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Graphical Abstract





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Structural Controlled Pure Metallo-triangular Assembly through Bisterpyridinyl Dibenzo[b,d]thiophene, Dibenzo[b,d]furan and Dibenzo[b,d]carbazole

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ABSTRACT

A novel family of metallocycles was constructed by a one-pot self-assembly of three analogous bis(terpyridine) ligand monomers **L1-L3**, having different bent angles, with metal ions $(Zn^{2+} \text{ or } Cd^{2+})$. The dibenzo[b,d]thiophene-containing ligand **L3** assembled with the metal ions to form a single trimer, whereas the dibenzo[b,d]furan-containing ligand **L2** and dibenzo[b,d]carbazole-containing ligand **L1** formed a mixture of trimers and tetramers. Heteroatoms (**N**, **O**, **S**) significantly contributed to the molecular size of the assemblies, owing to the bent angle of the bis-terpyridines ligands.

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1. Introduction

self-assembly has Coordination-driven supramolecular attracted the attention of researchers over the past few decades¹⁻¹⁴. Precisely control over the shape and size of the supramolecular architectures through spontaneous self-assembly process has always been a challenge for chemists, the crucial reason is that the assembled structures are influenced by many factors such as ligand geometry^{15,16}, temperature^{17,18}, concentration^{19,20}, and others²¹⁻²⁴. Among these, the geometry of the ligands is an important factor ²⁵. The self-assembly of the rigid ditopic tpy (tpy = 2,2':6',2"-terpyridine) ligands with the metal ions results in the products that include unexpected pentameric²⁶⁻²⁸, hexameric²⁹⁻³⁴, heptameric³⁵, octameric³⁶, nonameric³⁴, and decameric³² macrocycles. In certain studies, an equilibrating mixture of trimer and tetramer has been reported to be obtained instead of the single discrete structure when bidentate pyridyl ligands were treated with Pd(II)- and Pt(II)-based acceptors³⁷⁴⁰. Kinetical formation of the equilibrating selfassembled macrocycles is always resulted from the fact that slight entropy difference among similar structures. Moreover, the two terpyridyl ligand spacers often possess some degree of lability, which leads to the incorporation of some additional structures that disturb the pre-structure generated from the initially formed

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products; controlling the angle α between the two terpyridyl ligands is critical in the preorganized assembly stage.

In this paper, we successfully synthesized a series of the bisterpyridine ligands with benzo-carbazole (L1), benzofuran (L2) and benzothiophene (L3) as the bridge unit $^{41-45}$. The results of the energy-minimized computation revealed that the tpy-N-tpy and tpy-O-tpy angle of 92.5° and 93.5° deviates markedly from 60° and the angle α between the two terpyridines is 79.5° for L3, respectively (Scheme 1). It indicates that the heteroatomic radius definitely influenced the stretch angles of the organic building blocks L. According to the one-pot synthesis, it was treated with metal ions such as Zn^{2+} and Cd^{2+} to obtain $L1_3Zn_3\&L1_4Zn_4$ or $L1_3Cd_3\&L1_4Cd_4$, which has a predesigned angle of 92.5° between the two terpyridine moieties. When the dibenzofuranbased ditopic terpyridine was used as the ligand, $L2_3Zn_3\&L2_4Zn_4$ or $L2_3Cd_3\&L2_4Cd_4$ were obtained. The coordination monomer with the dibenzothiophene-based ditopic terpyridine (L3), due to its close 60° bend angle, resulted in the single and discrete ternary rings (L3₃Zn₃ or L3₃Cd₃).

Investigation of these macromolecules by NMR spectrometry, ESI-MS, UV-Vis absorption spectrum, and fluorescence spectroscopy provided information about their molecular size and shape, along with their photophysical properties. Our study showed the agreement between the resultant component of supramolecular self-assemblies and the heteroatomic radius,

which confirmed that the stretch angle was the crucial factor M signals in L_4M_4 (M = Zn²⁺ or Cd²⁺), presumably because of the that governed the properties of the supramolecular architectures.



Scheme 1. Energy-minimized structures of ligands L1-L3. Self-assembly process from L to $L_n M_n$ (M = Zn²⁺ or Cd²⁺; n = 3, 4).

By varying the heteroatom, which affected the stretch angle, the radius of the metallomacrocycles and their photophysical properties could be readily tuned.

