): δ 161.31, 146.53, 146.49, 142.10, 141.50, 137.72, 135.71, 134.63, 133.79, 133.76, 130.65, 127.12, 126.63, 124.75, 124.54, 124.22, 122.66, 120.68, 120.27, 120.11, 119.02, 110.03, 108.86 (Ar), 21.28 (CH₃) (ppm).

**Synthesis of L₁₁**

This compound was prepared by a similar procedure as described for L₂, except that 2-bromo-N-tolylcarbazole (1.43 g, 4.45 mmol) and 2-(tributylstannyl) pyridine (2.15 g, 6.68 mmol) were used as the starting materials. The product was obtained as a white solid (75%). *Spectral data: *$^1$H NMR (CDCl₃): δ 8.69-8.67 (m, 1H, Ar), 8.23-8.16 (m, 2H, Ar), 8.03 (m, 1H, Ar), 7.91-7.88 (m, 1H, Ar), 2.36 (s,
3H, CH₃) (ppm); ¹³C NMR (CDCl₃): δ 158.15, 149.61, 141.91, 141.59, 137.53, 137.43, 136.68, 134.83, 130.58, 127.19, 126.19, 123.87, 122.88, 121.81, 121.01, 120.51, 120.47, 119.91, 118.94, 109.91, 108.38 (Ar), 21.28 (CH₃) (ppm).

By using similar synthetic strategy, L₁₄ could be generated.

Synthesis of L₁₂ (68%)

Spectral data: ¹H NMR (CDCl₃): δ 8.67-8.65 (m, 1H, Ar), 8.35-8.20 (m, 3H, Ar), 7.90-7.88 (m, 1H, Ar), 7.81-7.80 (m, 1H, Ar), 7.71-7.65 (m, 3H, Ar), 7.56-7.47 (m, 5H, Ar), 7.70-7.36 (m, 3H, Ar). 2.37 (s, 3H, CH₃) (ppm); ¹³C NMR (CDCl₃): δ 161.49, 142.17, 141.81, 141.23, 137.52, 137.44, 136.91, 134.84, 130.55, 129.99, 127.97, 127.18, 127.14, 127.06, 126.96, 126.29, 123.51, 123.02, 122.09, 120.62, 120.04, 119.97, 119.85, 111.44, 110.03 (Ar), 21.23 (CH₃) (ppm).

Synthesis of L₁₃ (61%)

Spectral data: ¹H NMR (CDCl₃): δ 8.6116-8.5974 (m, 1H, Ar), 8.29-8.27 (m, 1H, Ar), 8.24-8.21 (m, 1H, Ar), 8.16-8.14 (m, 1H, Ar), 7.89-7.87 (m, 1H, Ar), 7.75 (m, 1H, Ar), 7.70-7.50 (m, 8H, Ar), 7.46-7.40 (m, 3H, Ar), 7.37-7.32 (m, 1H, Ar) (ppm); ¹³C NMR (CDCl₃): δ 161.43, 142.14, 141.62, 141.05, 137.54, 137.48, 136.89, 129.96, 129.91, 127.93, 127.56, 127.28, 127.14, 127.05, 126.93, 126.28,
Synthesis of L_{14} (70%)

Spectral data: $^1$H NMR (CDCl$_3$): $\delta$ 8.68-8.66 (m, 1H, Ar), 8.18-8.16 (m, 1H, Ar), 8.05-8.03 (m, 2H, Ar), 7.89-7.87 (m, 1H, Ar), 7.79-7.71 (m, 2H, Ar), 7.66-7.59 (m, 4H, Ar), 7.52-7.47 (m, 1H, Ar), 7.21-7.12 (m, 3H, Ar), 2.50 (s, 3H, CH$_3$) (ppm); $^{13}$C NMR (CDCl$_3$): $\delta$ 158.19, 149.59, 142.21, 141.49, 137.65, 136.99, 136.68, 136.64, 129.99, 127.56, 127.43, 124.10, 121.75, 121.64, 120.96, 120.70, 120.24, 120.16, 119.04, 109.96, 108.29 (Ar), 22.23 (CH$_3$) (ppm).

Synthesis of heteroleptic Ir(III) complexes 10-15

The heteroleptic complexes 10-15 were generated through two steps. First the Ir dimers were synthesized by the reaction between IrCl$_3$·3H$_2$O and 2.5 equivalent corresponding ligand. After heated at 90 °C in a mixture of 2-ethoxyethanol and water (3:1, v/v) overnight, the dimers were formed as precipitates and were collected by vacuum filtration, followed by washing with two portions of hexane (2 mL) and one portion of cold ethanol (1 mL). The crude products were put under vacuum until dried completely. Then each of the crude dimers and three equivalents of acetylacetone were reacted in 2-ethoxyethanol with the presence of
10 equivalents of Na₂CO₃. The reaction mixture was then heated at 90 °C overnight, and the resulting mixture was collected after extraction with CH₂Cl₂. The organic solvent was removed through reduced pressure evaporation and the crude product was purified by column chromatography followed by preparative TLC plates using CH₂Cl₂/hexane as eluent.

**10**: A bright orange red powder (yield: 26%).

*Spectral data:* MS (MALDI-TOF) m/z: 986.1 [M+H]+. ¹H NMR (CDCl₃): δ
8.47 (m, 2H, Ar), 7.81-7.79 (m, 2H, Ar), 7.66-7.64 (m, 2H, Ar), 7.61 (m, 2H, Ar), 7.59-7.56 (m, 2H, Ar), 7.38-7.33 (m, 8H, Ar), 7.20-7.13 (m, 4H, Ar), 7.00-7.96 (m, 2H, Ar), 6.88 (m, 2H, Ar), 5.24 (s, 1H, acac), 2.47-2.46 (m, 12H, CH₃), 1.81 (s, 3H, CH₃) (ppm); ¹³C NMR (CDCl₃): δ 184.44, 166.32, 148.16, 142.99, 141.41, 137.92, 137.31, 136.58, 135.63, 134.06, 131.05, 130.32, 126.99, 125.19, 125.10, 123.08, 122.61, 120.42, 118.63, 118.22, 108.99, 105.43, 100.53 (Ar), 29.00 (CH₃), 21.25 (CH₃), 18.63 (CH₃) (ppm).

