

## Synthesis and Electronic Properties of Novel Light-Emitting Materials Based on Aminostilbene Derivatives

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Aminostilbene is a stilbene, 1, 2-diphenylethene, containing amino group (NR<sub>2</sub>, R is either H, alkyl or aryl group). Based on Hammett constant, amino group serves as electron-rich substituent, and it brings aminostilbene significant intramolecular charge transfer (ICT) character. Upon photoexcitation, aminostilbene can undergo either fluorescence, *trans*→*cis* isomerization of C=C bond or twisted intramolecular charge transfer (TICT) of C-N bond. Many applications are extended based on these properties of excited state. Aminostilbenes showed significant CT character and their fluorescent behavior have been utilized in light-emitting materials and molecular probes. It has been reported that light-emitting materials incorporate *N,N*-diphenylaminostilbene<sup>1,2</sup>. On the other hand, charge transfer characters of aminostilbenes have been utilized in molecular probes according to luminescence response. The available approach for ion probes is to connect nucleophilic groups like crown ethers or pyridine into aminostilbene or use aminostilbazole (one of the phenyl ring of stilbene is substituted by pyridine). The intensity change or spectral shifts of fluorescence might function as indicators to monitor analytes.<sup>3-8</sup> 4-*N*-methylamino-4'-hydroxystilbene was reported for optical imaging to detect amyloid plaques in the patients with Alzheimer's disease.<sup>9</sup>

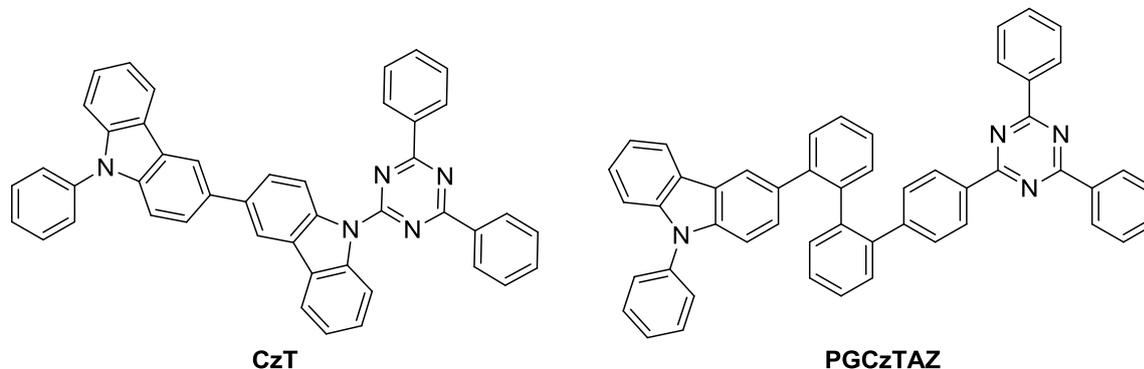
Photo-induced *trans*-*cis* isomerization is the other main deactivated channel of aminostilbene, and it involves structural change from linear to bent. The structural change of stilbene has been applied on molecular devices such as molecular brakes and supramolecular chemistry. For example, a light-driven molecular brake consisting of pentiptycene as stator restricts the rotational rate of pentiptycene for *cis* isomer but is free-rotating for *trans* form.<sup>10-12</sup> Unidirectional shuttling of stilbene in asymmetric  $\alpha$ -cyclodextrin was controlled by photo-induced isomerization.<sup>13</sup> Instead of fluorescence and isomerization, TICT is the other possible deactivated pathway for aminostilbene equipping stronger acceptor. The TICT concept originated from the interpretation of the dual fluorescence behavior of 4-(*N,N*-dimethylamino) benzonitrile (DMABN) in polar solvents.<sup>14,15</sup> The proposed TICT state is a successor of the locally excited (LE) state through the twisting of the C<sub>ph</sub>-N bond (D-A torsion). Because of the forbidden nature in optical transition for the charge-recombination process, the TICT state is characterized with low fluorescence quantum efficiency. In the case of 4-*N,N*-dimethylamino-4'-nitrostilbene (DNS),<sup>16,17</sup> it showed neither fluorescence nor C=C isomerization upon irradiating, and the deactivation is probably through TICT channel. However, the identification and characterization of TICT state is a challenging task because TICT state is a weak-emissive deactivation pathway.