2. Results and discussion

2.1. Analysis of ¹H NMR spectra

The ¹H NMR spectra of trimetallic cycles $L_{3}Zn_{3}$ and $L_{3}Cd_{3}$ (Fig. 1) reveal that the characteristic singlet peak of $tpyH^{3,5}$ shifted downfield from 8.83 ppm in L3 to 9.08 ppm in L3₃Zn₃ and 9.04 ppm in $L3_3Cd_3$. On the other hand, the indicative doublet peak of tpyH^{6,6"} shifted upfield from 8.76 ppm in L3 to 7.88 ppm in $L3_3Zn_3$ and 8.13 ppm in $L3_3Cd_3$, owing to the shielding effect.

As shown in Fig. S4, the ¹H NMR spectra of $L1_3Zn_3\&L1_4Zn_4$ shows a very obvious pattern with the two representative singlets corresponding to tpy $H^{3',5'}$ exhibiting an integration ratio of 0.4:1. Two downfield shifts at 9.07 and 9.09 ppm are assigned to the tpy $H^{3,5}$ protons in L1₃Zn₃ and L1₄Zn₄, respectively. The tpy $H^{3,5}$ protons of L1₃Cd₃&L1₄Cd₄ are observed as a single broad peak at 9.03 ppm, but the ESI-MS proved the presence of two patterns in L1₃Cd₃&L1₄Cd₄ (Fig. 2). The doublets at 7.84 and 7.91 ppm protons installed on attributed to the tpyH^{6,6}" are $L1_3Zn_3\&L1_4Zn_4$. The indistinguishable doublets corresponding to the tpy $H^{6,6^{\circ}}$ protons of L1₃Cd₃&L1₄Cd₄ appeared as multiplets at 8.14 ppm, indicating an upfield shift owing to the electronshielding effect. Similarly, the ¹H NMR spectra of $L2_3Zn_3\&L2_4Zn_4$ and $L2_3Cd_3\&L2_4Cd_4$ (Fig. S5) display the two independent singlets corresponding to the tpyH^{3',5'} protons. These peaks shifted downfield from 8.83 ppm in L2 to 9.06 ppm and 9.09 ppm in $L2_3Zn_3\&L2_4Zn_4$, and 9.03 ppm and 9.05 ppm in L2₃Cd₃&L2₄Cd₄, respectively.

The ¹H NMR spectrum of L_3M_3 (M = Zn²⁺ or Cd²⁺) exhibits a similar pattern, but the typical signals of tpyH^{3',5'} and tpyH^{6,'} protons show a slight upfield shift relative to the corresponding

combined influence of the metal-centered electron-withdrawing effect and the shielding effect of the perpendicular terpyridine



Fig. 1 ¹H NMR spectra of ligand L3 in CDCl₃ and complexes L3₃Zn₃ and $L3_3Cd_3$ in CD_3CN .

counterpart by the metal. Many other chemical shifts of the tpy^H protons merge together in the mixture of complexes and are hard to distinguish. For a better understanding of the complexes, the metallomacrocycles have been characterized additionally by MS as shown in Fig. 2 and Fig. 3 (Fig. S16-S21). And 2D COSY spectra further supported the formation of all complexes (Fig. S7-S13).

2.2. Analysis of ESI-MS spectra

ESI-MS spectra of $L1_3Zn_3\&L1_4Zn_4$ (Fig. 2) exhibit the desired charge state distributions corresponding to the successive loss of PF_6^- counterions, where the m/z peaks of $L1_3Zn_3$ at 479.6809, 604.6017, 791.9907, and 1104.6476 correspond to the charged moieties $[L1_{3}Zn_{3}-6PF_{3^{+}}]^{6+}$, $[L1_{3}Zn_{3}-5PF_{6^{-}}]^{5^{+}}$, $[L1_{3}Zn_{3}-6PF_{6^{-}}]^{5^{+}}$, $[L1_{3}Zn_{3}-6PF_{6^{-}}]^{5^{+}}$ $4PF_6^{-}$ ⁴⁺, and $[L1_3Zn_3-3PF_6^{-}]^{3+}$, respectively; the m/z peaks of $L1_4Zn_4$ at 479.6809, 568.9147, 687.7256, 854.6547, and 1104.6476 can be assigned to the charged moieties $[L1_4Zn_4]$ $8PF_6^{-}]^{8+}$, $[L1_4Zn_4-7PF_6^{-}]^{7+}$, $[L1_4Zn_4-6PF_6^{-}]^{6+}$, $[L1_4Zn_4-5PF_6^{-}]^{5+}$, and $[L1_4Zn_4-4PF_6^{-}]^{4+}$, respectively. The mass spectra of $L_{2_3}Zn_3\&L_{2_4}Zn_4$ (Fig. 2) reveals the m/z peaks at 537.9226, 708.6337, and 993.1747 corresponding to the structures $[L2_3Zn_3]$ - $5PF_6^{-1}^{5+}$, $[L2_3Zn_3-4PF_6^{-1}]^{4+}$, and $[L2_3Zn_3-3PF_6^{-1}]^{3+}$, respectively; the m/z peaks at 505.4118, 613.7965, 765.3454, and 993.1747 corresponding to the structures of $[L2_4Zn_4-8PF_6^-]^{8+}$, $[L2_4Zn_4 7PF_{6}^{-}]^{7+}$, $[L2_{4}Zn_{4}-6PF_{6}^{-}]^{6+}$, $[L2_{4}Zn_{4}-5PF_{6}^{-}]^{5+}$, and $[L2_{4}Zn_{4}-6PF_{6}^{-}]^{5+}$ $4PF_6^{-1}^{4+}$, respectively.