**11**: A bright red powder (yield: 22%).

*Spectral data:* MS (MALDI-TOF) m/z: 1094.0 [M+H]+. ¹H NMR (CDCl₃): δ
8.91 (m, 2H, Ar), 8.02-7.92 (m, 4H, Ar), 7.69-7.66 (m, 4H, Ar), 7.36 (m, 8H, Ar), 7.25-7.21 (m, 2H, Ar), 7.15-7.13 (m, 2H, Ar), 7.04-7.01 (m, 2H, Ar), 6.90 (m, 2H,
Ar), 5.31 (m, 1H, acac), 2.47 (s, 3H, CH₃), 1.83 (s, 3H, CH₃) (ppm); ¹³C NMR (CDCl₃): δ 185.37, 172.76, 145.46, 142.11, 140.45, 138.03, 137.07, 136.27, 135.23, 133.77, 130.47, 126.93, 126.33, 124.36, 124.09, 123.76, 123.26, 122.05, 121.66, 120.73, 119.18, 118.28, 109.26, 107.54, 100.95 (Ar), 28.74 (CH₃), 21.25 (CH₃) (ppm).

12: An orange red powder (yield: 25%).

Spectral data: MS (MALDI-TOF) m/z: 958.5 [M+H]⁺. ¹H NMR (CDCl₃): δ 8.67-8.65 (m, 2H, Ar), 7.92-7.90 (m, 2H, Ar), 7.78-7.74 (m, 2H, Ar), 7.66-7.64 (m, 4H, Ar), 7.38-7.33 (m, 8H, Ar), 7.21-7.13 (m, 6H, Ar), 7.01-6.97 (m, 2H, Ar), 6.91 (m, 2H, Ar), 5.25 (s, 1H, acac), 2.47 (s, 3H, CH₃), 1.80 (s, 3H, CH₃) (ppm); ¹³C NMR (CDCl₃): δ 184.56, 169.09, 148.40, 142.65, 141.57, 137.92, 136.67, 136.47, 135.56, 134.75, 130.33, 126.99, 125.58, 125.44, 123.05, 122.49, 121.38, 120.45, 118.75, 118.64, 109.06, 105.98, 100.50 (Ar), 28.89 (CH₃), 21.24 (CH₃) (ppm).

13: A deep red powder (yield: 22%).

Spectral data: MS (MALDI-TOF) m/z: 1049.8 [M+H]⁺. ¹H NMR (CDCl₃): δ 8.92-8.90 (m, 2H, Ar), 8.61-8.59 (m, 2H, Ar), 8.34 (m, 2H, Ar), 7.98-7.96 (m, 2H, Ar), 7.73-7.64 (m, 2H, Ar), 7.52-7.50 (m, 4H, Ar), 7.52-7.50 (m, 4H, Ar),
7.44-7.41 (m, 4H, Ar), 7.37-7.35 (m, 4H, Ar), 7.21-7.15 (m, 4H, Ar), 7.07 (m, 2H, Ar), 6.94-6.90 (m, 2H, Ar), 5.31 (s, 1H, acac), 2.47 (s, 3H, CH₃), 1.76 (s, 3H, CH₃) (ppm); ¹³C NMR (CDCl₃): δ 184.71, 169.87, 143.95, 141.80, 140.89, 138.45, 137.62, 137.22, 136.54, 135.62, 130.31, 130.28, 127.55, 127.31, 126.95, 126.62, 126.38, 125.74, 125.44, 123.73, 122.29, 120.78, 119.51, 118.84, 112.10, 109.11, 100.54 (Ar), 28.84 (CH₃), 21.25 (CH₃) (ppm).

14: A deep red powder (yield: 40%).

Spectral data: MS (MALDI-TOF) m/z: 1030.1 [M+H]+. ¹H NMR (CDCl₃): δ 8.91-8.89 (m, 2H, Ar), 8.61-8.60 (m, 2H, Ar), 8.37 (m, 2H, Ar), 7.97-7.95 (m, 2H, Ar), 7.71-7.68 (m, 2H, Ar), 7.65-7.61 (m, 2H, Ar), 7.56-7.50 (m, 12H, Ar), 7.41-7.37 (m, 2H, Ar), 7.24-7.16 (m, 4H, Ar), 7.09 (m, 2H, Ar), 6.95-6.91 (m, 2H, Ar), 5.21 (m, 1H, acac), 1.76 (s, 3H, CH₃) (ppm); ¹³C NMR (CDCl₃): δ 184.76, 171.19, 169.78, 144.04, 141.63, 140.87, 138.64, 138.31, 137.48, 137.23, 130.39, 129.71, 127.57, 127.35, 126.87, 126.80, 126.37, 125.86, 125.51, 123.78, 122.40, 120.84, 119.62, 119.06, 112.05, 109.11, 100.61 (Ar), 21.09 (CH₃) (ppm).

15: A deep red powder (yield: 40%).

Spectral data: MS (MALDI-TOF) m/z: 958.2 [M+H]+. ¹H NMR (CDCl₃): δ 8.66-8.65 (m, 2H, Ar), 7.90-7.88 (m, 2H, Ar), 7.78-7.74 (m, 2H, Ar), 7.64 (m, 2H,
Ar), 7.60-7.48 (m, 10H, Ar), 7.43-7.40 (m, 2H, Ar), 7.19-7.16 (m, 2H, Ar), 6.97 (m, 2H, Ar), 6.87-6.81 (m, 4H, Ar), 5.25 (m, 1H, acac), 2.36 (s, 3H, CH₃), 1.80 (s, 3H, CH₃) (ppm); ¹³C NMR (CDCl₃): δ 184.54, 169.13, 148.38, 142.10, 141.86, 138.40, 137.77, 136.44, 135.69, 135.05, 129.71, 127.19, 126.73, 125.84, 122.88, 121.23, 120.53, 120.43, 120.22, 118.51, 109.19, 105.85, 100.48 (Ar), 28.90, 21.09 (CH₃) (ppm).

8.5 Synthesis of the Key Compounds for Chapter 4

Synthesis of L₁₅

Trimethyl[(4-(1,2,2-triphenylvinyl)phenyl)ethynyl]silane (200 mg, 0.467 mmole) was stirred with K₂CO₃ (68 mg, 0.490 mmole) in a mixture of methanol and dichloromethane (1:1, v/v) at room temperature overnight. The solvent was removed by rota-evaporation under vacuum and the residue was further purified by column chromatography with hexane and dichloromethane (5:1, v/v) as eluent. The product L₁₅ was found to be a white crystal (85%). Spectral data: ¹H NMR (CDCl₃): δ 7.24-7.21 (m, 2H, Ar), 7.13-7.09 (m, 9H, Ar), 7.05-6.97 (m, 8H, Ar), 3.03 (s, 1H, C≡C-H) (ppm); ¹³C NMR (CDCl₃): δ 144.6, 143.5, 143.4, 143.3, 141.9, 140.2, 131.4, 131.3, 127.9, 127.8, 127.7, 126.8, 126.7 (Ar), 119.9 (C≡C), 83.9 (C=C) (ppm).
By using similar synthetic strategy, $L_{16}$ could also be generated.

