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Construction of metallo-complexes with 2,2′:6′,2″-terpyridine substituted triphenylamine in different modified positions and their photophysical properties

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ABSTRACT

The stable coordinated metallo-complexes based on 2,2′:6′,2″-terpyridine (tpy) and its derivatives have been widely researched for various wide-ranging applications in photoelectronics, catalysis, sensor, photoluminescence, and so on. However, the most reported studies ignored the comprehensive comparison between structures modified by different positions and photoluminescence. Herein, we design a series of metallo-complexes which were assembled with tpy substituted triphenylamine (TPA) at different positions and metal ions and explored their photophysical properties. In the solution state, **MLE$_2$** based on the 5,5″-positions modification showed the highest PLQYs and PL intensity. With the increase of solvent polarity, **MLB$_2$** exhibit the largest redshift. In the solid state, from **MLA$_2$** to **MLE$_2$**, the emission colours are gradually red-shifted from yellow to red. The findings in this work may pave a new way to design functional metallo-complexes, not just for PL properties.

Over the past decades, the customized design of functional coordination metallo-complexes with diverse and multiple coordination interactions have attracted considerable attention due to their structural diversity [1–3], which have played a unsubstitutable role in various wide-ranging applications, such as luminescence [4–7], photovoltaic [8], catalysis [9], gas separation [10], magnetic materials [11,12], and anion recognition [13]. For metal coordination complexes with unique structures and desired functional properties, various influence factors need be considered, such as predesigned structures of organic ligands [14], coordination arrangements of metal ions [15,16], anions [17], the reaction temperature [18], types of solvents [19], coordination positions [20], and the ratios of metal ions and ligands [21]. Among the aforementioned factors, the chemical structures of organic ligands have been proved as a key role in the construction of metallo-complexes with desired structures and founctions.

Recently, a large number of coordination complexes has been developed via diverse ligands with electronic-donor and electronic-acceptor groups as building blocks [22–28]. Among the various ligands, 2,2′:6′,2″-terpyridine (tpy), as a versatile and unique chelating building block [29–33], has three pyridine rings and several modified positions which could be designed and combined diverse chromophores. Different modified positions could offer a fine-tuning of different electronic absorption and further effect the photophysical properties. What is more, tpy could coordinate with diverse metal ions including transition and lanthanide metals to construct stable metallo-complexes. Thus, the stable coordinated complexes with tpy and its derivatives have exhibited potential applications in photoelectronics [34], catalysis [35], sensor [36], photoluminescence [37], and so on. In present study, many complexes based on tpy motifs substituted with different groups were reported. However, most studies focused on the 4′-position [38–40] modified with electron-donor or electron-acceptor substituents, including nitrogen- [41], phosphorus- [42], halogen- [43], oxygen- [44], naphthyl [45], phenanthrenyl [45], triphenylamine (TPA) [46], and tetraphenylethylene (TPE) [47], which will tune electronic structures for whole complexes. However, the most reported studies ignored the comprehensive comparison between structures and luminescence caused by the different modified positions and symmetrical or dissymmetrical modifications.

In this study, we designed a series of ligands **LA**-**LE** (Scheme 1) based on tpy substituted with TPA at 4′-, 4-, 4,4″-, 5,5″-positions of tpy, studied photophysical properties of each metallo-complexes with Zn^{2+} or Cd^{2+} and explored the influence of the position and