Fig. 2 ESI-MS spectra of $L1_3Zn_3\&L1_4Zn_4$, $L2_3Zn_3\&L2_4Zn_4$, M/h $L1_3Cd_3\&L1_4Cd_4$, and $L2_3Cd_3\&L2_4Cd_4$.



Fig. 3 ESI-MS spectra of $L3_3Zn_3$ with calculated and experimental isotope patterns for the 5+ and 4+ species (left); $L3_3Cd_3$ with calculated and experimental isotope patterns for the 5+ and 4+ species (right).

As shown in Fig. 2, the m/z peaks of $L1_3Cd_3$ at 503.1736, 632.9904, and 827.4867 correspond to the charged moieties $[L1_{3}Cd_{3}-6PF_{6}^{-}]^{6+}$, $[L1_{3}Cd_{3}-5PF_{6}^{-}]^{5+}$, and $[L1_{3}Cd_{3}-4PF_{6}^{-}]^{4+}$, respectively. The m/z peaks of $L1_4Cd_4$ at 503.1736 and 719.2076 correspond to the charged moieties $[L1_4Cd_4-8PF_6^{-1}]^{8+}$ and $[L1_4Cd_4-6PF_6]^{6+}$, respectively. Similarly, the m/z peaks of L2₃Cd₃ at 566.1246, 743.8853, and 1040.1736 correspond to the charged moieties $[L2_{3}Cd_{3}-5PF_{6}^{-}]^{5+}$, $[L2_{3}Cd_{3}-4PF_{6}^{-}]^{4+}$, and $[L2_3Cd_3-3PF_6]^{3+}$, respectively. The m/z peaks of $L2_4Cd_4$ at 654.1247 and 1140.1736 correspond to the charged moieties $[\mathbf{L2}_{4}\mathbf{Cd}_{4}-6\mathbf{PF}_{6}^{-}]^{6+}$ and $[\mathbf{L2}_{4}\mathbf{Cd}_{4}-4\mathbf{PF}_{6}^{-}]^{4+}$, respectively. The tricyclic structure L3₃Zn₃ is verified by the ESI-MS (Fig. 3) with the peaks at m/z 547.7024, 720.6109, and 1008.8078 corresponding to the charged moieties $[L3_3Zn_3-5PF_6^-]^{5+}$, $[L3_{3}Zn_{3}-4PF_{6}^{-}]^{4+}$, and $[L3_{3}Zn_{3}-3PF_{6}^{-}]^{3+}$, respectively; the corresponding isotope distributions of L3₃Zn₃ are shown in Fig. S18. Similarly, the ESI mass spectrometry of $L3_3Cd_3$ at 575.8367, 756.0364, and 1056.0194 correspond to the charged moieties $[L3_3Cd_3-5PF_6^-]^{5+}$, $[L3_3Cd_3-4PF_6^-]^{4+}$, and $[L3_3Cd_3 - 4PF_6^-]^{4+}$ $3PF_6^{-}$ ³⁺, respectively; all isotope patterns are in good accordance with the theoretical distribution (Fig. S21).

Such results from the ESI-MS data provide valuable information about the molecular composition and is useful for the identification of components in the compounds possessing different molecular weights. These results are consistent with the results of the NMR data mentioned above.