$L_{16}$: a white solid (yield: 79%).

*Spectral data:* $^1$H NMR (CDCl$_3$): $\delta$ 7.35-7.31 (m, 2H, Ar), 7.29-7.24 (m, 4H, Ar), 7.11-7.04 (m, 6H, Ar), 6.98-6.95 (m, 2H, Ar), 3.02 (s, 1H, $\text{C} \equiv \text{C}-\text{H}$) (ppm);

$^{13}$C NMR (CDCl$_3$): $\delta$ 148.6, 147.3, 133.3, 129.6, 125.2, 123.8, 122.2, 114.9 (Ar), 84.1 (C≡C), 76.3 (ppm).

**Synthesis of $L_{17}$**

[(2,4-Difluorophenyl)ethynyl]trimethylsilane (252 mg, 1.20 mmole) was stirred with NaOH (48 mg, 1.20 mmole) in a mixture of methanol and tetrahydrofuran (1:1, v/v) at room temperature overnight. The solvent was removed by rota-evaporation under vacuum and the crude product was used directly without further purification since it would decompose in a short time. The product $L_{15}$ (146 mg, 88%) was found to be a white oil. *Spectral data:* $\delta$ $^1$H NMR (CDCl$_3$): 7.50-7.44 (m, 1H, Ar), 6.88-6.82 (m, 2H, Ar), 3.27 (s, 1H, $\text{C} \equiv \text{CH}$) (ppm).
Synthesis of cis-[Pt(P\textsubscript{Bu\textsubscript{3}})\textsubscript{2}Cl\textsubscript{2}]

A mixture of water and ethanol (2:1, v/v) was prepared and stirred vigorously. K\textsubscript{2}PtCl\textsubscript{4} (1.00 g, 2.41 mmole) was added in and a red slurry was formed. Then tri-\textit{n}-butylphosphine (1.00 g, 4.94 mmole) was injected by syringe when the starting materials almost dissolved. The reaction was maintained for 2 days at ambient condition. And a slurry with lots of white participate can be observed. After that the ethanol was removed by rota-evaporation and the aqueous mixture left was extracted by dichloromethane for three times. The organic layers were combined and concentrated to provide the crude product as white needle crystals (92%). It was used directly without further purification.

Synthesis of trans-[Pt(P\textsubscript{Bu\textsubscript{3}})\textsubscript{2}Cl\textsubscript{2}]

Cis-Pt(PBu\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (1.48 g, 2.21 mmole) was dried thoroughly to remove organic solvents. Then it was put into a small round bottle flask and stirred at 130 °C for half an hour. After that the temperature was raised to above 200 °C and stayed for 3-6 h. It could be observed that the white crystals melted and turned into yellowish green in color. After cooling down, the mixture was purified by a short silica column with hexane and dichloromethane (4:1, v/v) as eluent. The product was generated as yellowish green crystals (1.38g, 91%).
**Synthesis of trans-[Pt(PEt$_3$)$_2$PhCl]**

Cis-[Pt(PEt$_3$)$_2$PhCl] was prepared by the similar procedure of cis-[Pt(P$^{n}$Bu$_3$)$_2$Cl$_2$] by using triethylphosphine and K$_2$PtCl$_4$ as the starting materials. Then it was reacted with 2.5 equivalents of freshly prepared phenyllithium to afford cis-[Pt(PEt$_3$)$_2$Ph$_2$]. The crude product was purified by column chromatography with hexane/diethyl ether (9:1, v/v). After that it was mixed with 1.2 equivalents of hydrochloride in diethyl ether solution and stirred in fresh benzene overnight to generate cis-[Pt(PEt$_3$)$_2$PhCl] . The solvent was removed by rota-evaporation and a catalytic amount of triethylphosphine was added. The mixture was heated to reflux in dry hexane overnight. The crude product was purified by column chromatography with hexane/diethyl ether (9:1, v/v) as eluent to afford trans-[Pt(PEt$_3$)$_2$PhCl] as a white solid.

**Synthesis of complex 16**

Ligand L$_{15}$ (46 mg 0.13 mmol) and trans-[Pt(PBu$_3$)$_2$Cl$_2$] (40 mg 0.06 mmol) was stirred overnight in triethylamine (8 mL) and CH$_2$Cl$_2$ (8 mL) mixture with catalytic amount CuI (2 mg). The solvent was removed through rota-evaporation and the product was purified by column chromatography with hexane and dichloromethane (4:1, v/v) as eluent. Complex 16 was generated as a white solid (72%). **Spectral data:** MS (MALDI-TOF) m/z: 1310.7 [M+H]$^+$; FTIR: 2096 cm$^{-1}$ (C≡C), 1597 cm$^{-1}$ (C=C); $^1$H NMR (CDCl$_3$): $\delta$ 7.12-7.00 (m, 34H, Ar), 6.88-6.86
Synthesis of complex 17

*Trans*-\([\text{Pt}(\text{PBu}_3)_2\text{Cl}_2]\) (500 mg, 0.746 mmole) was stirred in a triethylamine (8 mL) and dichloromethane (8 mL) solution with a catalyst amount of copper(I) iodide (2 mg). Then \(L_{16}\) (50 mg, 0.187 mmole) dissolved in the same solvent system was dropped in slowly and stirred at room temperature for three hours, after that the solvent was removed followed by column chromatography with hexane and dichloromethane as eluent to afford intermediate mono-substituted Pt complexes (34 mg, 20%). Then it was reacted with ligand \(L_{15}\) still in the mixture of triethylamine (8 mL) and dichloromethane (8 mL) with catalytic amount copper(I) iodide. The unsymmetrical product complex 17 can be generated after solvent rota-evaporation and column chromatography purification (hexane:dichloromethane = 8:1, v/v), and complex 17 was generated as a pale yellow oil (42%). Spectral data: MS (MALDI-TOF) \(m/z\): 1223.1 [M+H]+; FTIR: 2054 cm\(^{-1}\) (C≡C), 1634 cm\(^{-1}\) (C=C); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.24-7.20 (m, 3H, Ar), 2.15-2.09 (m, 12H, PBu\(_3\)), 1.64-1.56 (m, 12H, PBu\(_3\)), 1.47-1.40 (m, 12H, PBu\(_3\)), 0.93-0.90 (m, 18H, PBu\(_3\)) ppm; \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 144.04, 143.93, 143.91, 141.09, 140.35, 140.24, 131.49, 131.40, 131.38, 130.96, 130.13, 127.65, 127.56, 127.53, 127.10, 126.30, 126.23 (Ar), 109.24, 108.78 (C≡C), 26.35, 24.40, 23.89, 13.78 (PBu\(_3\)) \(\delta\) (ppm). \(^{31}\)P NMR (161 MHz, CDCl\(_3\)): 2.82 (\(^1J_{p-p} = 1173\) Hz) (ppm).
Synthesis of complex 18