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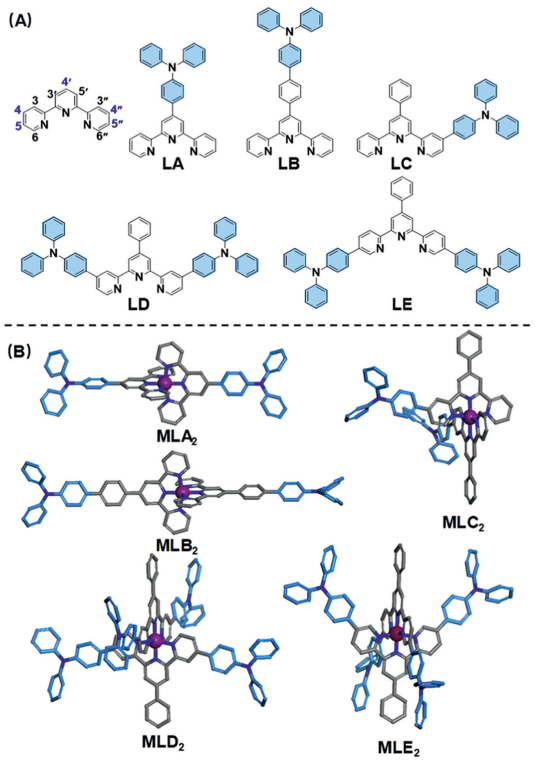

Scheme 1. The structural features of tpy and our design of ligands **LA-LE** (A) and the metallo-complexes $\mathbf{ML_2}$ (B).

number of TPA on the photoluminescent (PL) properties. These metallo-complexes with Zn^{2+} or Cd^{2+} have similar photoluminescent rule in different solvents. Compared with other metallo-complexes, the photophysical properties of 5,5″-positions modified metallo-complexes $\mathbf{ZnL_2}$ and $\mathbf{CdL_2}$ in dilute solution showed the highest PLQYs. What is more, the solvent effect on PL behaviour and the PL properties in solid state were investigated, and the metallo-complexes ranging from $\mathbf{MLA_2}$ to $\mathbf{MLE_2}$ followed the similar rules (Scheme 1). The peaks displayed red shift, corresponds to the colours' ranges from yellow-green to red.

All ligands are synthesized by Suzuki coupling reaction. It was mentioned that the key intermediate compound **5** (Supporting information) of dissymmetrical ligand **LC** was synthesized by the Kröhnke reaction. **LB** and **LC** were isomers by adjusting the modified positions of TPA, which were same for isomers **LD** and **LE**. The expected complexes were obtained by mixing the ligands and $Zn(NO_3)_2{\cdot}6H_2O$ (or $Cd(NO_3)_2{\cdot}4H_2O$) in a precise stoichiometric ratio of 2:1 in a mixed solvent of $CHCl_3$ and MeOH (1:3, v/v) at 50 °C for 12 h. After adding excess NH_4PF_6, yellow precipitates were obtained in quantitative yields. All ligands and complexes are completely characterized by NMR (^{1}H, ^{13}C, and COSY) and electrospray ionization-mass spectrometry (ESI-MS).

The complexes were first characterized by ^{1}H NMR spectroscopy. From the spectra, all complexes displayed sharp and narrow peaks (Fig. 1 and Figs. S1–S15 in Supporting information). Combining with 2D COSY, all peaks of the protons of complexes can be distinguished clearly, the proton of tpy-$H^{3',5'}$ exhibited a diagnostic downfield shift. And the proton of tpy-$H^{6,6''}$ showed a significant upfield shift on account of the electronic shielding effect, indicating the existence of coordination bonds. For symmetrical system, the NMR spectra showed two sets of pyridine signals due to the same chemical environment of the pyridines (Fig. 1A). However, owing to the unsymmetrical modification at 4-position of **LC**, there are three sets of pyridine signals corresponding with the unsymmetrical ligand **LC** (Fig. 1B). ESI-MS was employed to further characterize the composition of the complexes. In ESI-MS spectrum (Figs. 1C-F and Figs. S16–S25 in Supporting information), one prominent set of peaks with 2+ and 1+ charge states were observed by losing PF_6^- counterions. The molecular weights of all complexes were matching well with the calculated molecular weights with the expected chemical compositions.