2.3. Analysis of 2D DOSY NMR spectra

NMR spectroscopy Diffusion-ordered (DOSY-NMR) experiments were carried out to obtain the size information of the synthesized supramolecular assemblies. As shown in Fig. 4, $L1_3Zn_3\&L1_4Zn_4$ and $L2_3Zn_3\&L2_4Zn_4$ explicitly show two bands that suggest that the self-assemblies formed two different supramolecular architectures. The DOSY-NMR spectrum of $L3_3Zn_3$ shows the narrow bands that suggest that the selfassemblies formed a pure tri-metallocycle architecture. Different components in $L1_3Zn_3\&L1_4Zn_4$ and $L2_3Zn_3\&L2_4Zn_4$ have different diffusion degrees. The experimental diffusion coefficients derived from the spectra measured in CD₃CN at 298 K were $2.75 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ for $\mathbf{L1}_4 \mathbf{Zn}_4$ and $3.31 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ for $L1_3Zn_3$. The diffusion coefficient of $L1_4Zn_4$ was lower than that of L1₃Zn₃, suggesting an increase in the size. For all the polymers, the experimental hydrodynamic radius (r_H) was calculated via the Stokes-Einstein equation^{34,28}. Experimental hydrodynamic radius for $L1_4Zn_4$ and $L1_3Zn_3$ are calculated to be 2.16 nm and 1.80 nm, respectively. The same conclusion can be summarized for



Fig. 4 2D DOSY-NMR spectra of $L1_3Zn_3\&L1_4Zn_4$, $L2_3Zn_3\&L2_4Zn_4$, and $L3_3Zn_3$.

 $L_{2_3}Zn_3 \& L_{2_4}Zn_4$ that the diffusion coefficients are 2.63 × 10⁻¹⁰ m^2s^{-1} for $L2_4Zn_4$ and $3.47 \times 10^{-10} m^2s^{-1}$ for $L2_3Zn_3$, the radius are 2.26 nm for $L2_4Zn_4$ and 1.72 nm for $L2_3Zn_3$. The diffusion coefficient of $L3_3Zn_3$ is $3.63 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ and its radius is 1.64 nm. The typical tpyH^{3',5'} has been assigned. The ratio of content of each component (L_3M_3/L_4M_4) can be calculated from the integrated areas of tpyH^{3',5'} proton peaks in ¹H NMR. $L1_3Zn_3/L1_4Zn_4$ is appropriately 0.4 while $L2_3Zn_3/L2_4Zn_4$ is appropriately 0.6 (Table 1). The same regularity exists in the series of metallo-macrocycles $L1_3Cd_3\&L1_4Cd_4$ $L2_3Cd_3\&L2_4Cd_4$, and $L3_3Cd_3$ (Fig. S14 and S15). It is clear that the ratio (L_3M_3/L_4M_4) increased with the increasing radius of the heteroatom in the ligands. Moreover, in comparison with L1 and L2, the sulphur atom (S) of monomer L3 has more extrusion effects that makes the angle α closer to the bend angle (60°) caused by the adjacent ditopic terpyridyl ligands.

2.4. Analysis of UV-Vis spectra

UV-Vis spectra of complexes were examined in acetonitrile. The detailed photophysical characteristics are summarized in Table S1. The characteristic absorption bands around 340 nm and 400 nm in the spectra of all the complexes (**Fig. 5**) can be assigned to the spin-allowed $d\rightarrow\pi$ metal-to-ligand charge transfer (MLCT)

Table 1. Diffusion Coefficients, Hydrodynamic Radii, andRatio of L_3M_3 / L_4M_4 .

Complex	$D [10^{-10} m^2 s^{-1}]^a$	r _H [nm] ^b	Ratio (T/Q) ^c
$L1_3Zn_3$	3.31	1.80	0.4
$L1_4Zn_4$	2.75	2.16	
$L2_3Zn_3$	3.47	1.73	0.6
$L2_4Zn_4$	2.63	2.26	
$L3_3Zn_3$	3.63	1.64	
$L1_3Cd_3$	2.95	2.02	1.0
$\mathbf{L1}_{4}\mathbf{Cd}_{4}$	2.69	2.21	
$L2_3Cd_3$	3.24	1.84	1.8
$L2_4Cd_4$	3.02	1.97	
$L3_3Cd_3$	2.75	2.16	

^aDiffusion coefficient, deduced from the 2D DOSY NMR experiments

conducted in CD₃CN at 298 K. ^bHydrodynamic radii calculated via the Stokes-Einstein equation $D=k_BT/6\pi\eta r_H$ (k_B, Boltzmann constant; T, absolute temperature; $\eta = 0.367$ mPa·s). ^cRatio = A_T/A_Q; A is the area ratio of tpyH^{3',5'} of complex L₃M₃ and L₄M₄.