**Organic Light Emitting Diodes (OLEDs).** Recently, to circumvent the high-cost, limited sources, and potential health threats raised by the transition metal complexes incorporated in organic light emitting diodes (OLEDs), two upconversion mechanisms including triplet-triplet annihilation (TTA)\* and thermally activated delay-fluorescence (TADF)\* have been successfully utilized to yield high efficiency

OLEDs with tailor-made organic emitters. *The interest of developing these materials are growing and we are going to construct TADF chromophores based on aminostilbene scaffold.*

Particularly, the attainable 100% internal quantum efficiency (IQE) of TADF-based OLEDs has been receiving considerable attention. A key element for generating efficient TADF lies in the small singlet-triplet energy  $\Delta E_{ST}$  ( $<kT$ ), i.e., the small electron exchange energy. This can be achieved, in theory, by having orthogonality or slim overlap between HOMO and LUMO involved in the transition. Accordingly, organic molecules capable of demonstrating TADF are composed of structurally weak-coupled electron donor (D) and acceptor (A) components, inducing an intramolecular charge transfer (ICT) behavior. This makes the design of a new D/A molecule to attain efficient TADF a nontrivial matter, one requiring the subtle harnessing of the degree of ICT within the molecular framework. Alternatively, a similar result can be achieved by the formation of exciplex via intermolecular charge transfer between physically blended electronic donor and acceptor molecules. The realization of this simplicity has caused a rapid boom in exciplex applications in OLEDs. With the judicious selection of donor and acceptor materials, OLEDs with exceptionally high electroluminescence (EL) efficiencies have been achieved recently.

Adachi and Wong have reported CzT has significant TADF performance due to efficient upconversion from ICT state,<sup>18</sup> but **PGCzTAZ** shows no evident TADF property (structures seeing Figure 2).<sup>19</sup> The lack of TADF could be attributed to twisted conformation. However, the ICT character is also broken when twisting biphenyl group. The more evidence is need to make TDAF mechanism clear and predictable for future materials design.



**Figure 2.** Structures of **CzT** and **PGCzTAZ**.

**Aggregation-Induced Emission (AIE).** Fluorophores that display aggregation-induced emission (AIE) are fundamentally intriguing, because they are opposite to the majority of systems that undergo fluorescence quenching upon forming aggregates.<sup>20-23</sup> The AIE effect generally results from an effective restriction of the internal rotations (RIR) that are responsible for the fluorescence quenching in dilute solutions. In principle, all the low emissive fluorophores are potential candidates for AIE, provided that the underlying nonradiative decay channels can be substantially blocked upon forming aggregates. *However, the research of tuning emission color of AIE is needed to accomplished.*

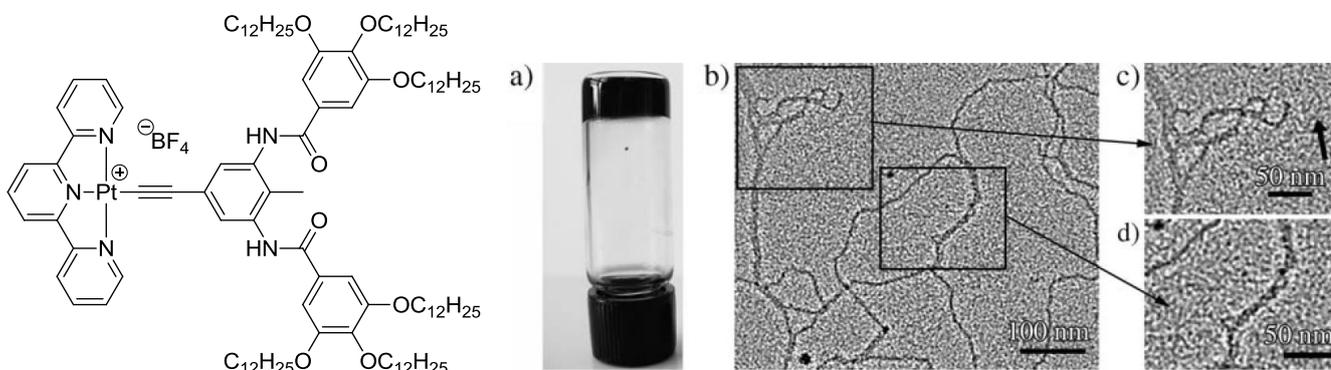
Square planar platinum complexes have stronger metal-metal interaction, which is suitable for

aggregation. Yam reported a series terpyridine platinum complexes which absorption and emission spectra are highly dependent on substituent. Dissolution of either of the two forms of  $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]\text{OTf}$  gave a yellow solution in acetonitrile with the same electronic absorption spectra that showed a MLCT absorption band at 416 nm, suggestive of the existence of monomeric species in solution. Upon increase of the diethyl ether content in the solution mixture of acetonitrile diethyl ether while the concentration of the platinum(II) complex is kept the same, the solution color of  $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]\text{OTf}$  changed dramatically from yellow to green to blue (Figure 3).<sup>24</sup> The corresponding electronic absorption spectral trace showed a growth of a new absorption band which was ascribed to ground-state self assembly or aggregate formation in the solution mixture as a result of reduced solvation, arising from an increase in the nonsolvent content of diethyl ether.