After confirming the composition of these metallo-complexes, the photophysical properties of ligands and complexes in different

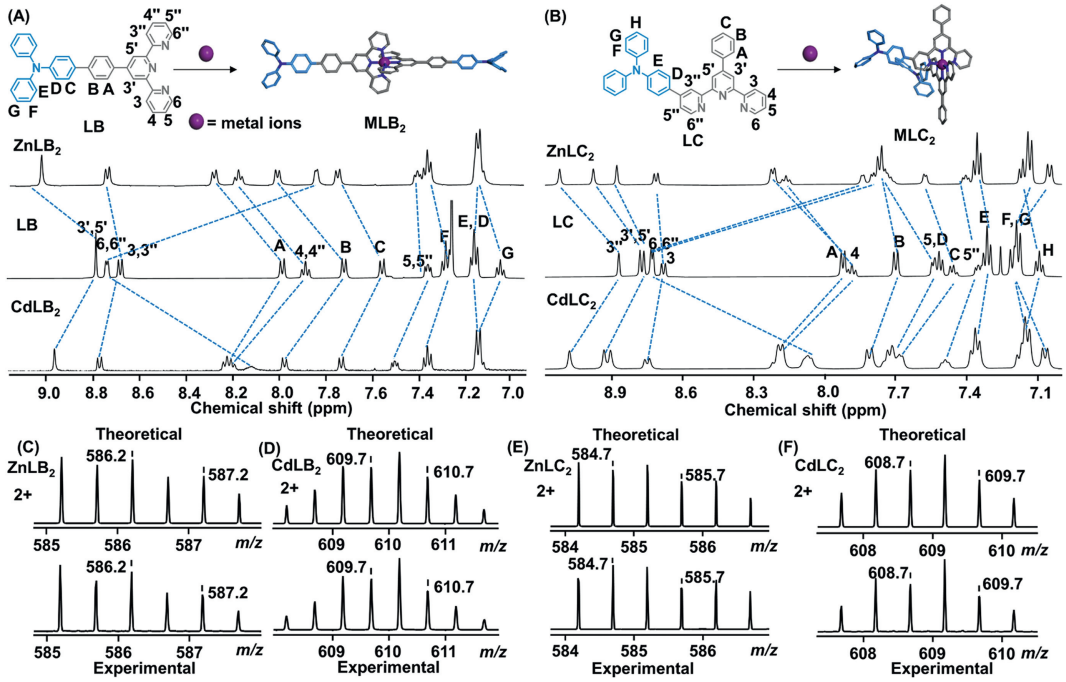

Fig. 1. The ^{1}H NMR spectra (500 MHz, 300 K) of **LB** in $\mathbf{CDCl_3}$ and metallo-complexes $\mathbf{ZnLB_2}$ and $\mathbf{CdLB_2}$ (A) in $\mathbf{CD_3CN}$, and **LC** in $\mathbf{CDCl_3}$ and metallo-complexes $\mathbf{ZnLC_2}$ and $\mathbf{CdLC_2}$ (B) in $\mathbf{CD_3CN}$; the isotope patterns of $\mathbf{ZnLB_2}$ (C), $\mathbf{CdLB_2}$ (D), $\mathbf{ZnLC_2}$ (E), and $\mathbf{CdLC_2}$ (F). The charge states of the intact assemblies are marked.