Fig. 5 The ultraviolet-visible spectra of compounds L_3M_3 and L_4M_4 recorded in CH₃CN (5.0×10⁻⁵ M).

transitions and ligand-centered $\pi \rightarrow \pi^*$ transitions⁴³.

UV-Vis spectra of $L1_3Zn_3\&L1_4Zn_4$ and The $L1_3Cd_3\&L1_4Cd_4$ reveal the broader and weaker absorption bands corresponding to the N-C₈H₁₇ substituted groups. The absorption spectra of other complexes tethered to O and S heteroatoms display smaller red-shift trends, but a more pronounced coverage of electron-donating groups (EDGs). The intensities of the absorption bands at 345 nm in $L1_3Zn_3\&L1_4Zn_4$ and $L1_3Cd_3\&L1_4Cd_4$ are relatively lower than those of $L3_3Zn_3$ and $L3_3Cd_3$ due to the presence of the EDGs. More importantly, the UV-Vis spectra of all the complexes are much more structured and show obvious red-shifts when compared to the monomeric ligand L at the room temperature (Fig. S29).

2.5. Analysis of fluorescence spectra

Under photon excitation, the fluorescence profiles of all complexes plotted in Fig. S30 show the wavelength-dependent emission bands. The peaks of fluorescence emission, which is the blue-green emission at the test temperature, are attributed to the MLCT in the complexes. This regularity coheres with that of typical UV absorption peaks. It should be noted that, in acetonitrile solution, complexes with **O** and **S** atoms show very similar emission spectra in terms of peak emission wavelength and spectra profile (Table S2). For complex $L_{13}Zn_3\&L_{14}Zn_4$ and $L_{13}Cd_3\&L_{14}Cd_4$, the large red-shift of emission from N-C₈H₁₇ substituted to the trimer or tetramer hints electron-donating effect, which has been extensively studied⁴³.

3. Conclusion

A family of well-defined macrocycles possessing $\langle tpy-M^{\Box}-tpy \rangle$ (**M** = Zn or Cd) connectivity has been prepared using heteroatom-containing bitopic terpyridine ligands in a one-pot, self-assembling procedure. The molecular compositions as well as the sizes of the macrocycles were confirmed by NMR spectroscopy and ESI-MS spectrometry. For the size characterization, the hydrodynamic radii of the supramolecular architectures have been obtained by the 2D DOSY NMR. Pure trimer compounds have been synthesized. Heteroatoms (**N**, **O**, **S**) significantly contributed to the molecular size of the assemblies by adjusting the stretch angles of the organic building blocks. The photochemical properties of the polymers were significantly modulated by the heteroatom and the metal ion center.

4.1. Materials and methods

4. Experimental section

Chemicals were purchased from Sigma/Aldrich, Fisher Scientific, Energy Chemical, Alfa Aesar and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al₂O₃ (IB-F) or SiO₂ (IB2-F). Column chromatography was conducted using neutral Al₂O₃ Brockman Activity I (60-325 mesh) or SiO₂ (60-200 mesh) from Fisher Scientific. NMR spectroscopy were recorded on a Bruker NMR 400 or 500 MHz spectrometer, using CDCl₃ for ligands and CD₃CN for metallo-products. ESI mass spectrometry (MS) experiments were performed on a Waters Synapt HDMS quadrupole/time-of-flight (Q/ToF) tandem mass spectrometer. This instrument contains a triwave device between the Q and ToF analyzers, consisting of three collision cells in the order trap cell, ion mobility cell, and transfer cell. Trap and transfer cells are pressurized with Ar, and the ion mobility cell is pressurized with N₂ flowing in a direction opposite to that of the entering ions.