**Figure 3.** Solution of  $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]\text{OTf}$  (concentration =  $1.47 \times 10^{-4}$  M) in acetonitrile diethyl ether mixture demonstrating the remarkable color changes. Diethyl ether composition (from left to right): 64%, 68%, 72%, 74%, 76%, 78%, 80%.

Gallate-substituted derivatives of  $\sigma$ -alkynyl platinum(II) terpyridine luminophoric complexes shown in Figure 4 was synthesized with a deliberate design by incorporating Pt(II) to favor spin-orbit coupling for phosphorescence and to facilitate metal-metal interactions.<sup>25</sup> The complex was found to be a good gelator of dodecane, and TEM and AFM studies confirmed the presence of linear fibrils with the length of several hundred nanometers and the width of 2 nm. The formation of elongated fibers suggests that the strong directional intermolecular interactions such as  $\text{Pt}\cdots\text{Pt}$  and hydrogen bonding of amide functions plays a crucial role in the self-assembly. The tridentate platinum complexes connecting stilbene are ideal to investigate the AIE and how the substituent affecting photophysical properties.

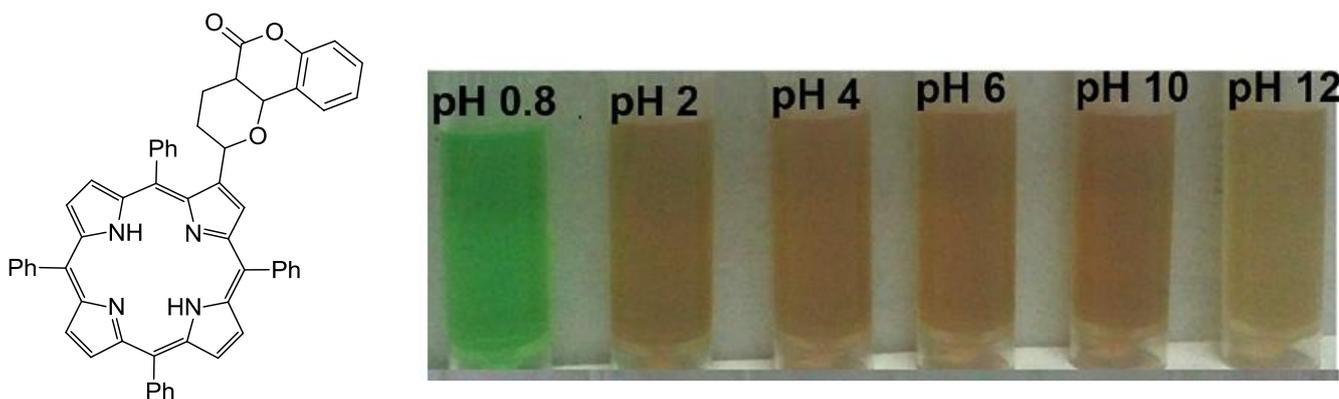


**Figure 4.** a) Gel obtained in dodecane ( $8.1 \text{ mmol L}^{-1}$ ). The gel does not flow when the test tube is turned upside down. b) TEM image of a diluted gel in dodecane ( $c=0.08 \text{ mmol L}^{-1}$ ) showing an interconnected

network of fibers. c) Zoom showing a fiber with the smallest observed diameter (2 nm; indicated by arrow). d) Zoom of intertwined bundles of fibers.

**Probes.** The development of chemosensors or biosensors for recognition of ions, radicals, small molecules, and biologically important molecules continue to be a hot topic at current chemistry community. The issues of sensitivity and selectivity are always the main concerns in designing a new sensor. However, the ease of detection provides an additional attribute for the application. Among the various possible signals for read out, fluorescence has been one of the most popular signals for sensor design due to its high sensitivity and multiple signaling mechanisms such as change in excited-state natures, electron transfer, and energy transfer and multiple types of signal readout such as on-off intensity change, ratiometric detection, and fluorescence lifetime. Color change is another popular method in view of the ease of detection with naked eyes. Many recognition mechanisms have been developed over the past years. Previous efforts emphasize the noncovalent interactions such as hydrogen bonding,  $\pi,\pi$ -interactions, and dipole-dipole interactions. *Considering the convenience and specificity, multifunctioned probes were desired in practical applications.*