L_{17} (103 mg, 0.746 mmole) was reacted with 2.5 M n-butyl lithium (0.3 mL, 0.750 mmole) at -78 °C in dry ether for 30 min first, then trans-[Pt(PBu_{3})_{2}Cl_{2}] (500 mg, 0.746 mmole) dissolved in dry ether was dropped in by syringe. The reaction mixture was stirred for another 3 h to afford a mono-substituted Pt complex, and it was purified by column chromatography with hexane and dichloromethane as eluent (219 mg, 38%). Then it (40 mg, 0.0518 mmole) was reacted with L_{15} in the mixture of triethylamine (6 mL) and dichloromethane (6 mL) with catalyst copper(I) iodide (2 mg) and stirred at room temperature for three hours, the solvent was then removed by rota-evaporation and the product was purified by column chromatography with hexane and dichloromethane as eluent to afford complex 17 (37%). Spectral data: MS (MALDI-TOF) m/z: 949.1 [M+H]^+; FTIR: 2100 cm$^{-1}$ (C≡C), 1601 cm$^{-1}$ (C=C); $^1$H NMR (CDCl$_3$): $\delta$ 7.24-7.18 (m, 1H, Ar), 7.11-6.99 (m, 17H, Ar), 6.85-6.84 (m, 2H, Ar), 6.75-6.69
(m, 2H, Ar), 2.15-2.10 (m, 12H, PBu₃), 1.58-1.53 (m, 12H, PBu₃), 1.47-1.37 (m, 12H, PBu₃), 0.92-0.88 (m, 18H, PBu₃) (ppm); ¹³C NMR (CDCl₃): δ 144.02, 143.90, 141.03, 140.35, 140.33, 133.22, 131.49, 131.41, 131.40, 130.99, 130.17, 127.68, 127.60, 127.57, 126.95, 126.35, 126.27 (Ar), 110.72, 110.68, 110.50, 110.47, 109.41, 108.36, 103.85, 103.59, 103.34, 99.92 (C≡C), 26.33, 24.37, 23.73, 13.83 (PBU₃) (ppm); ³¹P NMR (161 MHz, CDCl₃): δ 2.70 (1J_P-Pt = 1161 Hz) δ (ppm).

**Synthesis of complex 19**

*Trans*-[PhPt(PEt₃)₂Cl] (33 mg, 0.0621 mmole) and L₁₅ (22 mg, 0.0621 mmole) was stirred in a triethylamine (6 mL) and dichloromethane (6 mL) solution with a catalytic amount of copper(I) iodide (2 mg) overnight. Complex 19 can be generated as a white solid (41%) after removing solvent by rota-evaporation and column chromatography purification (hexane:dichloromethane = 4:1, v/v). **Spectral data**: MS (MALDI-TOF) m/z: 864.4 [M+H]⁺; FTIR: 2095 cm⁻¹ (C≡C), 1600 cm⁻¹ (C≡C); ¹H NMR (CDCl₃): δ 7.36-7.25 (m, 2H, Ar), 7.13-6.99 (m, 17H, Ar), 6.97-6.93 (m, 2H, Ar), 6.85-6.77 (m, 2H, Ar), 1.78-1.70 (m, 12H, PEt₃), 1.11-1.03 (m, 18H, PEt₃) (ppm); ¹³C NMR (CDCl₃): δ 144.10, 143.98, 143.96, 141.09, 140.14, 140.04, 139.18, 131.49, 131.40, 130.98, 130.32, 127.76, 127.57, 127.53, 127.29, 126.30, 126.26, 126.22,
121.20 (Ar), 110.16 (C≡C), 15.01, 8.04, (PEt₃) (ppm); ³¹P NMR (161 MHz, CDCl₃): δ 3.64 (¹J_P-Pt = 1312 Hz) (ppm).

8.6 Synthesis of the Key Compounds for Chapter 5

Synthesis of L₁₈

[2-(4-Bromophenyl)ethene-1,1,2-triyl]tribenzene (1.00 g, 2.44 mmole) was reacted with 2-(tributylstannyl)pyridine (1.07g, 2.93 mmole) through Stille coupling in the presence of Pd(PPh₃)₄ (70 mg, 0.061 mmole), the mixture was heated to reflux in toluene for two days. After that the solvent was removed by rota-evaporation and L₁₈ was generated as a white solid (79%) after column chromatography by using hexane and dichloromethane as eluent. Spectral data: 

¹H NMR (CDCl₃): δ 8.66-8.64 (m, 1H, Ar), 7.76-7.74 (m, 2H, Ar), 7.72-7.65 (m, 2H, Ar), 7.20-7.04 (m, 18H, Ar) (ppm); ¹³C NMR (CDCl₃): δ 157.17, 149.61, 144.65, 143.70, 143.60, 141.43, 140.46, 137.24, 136.65, 131.83, 131.43, 131.36, 127.81, 127.70, 127.66, 126.60, 126.53, 126.49, 126.19, 121.94, 120.43 (Ar) (ppm).

By using similar synthetic strategy, L₁₉ and L₂₀ could also be generated.
**L₁₉:** a white solid (657 mg, 80%).

*Spectral data:* $^1$H NMR (CDCl₃): $\delta$ 8.02 (m, 2H, Ar), 7.56 (m, 2H, Ar), 7.35 (m, 8H, Ar) (ppm); $^{13}$C NMR (CDCl₃): $\delta$ 140.43 (Ar), 136.63, 132.98, 128.59, 125.97, 123.35, 120.77, 120.27, 120.10, 109.46 (Ar) (ppm).

**L₂₀:** a white solid (832 mg, 77%).

*Spectral data:* $^1$H NMR (CDCl₃): $\delta$ 8.66-8.68 (m, 1H, Ar), 8.15-8.13 (m, 2H, Ar), 7.89-7.87 (m, 2H, Ar), 7.73-7.69 (m, 1H, Ar), 7.65-7.63 (m, 1H, Ar), 7.46-7.42 (m, 2H, Ar), 7.40-7.38 (m, 2H, Ar), 7.28-7.24 (m, 4H, Ar), 7.22-7.19 (m, 1H, Ar), 5.58 (s, 2H, CH₂) (ppm); $^{13}$C NMR (CDCl₃): $\delta$ 140.51, 137.22, 135.96, 129.53, 125.78, 122.87, 121.41, 119.82, 109.64 (Ar), 48.72 (CH₂) (ppm).