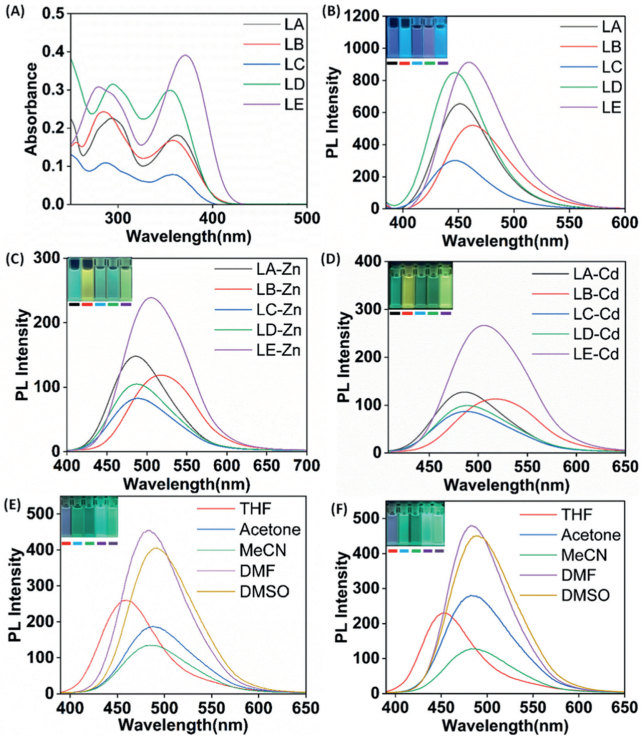

Fig. 2. The UV–vis (A) and PL (B) spectra of **LA**-**LE** in $CHCl_3$ at concentration of 5×10^{-6} mol/L, the PL spectra of metallo-complexes with Zn^{2+} (C) and Cd^{2+} (D) in CH_3CN at concentration of 5×10^{-6} mol/L, the PL spectra in different solvents of $\mathbf{ZnLA_2}$ (E) and $\mathbf{CdLA_2}$ (F) at concentration of 5×10^{-6} mol/L.

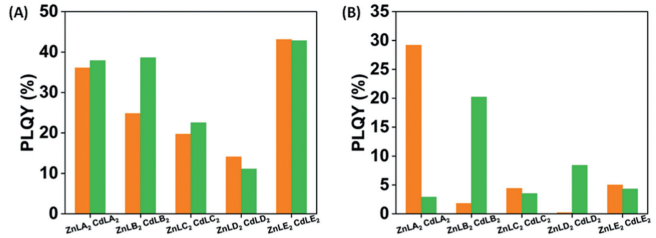

Fig. 3. The PLQY of $\mathbf{ML_2}$ in MeCN at concentration of 5×10^{-6} mol/L (A), $\mathbf{ML_2}$ in solid state (B).

modified positions in dilute solution were investigated firstly. The absorption bands of ligand **LA**-**LE** in chloroform (Fig. 2A) exhibited main bands at 250–300 nm, attributing to the π–π^* transition of tpy and TPA motifs. The absorption band in the range of 350–400 nm was ascribed to the intramolecular charge transfer (ICT) absorption from the electron donor (TPA) to the electron acceptor (tpy) moieties. The PL spectra of ligands **LA**-**LE** displayed weak emission at a range of 430–475 nm in chloroform (Fig. 2B). For the ligands, compared to the D-A structures of **LA** and the isomer **LC**, the D-π-A structure of **LB** increased the degree of conjugation and enhanced ICT and the PL band was further bathochromically shifted [48]. **LD** and **LE** with two TPA motifs have the stronger PL intensity because the D-A-D structure causes the radiative leap to take a greater part in the deactivation of the excited state, resulting in a higher photoluminescent quantum yield (PLQY) [49], meanwhile the steric hindrance of **LE** is smaller than that of **LD** which may cause weaker quenching of **LE** in dilute solution, the PLQY of **LE** reached up to 67.43% which was the highest among the ligands (Fig. S37A in Supporting information). Compared with ligands, the absorption bands of metallo-complexes were bathochromically shifted about 50 nm which may should be attributed to the metal to ligand charge transfer (MLCT) after coordination (Figs. S27A and B in Supporting information).