Santos reported new porphyrinecoumarin conjugate was successfully obtained and fully characterized. The photophysics was characterized in dichloromethane, DMSO, toluene, and ethanol. A strong color change from purple to yellow (colorimetric effect) and an unprecedented selectivity for  $\text{Hg}^{2+}$  was detected in EtOH/ $\text{H}_2\text{O}$  (50:50). In addition, it was able to detect and quantify the minimal amount of 0.6 ppm and 1.2 ppm of  $\text{Hg}^{2+}$  in aqueous solution (EtOH/ $\text{H}_2\text{O}$ , 50:50). The naked eye sensorial ability of the colorimetric effect of 5 for  $\text{Hg}^{2+}$  was successfully applied in a solid support material, a cellulose paper (filter paper). Moreover, pH studies carried out with the porphyrinecoumarin conjugate showed a green color at low pH and a yellow color at high pH values in solution and solid supports.

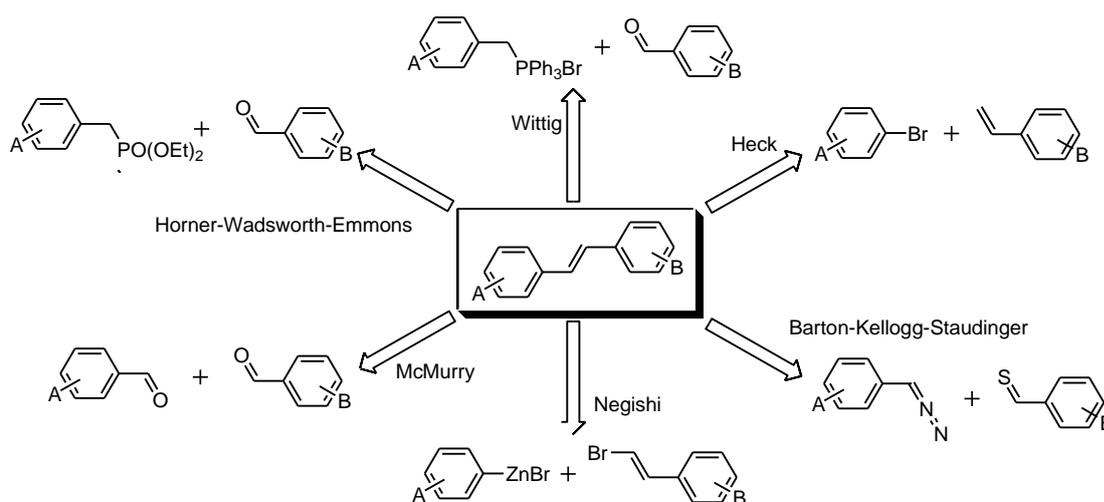


**Figure 5.** Color change (from green to yellow) at different pH in EtOH/ $\text{H}_2\text{O}$  (50:50).

- (一) 研究方法、進行步驟及執行進度。請分年列述：1.本計畫採用之研究方法與原因。2.預計可能遭遇之困難及解決途徑。3.重要儀器之配合使用情形。4.如為整合型研究計畫，請就以上各點分別說明與其他子計畫之相關性。5.如為須赴國外或大陸地區研究，請詳述其必要性以及預期成果等。

In the past decades, my group has extensively studied the photophysics and photochemistry of aminostilbenes. Our synthetic methods and skills are well-developed to modify aminostilbene. The synthesis of aminostilbene is feasible and the aminostilbene with different substituent could be constructed by C-N coupling using the same starting material. Moreover, the common strategy to construct C=C bond is using commercially available aldehydes as starting materials to construct stilbenes. The synthetic methods were showed in Scheme 1. The methods include Wittig, Horner-Wadsworth-Emmons, and McMurry reactions. The other reactions such as Heck and Negishi reactions are constructed C-C bond between arene and styrene. Barton-Kellogg-Staudinger reaction is an useful reaction between thioketone and diazoarene to prepare unsymmetrical and sterically hindered alkenes. We want to investigate the position effect by altering substituent at ortho, meta, or para position and electronic effect of substituent.