**Synthesis of heteroleptic Ir(III) complex 20**

The dimer corresponding to complex 20 was synthesized by reacting IrCl₃·3H₂O (103 mg, 0.293 mmole) with 2.5 equivalents of ligand L₁₈ (300 mg, 0.732 mmole) in a mixture of 2-ethoxyethanol (6 mL) and water (2 mL). The mixture was heated overnight at 80°C. The dimer was formed as a precipitate and collected by vacuum filtration, followed by washing with two portions of hexane (2 mL) and one portion of cold ethanol (1 mL). The crude dimer (280 mg, 0.134
mmole) were put under vacuum and dried thoroughly for three days. After that, it was reacted with Na$_2$CO$_3$ (142 mg, 1.34 mmole) and acetylacetone (40 mg, 0.402 mmole) in 2-ethoxyethanol at 100 °C overnight. Then the mixture was extracted with CH$_2$Cl$_2$ and the organic layers were collected. The product was concentrated by reduced pressure evaporation and purified by column chromatography and preparative TLC plates using CH$_2$Cl$_2$/hexane solution mixture as eluent. The product was an orange red powder (89 mg, 30%). *Spectral data:* MS (MALDI-TOF) m/z: 1108.6 [M+H]$^+$; $^1$H NMR (CDCl$_3$): δ 8.80-8.79 (m, 3H, Ar), 7.46-7.37 (m, 6H, Ar), 7.14-7.12 (m, 3H, Ar), 7.01-6.90 (m, 18H, Ar), 6.87-6.80 (m, 15H, Ar), 6.76-6.72 (m, 12H, Ar), 6.46-6.38 (m, 6H, Ar), 5.51 (m, 3H, Ar) (ppm); $^{13}$C NMR (CDCl$_3$): δ 167.43, 151.33, 144.37, 144.23, 143.87, 143.84, 143.39, 142.05, 141.45, 139.75, 135.24, 133.44, 131.44, 130.95, 127.42, 127.17, 126.32, 126.03, 125.87, 124.22, 123.00, 121.54, 118.50 (Ar) (ppm).

**Synthesis of homoleptic Ir(III) complex 21**

Complex 21 was synthesized by directly heating L$_{18}$ (300 mg, 0.293 mmole) and Ir(acac)$_3$ (41 mg, 0.0837 mmole) in ethylene glycerol and refluxed overnight. Complex 21 was generated as an orange red powder (28%) after column chromatography and preparative TLC plates by using hexane and dichloromethane as eluent. *Spectral data:* MS (MALDI-TOF) m/z: 1418.0 [M+H]$^+$; $^1$H NMR (CDCl$_3$): δ 8.80-8.79 (m, 3H, Ar), 7.46-7.37 (m, 6H, Ar),
7.14-6.91 (m, 18H, Ar), 6.84-6.81 (m, 15H, Ar), 6.76-6.72 (m, 12H, Ar), 6.46-6.38 (m, 6H, Ar), 5.51 (m, 3H, Ar) (ppm); $^{13}$C NMR (CDCl$_3$): $\delta$ 167.43, 151.33, 144.37, 144.23, 143.87, 143.84, 143.39, 142.05, 141.45, 139.75, 135.24, 133.44, 131.44, 130.95, 127.42, 127.17, 126.32, 126.03, 125.87, 124.22, 123.00, 121.54, 118.50 (Ar) (ppm).

Synthesis of Pt(II) complex 22

The corresponding dimer of complex 22 was synthesized by reacting K$_2$PtCl$_4$ (169 mg, 0.407 mmole) with ligand L$_{18}$ (200 mg, 0.489 mmole) in a mixture of 2-ethoxyethanol (6 mL) and water (2 mL). The mixture was heated overnight at 80°C. Then the precipitates were filtered under vacuum and washed with several portions of hexane (2 mL). The crude dimer (364 mg, 0.285 mmole) was dried thoroughly under vacuum for three days and used directly for the next step. It was heated with Na$_2$CO$_3$ (148 mg, 2.85 mmole) and acetylacetone (42.8 mg, 0.427 mmole) in 2-ethoxyethanol at 80 °C overnight. After that water (20 mL) was added into the mixture and the precipitate was collected by centrifugation. The product was a bright yellow powder (84 mg, 42%) and was purified by column chromatography using CH$_2$Cl$_2$/hexane as eluent. Spectral data: MS (MALDI-TOF) m/z: 703.2 [M+H]$^+$; $^1$H NMR (CDCl$_3$): $\delta$ 8.92-8.90 (m, 1H, Ar), 7.74-7.70 (m, 1H, Ar), 7.49-7.47 (m, 1H, Ar), 7.17-7.03 (m, 18H, Ar), 6.76-6.73 (m, 1H, Ar), 5.37 (s, 1H, Ar), 1.95 (s, 3H, CH$_3$), 1.80 (s, 3H, CH$_3$) (ppm); $^{13}$C NMR (CDCl$_3$): $\delta$ 184.41,
182.95, 166.81, 146.12, 143.39, 143.04, 142.96, 142.91, 141.62, 140.51, 139.74, 136.85, 136.42, 132.44, 130.41, 130.37, 130.24, 126.60, 126.47, 126.43, 125.88, 125.34, 125.13, 125.10, 121.12, 119.78, 117.31 (Ar), 101.25 (C=C) (ppm).

By using similar synthetic strategy, complexes 23 and 24 could also be generated.

23: A greenish yellow powder (42 mg, 38%).

*Spectral data:* MS (MALDI-TOF) m/z: 613.2 [M+H]+; ¹H NMR (CDCl₃): δ 9.06-9.05 (m, 1H, Ar), 8.16-8.14 (m, 2H, Ar), 7.89-7.82 (m, 2H, Ar), 7.70-7.65 (m, 2H, Ar), 7.58-7.56 (m, 2H, Ar), 7.43-7.39 (m, 2H, Ar), 7.30 (m, 2H, Ar), 7.20-7.16 (m, 1H, Ar), 5.46 (m, 1H, acac), 2.02 (s, 3H, CH₃), 1.87 (s, 3H, CH₃) (ppm); ¹³C NMR (CDCl₃): δ 184.80, 183.39, 166.41, 146.44, 142.72, 139.85, 137.31, 136.76, 127.57, 124.75, 123.04, 122.29, 121.01, 120.40, 119.04, 118.61, 117.60, 109.43, 101.54 (Ar), 27.18, 26.03 (CH₃) (ppm).

24: An orange yellow powder (37 mg, 43%).