As shown in Figs. 2C and D, PL spectra of metallo-complexes underwent a moderate redshift and displayed at a range of 480–530 nm, which should be attributed to the MLCT after coordination. The two series of metallo-complexes with Zn^{2+} and Cd^{2+} have a popular regulation: the complexes constructed with ligand **LE** modified in 5,5″-positions had the highest PLQY and PL intensity which may be attributed to the MLCT after coordination and the D-A-D structure of **LE**, the PLQYs of $\mathbf{CdLE_2}$, $\mathbf{ZnLE_2}$ were 42.82%, 43.14%, respectively (Fig. 3A). Meanwhile, from the DFT calculations (Fig. 4E), the overlapping area of HOMO and LUMO of $\mathbf{MLE_2}$ is largest, which may cause strongest locally excited (LE) emission supported the above conclusion [50–52]. Surprisingly, $\mathbf{MLB_2}$ exhibits red shift in greatest extent due to the balance between MLCT and ICT, and it is known from the DFT calculations that the $\mathbf{MLB_2}$ has the smallest band gap ($\mathbf{MLB_2}$ < $\mathbf{MLE_2}$ < $\mathbf{MLA_2}$ < $\mathbf{MLD_2}$ < $\mathbf{MLC_2}$) leading to the maximum emission redshift [53]. Meanwhile, from the DFT calculations (Figs. 4A and B), it can be seen that the photoluminescence of $\mathbf{MLA_2}$ is mainly attributing to the tpy part, and the luminescence emission band of $\mathbf{MLB_2}$ is mainly attributing to the tpy and the conjugated benzene ring part. It is also evident that the π-conjugated bridging portion plays an important role in $\mathbf{MLB_2}$, its electronic state is more delocalized than others enhancing the ICT and maximizing the redshift [54,55]. All the results showed that the different positions of donor TPA motif will affect the optical properties of the metallo-complexes.

To further exploring the PL properties in dilute solution, the UV–vis and PL spectra of these complexes in solvents ranging from low to high polarity (THF, acetone, MeCN, DMF, and DMSO) were investigated (Figs. 2E, F, Figs. S28–S36 in Supporting information). All metallo-complexes in THF exhibit a regular blue shift, compared with the metallo-complexes in other solvents, due to the reduced extent of ICT in THF. And the emission bands of metallo-complexes in high polar solvents (DMF and DMSO) are red-shifted. Notably, the solvent polarities have the most significant influence on $\mathbf{MLB_2}$ which exhibit the largest redshift range from 475 nm to 540 nm, and span the colour from blue to orange, indicating the larger dipole moment change occurred in $\mathbf{MLB_2}$ relative to that of others upon excitation [49]. TPA motif is a classical group with aggregation-caused quenching (ACQ) effect [56], and according to the experimental results (Fig. S38 in Supporting information), the assemblies $\mathbf{ML_2}$ modified with TPA exhibit ACQ behavior.

Finally, the PL properties in solid state were further explored (Fig. 5, Figs. S26, S27C and D). As shown in Figs. S27C and D, and Fig. 5, all complexes exhibited a similar intense broad absorption band in the range of 200–700 nm, the main absorption peaks of $\mathbf{ZnL_2}$ were bathochromically shifted and the PL intensity decreased because of the MLCT after coordination. Compared to the solution state, PL intensity is enhanced in solid states which may be attributed to restricted intramolecular rotation. Although TPA is an aggregation-caused quenching motif, however, solid state of the complexes also exhibit high PLQYs, which should be attributed to the large steric hindrance of pseudo-octahedral <tpy-M-tpy> motifs (M = Zn^{2+} or Cd^{2+}). Surprisingly, from the PL spectra, $\mathbf{MLE_2}$ exhibits the largest redshift which may be attributed to a better π-conjugation and intermolecular interactions of $\mathbf{MLE_2}$ [57,58], and from $\mathbf{MLA_2}$ to $\mathbf{MLE_2}$, the emission colours are gradually redshifted from yellow to red under 365 nm UV light irradiation. In contrast to the dilute solution state, the highest PLQY was 20.22% for $\mathbf{CdLB_2}$ and 29.17% for $\mathbf{ZnLA_2}$ with D-A structure, respectively (Fig. 3B).