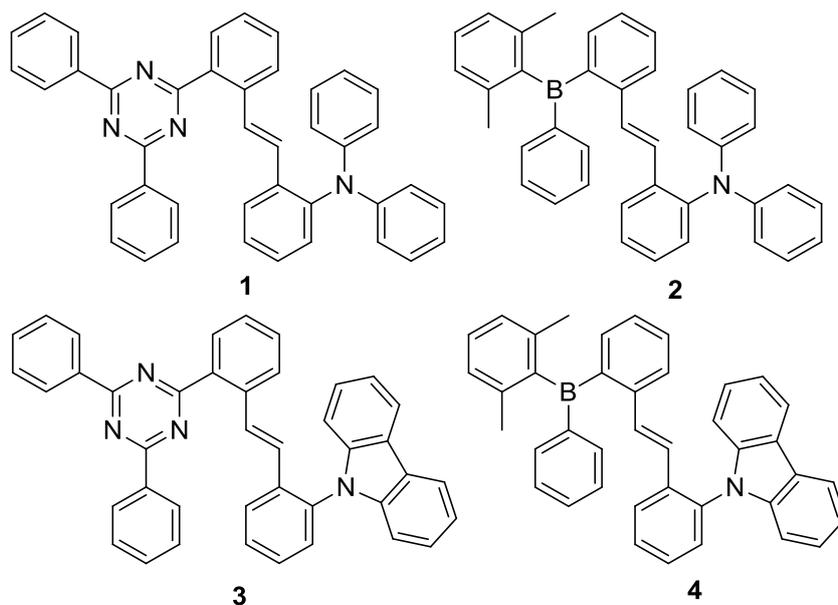
**Scheme 1.** Typical synthetic method for stilbene.



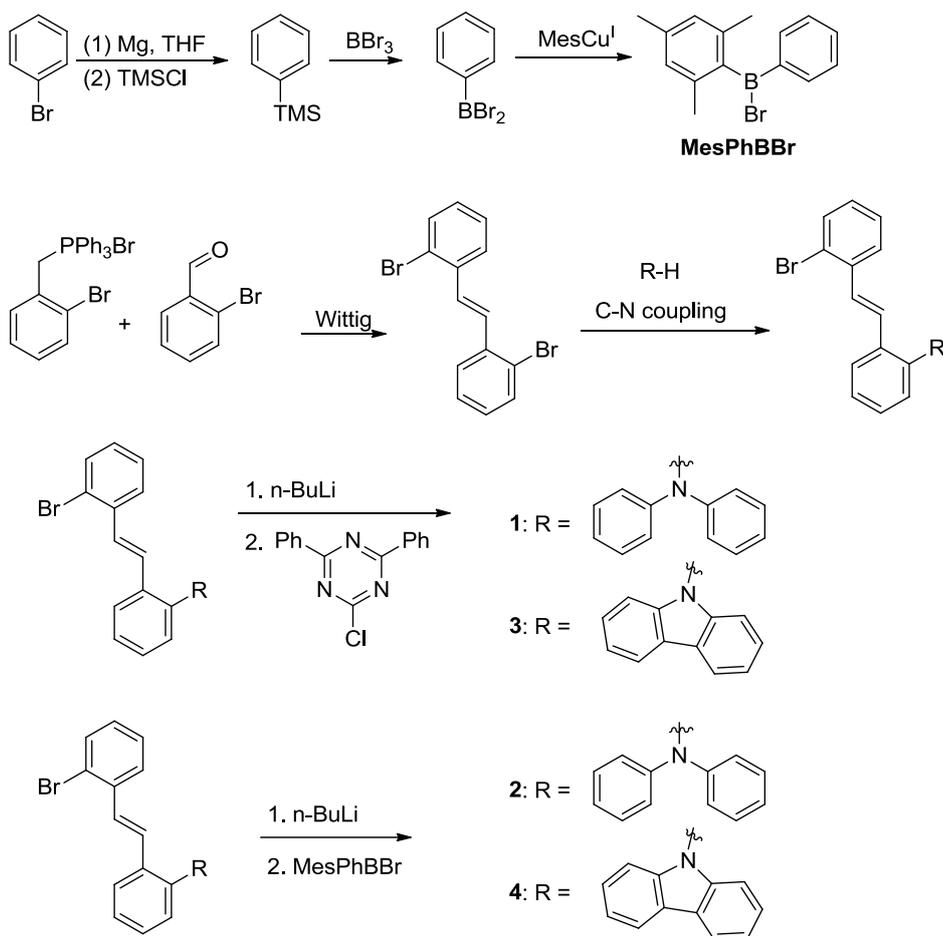
(A) **OLED:** We found the *o*-*N,N*-diphenylaminostilbene has extra long fluorescence lifetime (24.5 ns),<sup>26</sup> and it might be comprised from its congested structure and activated intersystem crossing. These properties are consistent with previous TADF materials CzT. We would like to lower the energy gap between singlet and triplet states and investigate *o*-aminostilbene would be a TADF-active fluorophore. We expected the light-emitting efficiency would be higher in the case of aminostilbene derivatives.