*Spectral data:* MS (MALDI-TOF) m/z: 627.1 [M+H]+; ¹H NMR (CDCl₃): δ 8.94-8.92 (m, 1H, Ar), 8.13-8.11 (m, 2H, Ar), 7.72-7.68 (m, 1H, Ar), 7.58-7.57 (m, 1H, Ar), 7.48-7.39 (m, 5H, Ar), 7.25-7.18 (m, 3H, Ar), 7.06-7.02 (m, 1H, Ar), 6.62-6.59 (m, 1H, Ar), 5.57 (s, 2H, CH₂), 5.44 (s, 1H, acac), 1.98 (s, 3H, CH₃), 1.90 (s, 3H, CH₃) (ppm); ¹³C NMR (CDCl₃): δ 185.86, 184.20, 147.29, 143.99,
8.7 Synthesis of the Key Compounds for Chapter 6

Ligands \( \text{L}_{21} \)-\( \text{L}_{23} \) were prepared by the similar procedure as described for \( \text{L}_{15} \).

\( \text{L}_{21} \): a white solid (200 mg, 66%).

\textit{Spectral data:} \(^1\text{H} \) NMR (CDCl\(_3\)): \( \delta \) 7.73-7.69 (m, 1H, Ar), 7.68-7.65 (m, 1H, Ar), 7.51-7.48 (m, 2H, Ar), 7.37-7.33 (m, 3H, Ar), 3.14 (s, 1H, C≡C-H), 2.06-2.00 (m, 4H, CH\(_2\)), 0.34-0.30 (m, 6H, CH\(_3\)) (ppm); \(^{13}\text{C} \) NMR (CDCl\(_3\)): \( \delta \) 147.53, 140.65, 141.02, 129.95, 129.58, 128.04, 126.73, 123.11 (Ar), 81.24, 75.31 (C≡C), 51.24 (quat. C), 35.13, 9.02 (Et) (ppm).

\( \text{L}_{22} \): a white solid (228 mg, 58%).

\textit{Spectral data:} \(^1\text{H} \) NMR (CDCl\(_3\)): \( \delta \) 7.58-7.56 (m, 2H, Ar), 7.49-7.44 (m, 2H, Ar), 7.30-7.25 (m, 4H, Ar), 7.15-7.11 (m, 5H, Ar), 7.06-7.01 (m, 3H, Ar), 3.13 (s, C≡C-H, 1H), 2.00-1.84 (m, 4H, CH\(_2\)), 0.38-0.35 (m, 6H, CH\(_3\)) (ppm); \(^{13}\text{C} \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 147.96, 148.37, 146.51, 139.90, 133.14, 130.06, 125.54, 122.88, 121.60 (Ar), 76.38, 72.59 (C≡C), 57.56 (quat. C), 35.23, 8.66 (Et) (ppm).
L\textsubscript{25}: a pale yellow oil (225 mg, 62%).

*Spectral data:* \(^1\)H NMR (CDCl\textsubscript{3}): \(\delta\) 7.74-7.56 (m, 4H, Ar), 7.38-7.25 (m, 5H, Ar), 3.45 (s, C≡C-H, 1H), 2.11-2.06 (m, 4H, CH\textsubscript{2}), 0.40-0.36 (m, 6H, CH\textsubscript{3}) (ppm); \(^{13}\)C NMR (CDCl\textsubscript{3}): \(\delta\) 151.61, 149.77, 147.84, 147.71, 142.11, 135.56, 131.23, 129.19, 126.38, 123.95, 123.37, 122.64, 120.72, 119.22, 118.91, 118.87 (Ar), 84.77, 76.69 (C≡C), 56.07 (quat. C), 32.53, 8.47 (Et) (ppm).

**Synthesis of symmetric Pt(II) complex 25**

Complex 25 were prepared by the similar procedure as described for 16.

25: a pale yellow powder (32 mg, 43%).

*Spectral data:* FTIR: MS (MALDI-TOF) m/z: 1253.7 [M+H]\(^+\); 2100 cm\(^{-1}\) (C≡C); \(^1\)H NMR (CDCl\textsubscript{3}): \(\delta\) 7.70-7.65 (m, 4H, Ar), 7.54-7.49 (m, 4H, Ar), 7.35-7.27 (m, 6H, Ar), 7.18-7.17 (m, 2H, Ar), 6.84-6.83 (m, 2H, Ar), 2.16-2.12 (m, 12H, PBu\textsubscript{3}), 2.07-2.01 (m, 8H, Et), 1.64-1.59 (m, 12H, PBu\textsubscript{3}), 1.56-1.47 (m, 12H, PBu\textsubscript{3}), 1.00-0.96 (m, 18H, PBu\textsubscript{3}), 0.37-0.33 (m, 12H, Et) (ppm); \(^{13}\)C NMR (CDCl\textsubscript{3}): \(\delta\) 150.55, 150.01, 141.46, 141.16, 140.57, 133.53, 129.08, 128.33, 126.95, 126.87, 124.39, 122.87, 122.41, 119.94, 119.65, 119.57 (Ar), 56.12 (quat. C), 32.80 (Et), 26.43, 24.47, 24.04, 13.84 (PBu\textsubscript{3}), 8.57 (Et) (ppm); \(^{31}\)P NMR (161 MHz, CDCl\textsubscript{3}): \(\delta\) 2.77 (\(^1\)J\textsubscript{P-Pt} = 1201 Hz) (ppm).
Synthesis of unsymmetric Pt(II) complexes 26-28

Complex 26-28 were prepared by the similar procedure as described for 18.

26: a pale yellow oil (22 mg, 23%).

Spectral data: MS (MALDI-TOF) m/z: 982.0 [M+H]⁺; FTIR: 2104 cm⁻¹ (C≡C); ¹H NMR (CDCl₃): δ 7.64-7.61 (m, 1H, Ar), 7.55-7.52 (m, 1H, Ar), 7.31-7.18 (m, 5H, Ar), 6.76-6.70 (m, 2H, Ar), 2.20-2.14 (m, 12H, PBu₃), 0.94-0.90 (m, 18H, PBu₃), 0.33-0.28 (m, 6H, Et) (ppm); ¹³C NMR (CDCl₃): δ 149.85, 149.41, 141.70, 129.65, 126.73, 126.43, 125.40, 122.76, 119.30, 119.09 (Ar), 110.51, 103.60 (C≡C), 55.85 (quat. C), 32.83 (Et), 26.36, 24.41, 23.83, 13.83 (PBu₃), 8.44 (Et) (ppm); ³¹P NMR (161 MHz, CDCl₃): δ 2.77 (¹Jₚ-ₚt = 1166 Hz) (ppm).

27: a pale yellow oil (24 mg, 19%).