4.2. Synthesis and characterizations of L1

To a solution of 3,6- Dibromo carbazole (3.25 g, 10 mmol) and 1-bromooctane (2.12 g, 11 mmol) in acetonitrile (100 mL), K₂CO₃ powder (2.76 g, 20 mmol) was added. The resultant suspension was refluxed for 20 hours under nitrogen. After cooling to 25 °C, the acetonitrile was concentrated in vacuo to give a grey residue, which was purified by column chromatography (neutral Al₂O₃) eluting with a 1:1 mixture of dichloromethane and petroleum ether to give 1, as a white solid: (3.80 g, 8.7 mmol, 87%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.13 (s, 2H), 7.57 (d, J = 4.0 Hz, 2H), 7.28 (d, J = 4.0 Hz, 2H), 4.23 (t, J = 6.0 Hz, 2H), 1.84-1.80 (m, 2H), 1.33-1.23 (m, 10H), 0.89 (t, J = 3.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 139.23, 128.99, 123.47, 123.24, 111.98, 110.39, 43.34, 31.78, 29.33, 29.16, 28.81, 27.24, 22.67, 14.11. MS: Found For: 436.0786 [M-H⁺] (Calcd. For: 437.2201) (Fig. S26). To a solution of 1 (0.44 g, 1.0 mmol) and (4- ([2,2': 6', 2"- terpyridyl]-4'-) - benzene boric acid (0.92 g, 2.60 mmol) in THF (100 mL), aqueous NaOH (200 mg, 5.0 mmol) was added. The mixture was degassed for 10 minutes, then Pd(PPh₃)₄ (130 mg, 0.11 mmol) was added. After refluxing for 48 hours under N2, the solvent was removed in vacuo to give a residue that was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous MgSO₄, concentrated in vacuo to give a residue that was purified by flash column chromatography (neutral Al₂O₃) eluting with dichloromethane and petroleum ether (1:1, v:v) to give L1, as a white solid: (0.67 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.87 (s, 4H), 8.79 (d, J = 4.0 Hz, 4H), 8.72 (d, J = 5.0 Hz, 4H), 8.51 (s, 2H), 8.08 (d, J = 4.0 Hz, 4H), 7.93 (d, J = 5.0 Hz, 4H), 7.91 (t, J = 4.0 Hz, 4H), 7.86 (d, J = 4.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 5.0 Hz, 4H), 4.39 (t, J = 6.0 Hz, 2H), 2.0-1.92 (m, 2H), 1.45-1.26 (m, 10H), 0.90 (t, J = 6.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 158.96, 156.37, 155.96, 155.48, 149.87, 149.18, 142.77, 140.71, 136.91, 136.33, 132.60, 131.62, 127.76, 127.68, 123.85, 123.57, 121.42, 119.05, 118.67, 109.26, 47.42, 31.81, 29.47, 29.27, 27.38, 25.53, 25.15, 22.65, 14.13. ESI/MS (m/z): Found For: 894.4404 (Calcd. For: 893.6797) (Fig. S22-S25).

4.3. Synthesis and characterizations of L2

To a round bottom flask, Diphenylene-oxide (8.40 g, 50 mmol), bromine (2.6 mL) dissolved in 30 mL glacial acetic acid were added. The resultant suspension was heating for 6 hours under nitrogen at 120 °C. After cooling to 25 °C, the intermediate product **2** was recovered by filtration and recrystallization in

acetic acid and vacuum drying as a white solid (12.2 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.03 (s, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8 Hz, 2H) (Fig. S27)⁴⁶. To a solution of **2** (0.324 g, 1.0 mmol) and (4- ([2,2': 6', 2"- terpyridyl]-4'-) - benzene boric acid (0.88 g, 2.50 mmol) in THF (100 mL), aqueous NaOH (160 mg, 4.0 mmol) was added. The mixture was degassed for 10 minutes, then Pd(PPh₃)₄ (115 mg, 0.10 mmol) was added. Following the procedure **L1**, the pure product **L2** was obtained as a white solid (0.55 g, 70%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.81 (s, 4H), 8.74 (d, J = 4.0 Hz, 4H), 8.68 (d, J = 4.0 Hz, 4H), 7.84 (d, J = 5.0 Hz, 4H), 7.78 (d, J = 5.0 Hz, 2H), 7.35 (t, J = 5.0 Hz, 4H) (Fig. S28)²⁸.