We would to increase the donor-acceptor ability of *o*-aminostilbene. By mimicking the structure of CzT and PGCzTAZ, the electronic-withdrawing substituent was placed on 2' position of *o*-aminostilbene. The electronic-withdrawing substituent is would be good electron acceptor in OLED such as diphenylboron

and diphenyltriazine. The structures **1–4** were provided below and the synthetic route was shown in Scheme 2. 2,2'-dibromostilbene was constructed by Wittig reaction and underwent C-N coupling with *N,N*-diphenylamine or carbazole. Compound **1–4** were synthesized after nucleophilic substitution of 2-amino-2'-bromostilbene with MesPhBBr or 2-chloro-4,6-diphenyl-1,3,5-triazine. The absorption, emission properties, emission quantum yield, radiative decay lifetime and electrochemical properties would be measured. Density functional theory (DFT) and time-dependent DFT would be used to understand the distribution of orbitals and excitation, respectively. We would collaborate with other groups for device fabrication and measurement of electroluminescence properties. We would compare the performance of compound **1–4** and also compare with **CzT**.



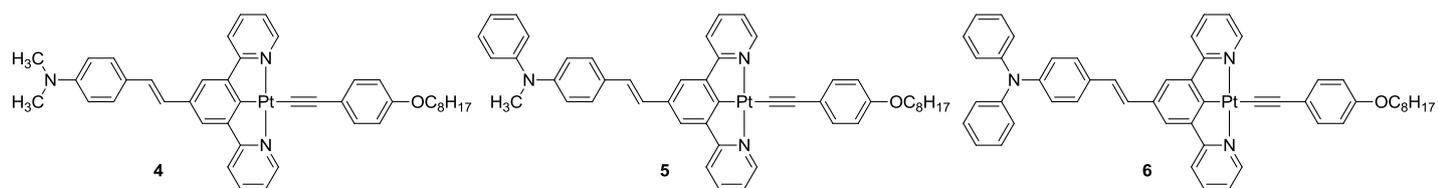
## Scheme 2.



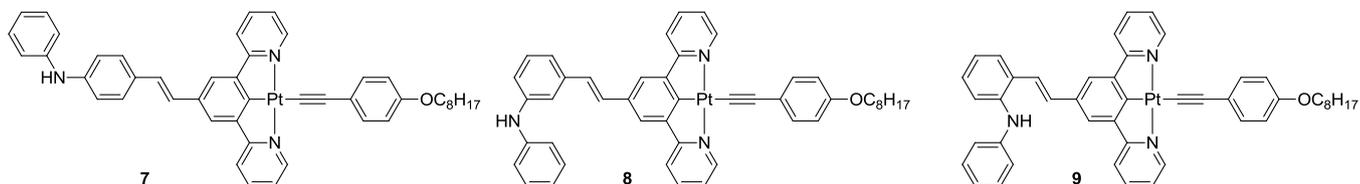
(B) **AIE chromophores.** We would like to combine aminostilbene to platinum, but the isomerization dominates the triplet deactivation. Thus, we try to restrict the double isomerization by inducing strong metal-metal interaction. In the aggregation form, the bond flipping would be restricted, and we expected to observed emission from aminostilbene at room temperature. We also curious about (1) amino conjugation effect, (2) ortho-meta effect, and (3) TICT behavior of aminostilbene in this system. Thus, the designed platinum complexes were shown below. In order to avoid counter ion effect, our study focus on neutral tridentate platinum complexes. The synthetic route was shown in Scheme 3. The NCN pincer ligands were synthesized by 1,3,5-tribromobenzene and 2-bromopyridine through Negishi coupling and followed by C-N coupling with aminostyrene. The complexes were obtained by coordinating to platinum and then replacing chloride to 4-octoxyphenylacetylde. The photophysical properties of monomers and aggregated forms would be obtained at room temperature and 77 K, respectively. We expected the emission would be recovered in the case of group 1 and 2 because the double bond flipping was restricted in the aggregated form. However, the TICT channel of group 3 might not be block because the volume of twisting C-N bond is relative small.