Spectral data: FTIR: MS (MALDI-TOF) m/z: 1004.4 [M+H]⁺; 2100 cm⁻¹ (C≡C); ¹H NMR (CDCl₃): δ 7.51-7.45 (m, 2H, Ar), 7.25-7.21 (m, 7H, Ar), 7.12-7.07 (m, 5H, Ar), 7.01-6.96 (m, 3H, Ar), 6.76-6.69 (m, 2H, Ar), 2.20-2.15 (m, 12H, PBu₃), 1.93-1.80 (m, 4H, Et), 1.63-1.57 (m, 12H, PBu₃), 1.49-1.41 (m, 12H, PBu₃), 0.94-0.91 (m, 18H, PBu₃), 0.36-0.32 (m, 6H, Et) (ppm); ¹³C NMR (CDCl₃): δ 150.24, 148.39, 147.04, 137.35, 136.06, 132.07, 128.71, 128.09,
125.77, 124.27, 122.83, 122.60, 121.24, 118.94, 118.58, 117.55 (Ar), 109.64, 109.43, 102.81, 102.55 (C≡C), 54.81 (quat. C), 31.68 (Et), 25.32, 23.36, 22.78, 12.72 (PBu$_3$), 7.45 (Et) (ppm); $^{31}$P NMR (161 MHz, CDCl$_3$): $\delta$ 2.85 ($^1J_{P, Pt} = 1164$ Hz) (ppm).

28: a pale yellow oil (21 mg, 23%).

_Spectral data:_ MS (MALDI-TOF) $m/z$: 753.4 [M+H]$^+$; FTIR: 2104 cm$^{-1}$ (C≡C); $^1$H NMR (CDCl$_3$): $\delta$ 7.25-7.14 (m, 7H, Ar), 7.08-7.06 (m, 4H, Ar), 7.00-6.92 (m, 4H, Ar), 6.75-6.69 (m, 2H, Ar), 2.17-2.11 (m, 12H, PBu$_3$), 1.60-1.58 (m, 12H, PBu$_3$), 1.48-1.39 (m, 12H, PBu$_3$), 0.93-0.89 (m, 18H, PBu$_3$) (ppm); $^{13}$C NMR (CDCl$_3$): $\delta$ 146.76, 143.71, 132.09, 130.60, 128.08, 122.96, 122.90, 122.51, 121.38 (Ar), 109.65, 109.41, 102.79, 102.53 102.28 (C≡C), 25.29, 23.34, 22.67, 12.79 (PBu$_3$) (ppm); $^{31}$P NMR (161 MHz, CDCl$_3$): $\delta$ 2.72 ($^1J_{P, Pt} = 1167$ Hz) (ppm).

**Synthesis of unsymmetric Pt(II) complexes 29-33**

Complex 29-33 were prepared by the similar procedure as described for 19.

29: a pale yellow solid (24 mg, 46%).

_Spectral data:_ MS (MALDI-TOF) $m/z$: 776.3 [M+H]$^+$; FTIR: 2101 cm$^{-1}$ (C≡C); $^1$H NMR (CDCl$_3$): $\delta$ 7.64-7.62 (m, 1H, Ar), 7.54-7.52 (m, 1H, Ar),
7.40-7.22 (m, 7H, Ar), 6.99-6.95 (m, 2H, Ar), 6.83-6.80 (m, 1H, Ar), 2.01-1.96 (m, 4H, Et), 1.83-1.76 (m, 12H, PEt₃), 1.16-1.08 (m, 18H, PEt₃), 0.36-0.32 (m, 6H, Et) (ppm); ¹³C NMR (CDCl₃): δ 149.92, 149.50, 141.73, 139.20, 138.26, 129.85, 127.95, 127.30, 126.68, 126.26, 125.34, 122.78, 121.22, 119.25, 119.05 (Ar), 111.28 (C≡C), 55.79 (quat. C), 32.73 (Et), 15.11 (PEt₃), 8.57 (Et), 8.12 (PEt₃) (ppm); ³¹P NMR (161 MHz, CDCl₃): δ 9.67 (¹J_P,Pt = 1311 Hz) (ppm).

30: a pale yellow solid (22 mg, 37%).

Spectral data: MS (MALDI-TOF) m/z: 776.4 [M+H]^⁺; FTIR: 2096 cm⁻¹ (C≡C); ¹H NMR (CDCl₃): δ 7.51-7.49 (m, 1H, Ar), 7.46-7.44 (m, 1H, Ar), 7.40-7.26 (m, 2H, Ar), 7.25-7.21 (m, 5H, Ar), 7.12-7.07 (m, 5H, Ar), 7.01-6.95 (m, 5H, Ar), 6.83-6.79 (m, 1H, Ar), 1.96-1.76 (m, 16H, Et+PEt₃), 1.16-1.08 (m, 18H, PEt₃), 0.39-0.35 (m, 6H, Et) (ppm); ¹³C NMR (CDCl₃): δ 151.33, 149.50, 148.07, 146.42, 139.19, 138.06, 137.17, 129.94, 129.11, 127.29, 125.27, 123.84, 123.59, 122.23, 121.21 119.92, 119.70, 118.56 (Ar), 113.04, 111.29 (C≡C), 55.79 (quat. C), 32.66 (Et), 15.09 (PEt₃), 8.61 (Et), 8.11 (PEt₃) (ppm); ³¹P NMR (161 MHz, CDCl₃): δ 9.77 (¹J_P,Pt = 1312 Hz) (ppm).

31: a pale yellow solid (26 mg, 48%).

Spectral data: MS (MALDI-TOF) m/z: 835.3 [M+H]^⁺; FTIR: 2107 cm⁻¹ (C≡C); ¹H NMR (CDCl₃): δ 7.74-7.32 (m, 2H, Ar), 7.27-7.17 (m, 6H, Ar),
1.80-1.72 (m, 12H, PEt₃), 1.13-1.05 (m, 18H, PEt₃) (ppm); $^{13}$C NMR (CDCl₃): $\delta$
147.84, 144.43, 139.22, 131.75, 129.31, 129.10, 127.28, 124.27, 124.13, 123.81,
122.30, 121.17 (Ar), 112.16, 109.69 (C≡C), 15.06, 8.07 (PEt₃) (ppm); $^{31}$P NMR
(161 MHz, CDCl₃): $\delta$ 9.76 ($^1J_{P,Pt} = 1312$ Hz) (ppm).

32: a pale yellow solid (19 mg, 32%).