4.4. Synthesis and characterizations of L3

To a round bottom flask, Dibenzothiophene (8.40 g, 45.6 mmol), bromine (2.6 mL) dissolved in 100 mL glacial acetic acid were added. Following the procedure intermediate 2, the intermediate product 3 was obtained as a white solid (12.2 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.26 (s, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), (Fig. S27)⁴⁶. To a solution of 3 (0.34 g, 1.0 mmol) and (4- ([2,2': 6', 2"- terpyridyl]-4'-) - benzene boric acid (0.88 g, 2.50 mmol) in THF (100 mL), aqueous NaOH (160 mg, 4.0 mmol) was added. The mixture was degassed for 10 minutes, then Pd(PPh₃)₄ (132 mg, 0.11 mmol) was added. Following the procedure L2, the pure product L3 was obtained as a white solid (0.6 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.80 (s, 4H), 8.74 (d, J = 5.0 Hz, 4H), 8.68 (d, J= 5.0 Hz, 4H), 8.50 (s, 2H), 8.05 (d, J = 4.0 Hz, 4H), 7.95 (d, J = 5.0 Hz, 2H), 7.88 (d, J = 5.0 Hz, 4H), 7.87 (t, J = 5.0 Hz, 4H), 7.79 (d, J = 4.0 Hz, 2H), 7.35 (t, J = 5.0 Hz, 4H) (Fig. S28)²⁸.

4.5. Synthesis and characterizations of $L1_3Zn_3\&L1_4Zn_4$

Zn(NO₃)₂·6H₂O (3.72 mg, 0.0125 mmol) in MeOH was added to a stirred solution of L1 (11.18 mg, 0.0125 mmol) in $CHCl_3/MeOH$ (v:v = 1:1, 20 mL). The colour instantly changed to yellow, and the mixture was heated at reflux for 10 hours at 70 \Box . After cooling to room temperature, the expectant product was deposited by NH₄PF₆ (20 times) which was filtered and washed with MeOH (3×20 mL) and water thoroughly to give a yellow solid (13.5 mg, 91%). ¹H NMR (400 MHz, CD₃CN) δ (ppm): 9.09 (s, 20H), 9.07 (s, 8H), 8.78 (m, 28H), 8.74 (s, 10H), 8.38 (m, 28H), 8.22 (m, 56H), 8.06 (d, 16H), 7.91 (d, 20H), 7.84 (d, 10H), 7.79 (m, 14H), 7.44 (t, 28H), 4.45 (t, 14H), 1.42 (m, 14H), 1.28 (m, 70H), 0.88 (t, 21H) (Fig. S1), ESI/MS (m/z): Found For: 479.6809 $[L1_3Zn_3-6PF_6^-]^{6+}$ (Calcd. For: 479.7001), 604.6017 $[L1_3Zn_3-5PF_6^{-}]^{5+}$ (Calcd. For 604.6024), 791.9907 $[L1_3Zn_3^{-}]^{3+}$ $4PF_6^{-1}^{4+}$ (Calcd. For: 792.0015), 1104.6476 [L1₃Zn₃-3PF₆⁻¹] (Calcd. For: 1104.3976), respectively and Found For: 479.6809 $[\mathbf{L1}_{4}\mathbf{Zn}_{4}-8PF_{6}^{-}]^{8+}$ (Calcd. For: 479.7021), 568.9147 $[\mathbf{L1}_{4}\mathbf{Zn}_{4}-7PF_{6}^{-}]^{7+}$ (Calcd. For: 568.9087), 687.7256 $[\mathbf{L1}_{4}\mathbf{Zn}_{4}-6PF_{6}^{-}]^{6+}$ (Calcd. For: 687.9014), 854.6547 [$L1_4Zn_4$ -5PF₆]⁵⁺ (Calcd. For: $[L1_4Zn_4-4PF_6^{-}]^{4+}$ (Calcd. 854.5986), 1104.6476 For: 1104.5876), respectively.

4.6. Synthesis and characterizations of $L2_3Zn_3\&L2_4Zn_4$

L2 (9.78 mg, 0.0125 mmol) was dissolved in a mixed solvent of CHCl₃ and CH₃OH at the ratio of 1:1 in 20 mL, Zn(NO₃)₂· $6H_2O$ (3.72 mg, 0.0125 mmol) in 20 mL MeOH was added. After refluxing for 10 hours at 70 \Box . After cooling to room temperature, the expectant product was deposited by NH₄PF₆ (20 times) which was filtered and washed with MeOH (3 × 20 mL) and water thoroughly to give a grey solid (12.8 mg, 95%). ¹H NMR (400 MHz, CD₃CN) δ (ppm): 9.12 (s, 18H), 9.09 (s, 10H), 8.82 (m, 18H), 8.80 (m, 10H), 8.68 (s, 9H), 8.61 (s, 5H), 8.39 (m, 28H), 8.19 (m, 56H), 8.07 (d, 18H), 7.90 (m, 28H), 7.82 (m, 10H), 7.44 (t, 28H) (Fig. S2). ESI/MS (m/z): Found For: 537.9226 [$L2_3Zn_3$ -5PF₆⁻]⁵⁺ (Calcd. For: 537.9276), 708.6337 [$L2_3Zn_3$ -4PF₆⁻]⁴⁺ (Calcd. For: 708.6297), 993.1747 [$L2_3Zn_3$ -3PF₆⁻]³⁺ (Calcd. For: 993.2076), respectively and Found For: 505.4118 [$L2_4Zn_4$ -7PF₆⁻]⁷⁺ (Calcd. For: 505.4098), 613.7965 [$L2_4Zn_4$ -6PF₆⁻]⁶⁺ (Calcd. For: 613.8054), 765.3454 [$L2_4Zn_4$ -5PF₆⁻]⁵⁺ (Calcd. For: 765.5063), 993.1747 [$L2_4Zn_4$ -4PF₆⁻]⁴⁺ (Calcd. For: 993.1875), respectively.