We would like to further test AIE in the metallogel system, and we expected to turn on emission upon sol-gel transition. The structures of compounds **12** and **13** were shown below. The gelator was synthesized according to literature.<sup>27</sup>

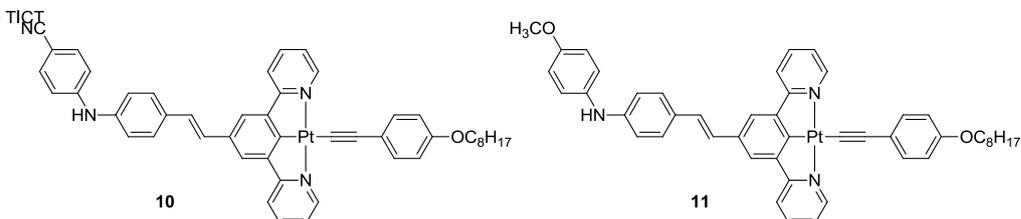
(Group 1) Amino conjugation effect



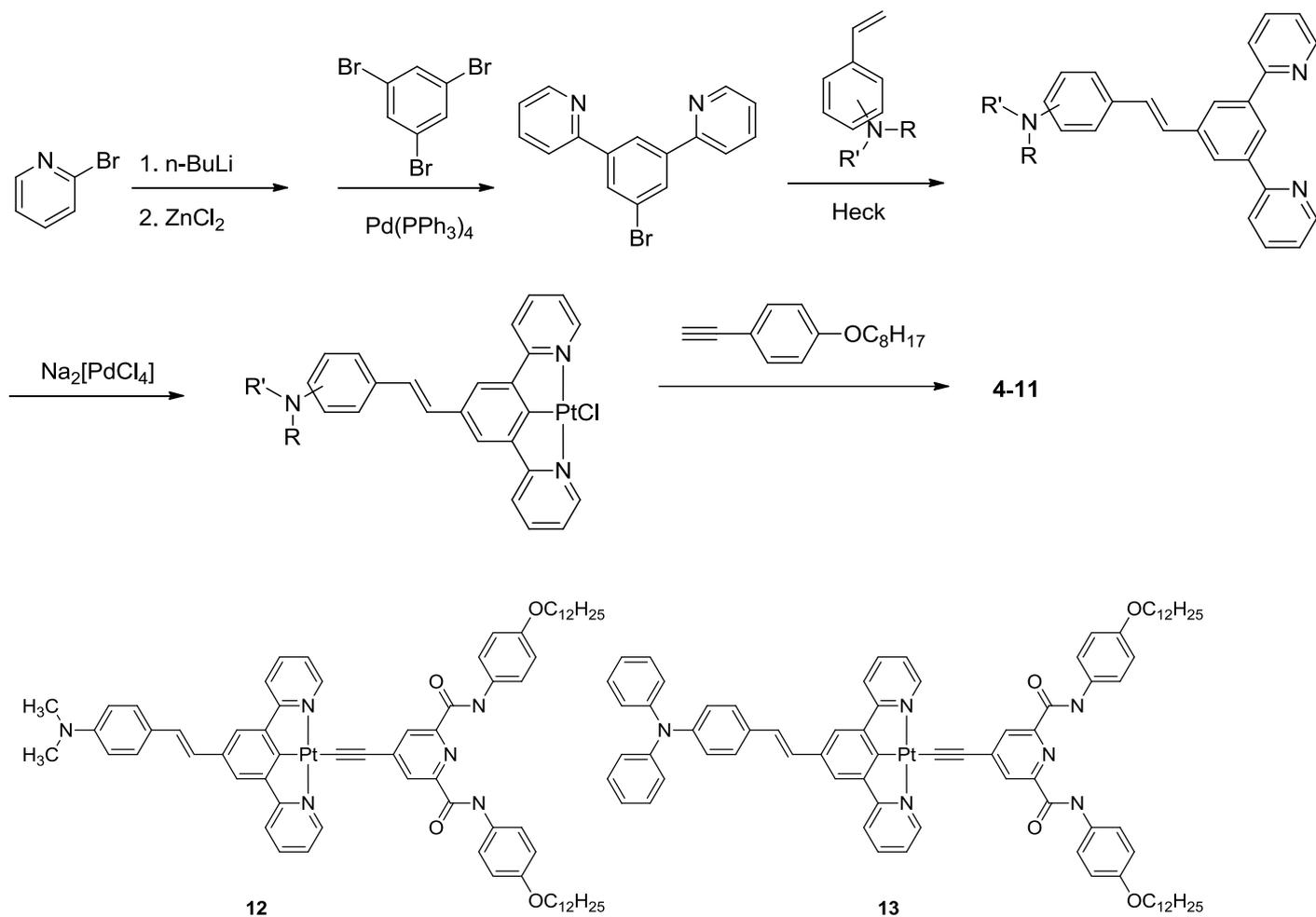
(Group 2) ortho-meta effect



(Group 3) TICT



### Scheme 3.



(C) **Multifunctional probes.** TICT-based aminostilbenes could act as multifunctional probes, and the synthesis of chromophores **14** was shown in Scheme 4. This probe would have four fluorescence responses according to environment and the response was organized as Table 1. In the absence of metal ions, the emission would be quenched in polar environment but is observable in non-polar environment. In the presence of metal ions, fluorescence would be observed in both polar and non-polar solvent, and the emission maxima would be different due to solvation. This probe would be sensitive to environment and analytes and we expected this could be function in vivo to monitor subtle environmental change and concentration of analytes.

**Scheme 4.**

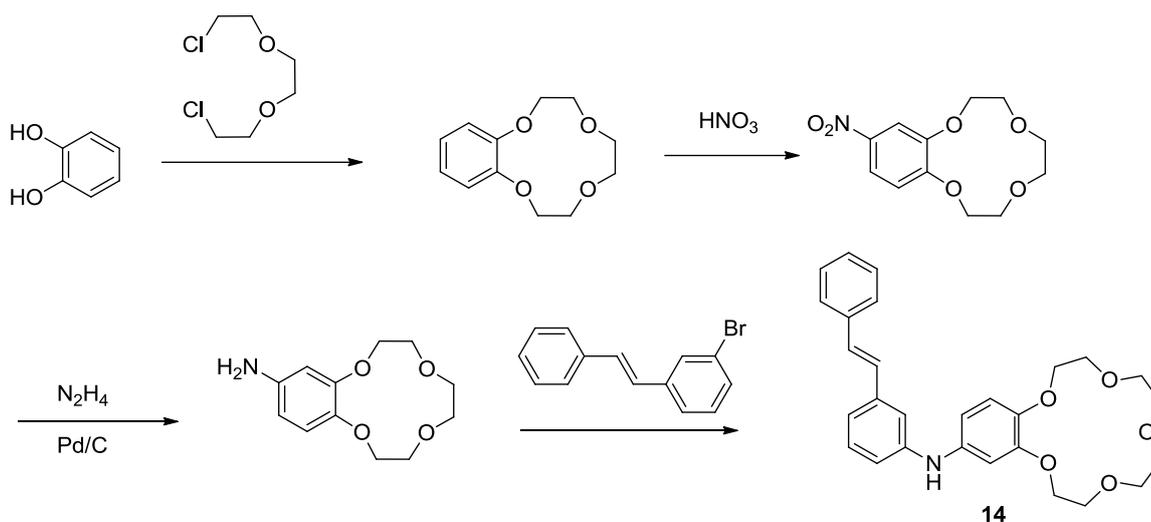


Table 1.

	With metal ions	Without metal ions
Polar environment	Less CT emission	Non-emission
Non-polar environment	Less CT emission	CT emission

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(四) 預期完成之工作項目、成果及績效。請分年列述：1.預期完成之工作項目。2.對於學術研究、國家發展及其他應用方面預期之貢獻。3.對於參與之工作人員，預期可獲之訓練。4.預期完成之研究成果及績效（如期刊論文、研討會論文、專書、技術報告、專利或技術移轉等質與量之預期績效）5.本計畫如為整合型研究計畫之子計畫，請就以上各點分別說明與其他子計畫之相關性。

My research group is pioneered in the aminostilbene chemistry. One of the purposes of this proposal is to reinforce our accomplishments and thus become a leading group on this field. In addition, the knowledge gained from this work should not only benefit the chemistry community but also have potential inputs to the progress of current technology. The education and training to the young people on molecular design, organic synthesis, structural characterization, data analysis, computational simulation, and oral and writing presentation are of the prime importance.

The research plan described above contains five sections. We plan to carry out each section simultaneously, since each section is more or less complementary to one another. Our investigation for most of the above proposed systems will include (a) synthesis of the target compounds, (b) characterization of the molecular and supramolecular structures, (c) electronic property characterization and/or performance test in optoelectronic devices, the latter part will through collaboration with the other groups at Academia Sinica or NTU. (d) data analysis with the assistance of computations, and (e) structural modification based on the preliminary results or conclusions until reaching conclusive results or optimized materials performance. Finally, publish the results in prestigious journals.

The above-proposed jobs will be divided into three parts more or less equally for each fiscal year. The great financial support from Ministry of Science and Technology will be the most critical issue for its success. Thank you for your reviewing and we sincerely wish a good support from you!

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