Spectral data: MS (MALDI-TOF) m/z: 508.7 [M+H]$^+$; FTIR: 2084 cm$^{-1}$
(C≡C); $^1$H NMR (CDCl₃): $\delta$ 7.69-7.64 (m, 2H, Ar), 7.55-7.53 (m, 1H, Ar), 7.48 (m, 1H, Ar), 7.38-7.27 (m, 5H, Ar), 7.17-7.16 (m, 1H, Ar), 6.99-6.96 (m, 2H, Ar),
6.85-6.80 (m, 2H, Ar), 2.07-2.02 (m, 4H, Et), 1.80-1.72 (s, 12H, PEt₃), 1.15-1.07 (m, 18H, PEt₃), 0.35-0.32 (m, 6H, Et) (ppm); $^{13}$C NMR (CDCl₃): $\delta$ 150.55, 150.00,
141.26, 140.99, 140.46, 139.11, 133.71, 129.62, 128.04, 127.38, 126.90, 126.87,
124.36, 122.87, 122.50, 121.63, 121.36, 119.92, 119.67, 119.55 (Ar), 102.51 (C≡C), 56.15 (quat. C), 32.83 (Et), 15.15 (PEt₃), 8.56 (Et), 8.10 (PEt₃) (ppm); $^{31}$P
NMR (161 MHz, CDCl₃): $\delta$ 9.88 ($^1J_{P,Pt} = 1312$ Hz) (ppm).

8.8 Device Fabrications and TRIR application

8.8.1 Fabrication Process for OLEDs

All of the OLED devices were fabricated by a similar procedure as described
below. The multilayer architecture consists of anode, hole blocking layer (HBL),
hole transporting layer (HTL), emission layer (EML), electron transporting layer (ETL), electron injection layer (EIL) and cathode. The devices were fabricated on ITO coated glass (80 nm in thickness) with a sheet resistance of 25Ω/□. Firstly, the ITO coated glass were cleaned by soaking in ultrasonic detergent for 30 minutes, spraying with D. I. water for 10 minutes, soaking in ultrasonic D. I. water for another 30 minutes and followed by drying in oven for 1 hour. When the coated glass was loaded into the pretreatment chamber, CF₄ plasma was applied for the Ir(III) samples with a power of 100 W, gas flow of 50 sccm and pressure of 0.2 Torr for 10 s. After that, staying in the vacuum with a base pressure of 7×10⁻⁷ Torr, the samples were transferred to the organic chamber, and HTL material 4, 4’-bis [N-(1-naphthyl-1-)-N-phenyl-amino]-biphenyl (NPB) (60 nm in thickness), EML material Ir(III) complexes doped emitter (20 nm in thickness), and HBL/ETL material 2,2’,2’-(1,3,5-benzinetriyl) tris(1-phenyl-1-H-benzimidazole) (TPBi) (20 nm in thickness) were deposited. Then the deposited samples were transferred to the metal chamber, and the cathode material LiF (1 nm in thickness) was also deposited followed by capped with Al (100 nm in thickness). By using the overlap of cathode and anode the light-emitting area was controlled to 4 mm². At last the current density-voltage results of the devices were recorded by the HP4145B semiconductor parameter analyzer, the electroluminescent (EL) spectra were obtained from the PR650 spectrophotometer, the forward direction photons emitted from the devices were
detected by a calibrated UDT PIN-25D silicon photodiode. The luminance and external quantum efficiencies of the devices were inferred from the photocurrent of the photodiode.

**8.8.2 Fabrication Process for DSSCs**

All of the DSSC devices were fabricated by a similar procedure as described below. They all consist of anode, cathode, and the dye-deposited mesoscopic TiO$_2$ in between. The anode films consist of two layers of TiO$_2$ nanoparticles with thickness of 12 μm (transparent, particles with 20 nm in diameter) and 6 μm (scattering, particles with 200 nm in diameter). They were prepared by a doctor-blade technique. Firstly the transparent conducting glass (SnO$_2$:F, FTO glass, 15 Ω$^{-1}$) were thoroughly cleaned by soaking and sonicated for 20 minutes in ethanol, acetone and D. I. water, respectively. Then, the first layer was doctor-bladed onto the cleaned FTO glass with 6 μm thick TiO$_2$ paste (200 nm in diameter) and followed by relaxation for 3 min at room temperature, after that the coated glass were heated for 6 min at 150 °C. The above procedure was repeated until the transparent layer got 12 μm in thickness. After that, the scattering layer of TiO$_2$ nanoparticles (200 nm in diameter) was doctor-bladed on the surface of the first layer and got 6 μm in thickness. The electrodes consist of a three-dimensional TiO$_2$ naoparticle-network. They were accomplished after a series of heating process in air flow: 275 °C for 5 minutes, 325 °C for 5 minutes,
375 °C for 5 minutes, and 480 °C for 30 minutes. Then the resulting films were put into a 0.02 M TiF$_4$ aqueous solution and stayed at 70 °C for 45 minutes. An annealing process was performed at 450 °C for 30 min. After that the electrodes were soaked into a dye bath with 0.5 mM in concentration of an acetonitrile/tert-butyl alcohol (volume ratio, 1:1) mixture at 80 °C in dark condition for 18 hours, rinsed by ethanol and acetonitrile and dried in the air. Platinum counter electrodes were treated with sputtering method, staying at 15 mA for 90 s with a power of 150 W. A sandwich-structured cell was assembled with the dye-adsorbed TiO$_2$ and Pt-counter electrodes prepared above. The liquid electrolyte is a mixture of acetonitrile/4-tert-butylpyridine (volume ratio, 1:1) containing 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M lithium iodide, and 0.05 M iodine.

8.8.3 TRIR Measurements

A Perkin Elmer rectangular semi-demountable cell consists of a 4mm thick CaF$_2$ back window and 2 mm thick CaF$_2$ front window was used for TRIR measurement. The sample was firstly dissolved by THF in a concentration with the absorbance between 1.0 and 2.0, followed by sealing in the 0.1 mm Teflon spacer between the front and back windows in a glove box. The initial laser was output by a mode-locked titanium sapphire oscillator and regenerative amplifier.
combination operating at 1 kHz. Then the pump pulses was generated after the fundamental laser beam pumping through a sum frequency generation (SFG) optical parametric amplifier (OPA) or a UV/vis OPA; and the mid-IR laser was produced after the fundamental beam passing through a difference frequency generation (DFG) OPA. A Ge beamsplitter was used to further split the IR beam into a probe and a reference. Both of them were applied onto the sample cell but only the probe is overlapped with the pumped pulses. A grating spectrometer (Triax 320) and separate Hg/Cd/Te array (32 elements) detectors were used to analyze the results. A chopper operating at 500 Hz was applied for time-dependent measurement of the probe signal. And the overall spectra were accomplished after corresponding the absorbance from the reference beam signals.
Reference:


CURRICULUM VITAE

Academic qualifications of the thesis author, Ms. WU Hao:

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