In summary, a series of metallo-complexes modified by TPA at different positions were self-assembled with ligands and Zn^{2+} or Cd^{2+}. The structural information of ligands and metallo-complexes

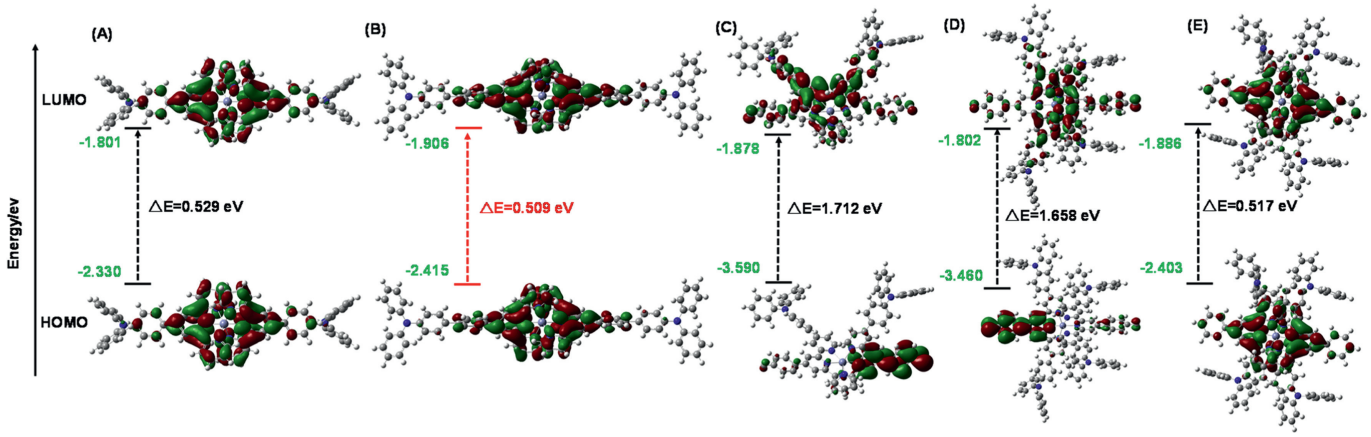

Fig. 4. The DFT calculation of $\mathbf{MLA_2}$ (A), $\mathbf{MLB_2}$ (B), $\mathbf{MLC_2}$ (C), $\mathbf{MLD_2}$ (D) and $\mathbf{MLE_2}$ (E).

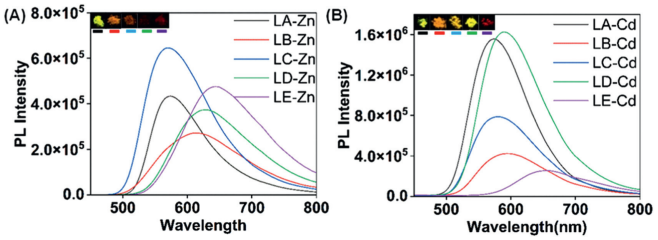

Fig. 5. The PL spectra in solid state of metallo-complexes with Zn^{2+} (A) and Cd^{2+} (B).

is confirmed by NMR (^1H, ^{13}C, COSY) and ESI-MS. After confirming the structures, the PL properties of ligands and metallo-complexes were studied. The luminescent behaviour of metallo-complexes with different metal ions followed the similar rule in different solvents. Compared with other metallo-complexes, the photophysical properties of metallo-complexes assembled with 5,5″-positions modified ligand **LE** in dilute solution were with the highest PLQYs. What's more, the solvent effect was investigated in different solvents. Finally, the PL behavior in solid state was studied, and the metallo-complexes ranging from $\mathbf{MLA_2}$ to $\mathbf{MLE_2}$ followed the similar rules, the PL band of metallo-complexes displayed red shift. The relationship between structural design and PL properties of metallo-complexes are clear. This study will pave a new way to design functional metallo-complexes, not just for PL properties.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.109348.

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