4.7. Synthesis and characterizations of $L3_3Zn_3$

L3 (9.98 mg, 0.0125 mmol) was dissolved in a mixed solvent of CHCl₃ and CH₃OH at the ratio of 1:1 in 20 mL, Zn(NO₃)₂· 6H₂O (3.72 mg, 0.0125 mmol) in 20 mL MeOH was added. After refluxing for 10 hours at 70 \square . After cooling to room temperature, the expectant product was deposited by NH₄PF₆ (20 times) which was filtered and washed with MeOH (3 × 20 mL) and water thoroughly to give a solid (12.5 mg, 91%). ¹H NMR (400 MHz, CD₃CN) δ (ppm): 9.11 (s, 12H), 8.94 (s, 6H), 8.81 (d, 12H), 8.41 (d, 12H), 8.30 (d, 12H), 8.25 (m, 18H), 8.12 (d, 6H), 7.91 (d, 12H), 7.47 (t, 12H) (Fig. S3). ESI/MS (m/z): Found For: 547.7024 [L3₃Zn₃-5PF₆]⁵⁺ (Calcd. For: 547.5978), 720.6109 [L3₃Zn₃-4PF₆]⁴⁺ (Calcd. For: 720.6001), 1008.8078 [L3₃Zn₃-3PF₆]³⁺ (Calcd. For: 1009.0127), respectively.

4.8. Synthesis and characterizations of L1₃Cd₃&L1₄Cd₄

L1 (11.18 mg, 0.0125 mmol) was dissolved in a mixed solvent of CHCl₃ and CH₃OH at the ratio of 1:1 in 20 mL, Cd(NO₃)₂. 4H₂O (3.86 mg, 0.0125 mmol) in 20 mL MeOH was added. The colour instantly changed to yellow, and the mixture was heated at reflux for 10 hours at 70 \Box . After cooling to room temperature, the expectant product was deposited by NH_4PF_6 (20 times) which was filtered and washed with MeOH $(3 \times 20 \text{ mL})$ and water thoroughly to give a yellow solid (14.7 mg, 98%). ¹H NMR (400 MHz, CD₃CN) δ (ppm): 9.03 (m, 28H), 8.82 (d, 28H), 8.75 (m, 14H), 8.33 (d, 28H), 8.23 (t, 28H), 8.18 (d, 28H), 8.14 (m, 28H), 8.03 (d, 14H), 7.77 (d, 14H), 7.53 (t, 28H), 4.45 (t, 14H), 1.42 (m, 14H), 1.28 (m, 70H), 0.88 (t, 21H) (Fig. S1). ESI/MS (m/z): Found For: 503.1736 [L1₃Cd₃-6PF₆⁻]⁶⁺ (Calcd. For: 503.3001), 632.9904 $[L1_3Cd_3-5PF_6^-]^{5+}$ (Calcd. For: 633.0012), 827.4867 $[L1_{3}Cd_{3}-4PF_{6}^{-}]^{4+}$ (Calcd. For: 827.5013), respectively and Found For: 503.1736 [L1₄Cd₄-8PF₆⁻]⁸⁺ (Calcd. For: 503.2976), 719.2076 $[L1_4Cd_4-6PF_6^-]^{6+}$ (Calcd. For: 719.4014), respectively.

4.9. Synthesis and characterizations of $L2_3Cd_3\&L2_4Cd_4$

L2 (9.78 mg, 0.0125 mmol) was dissolved in a mixed solvent of CHCl₃ and CH₃OH at the ratio of 1:1 in 20 mL, Cd(NO₃)₂. 4H₂O (3.86 mg, 0.0125 mmol) in 20 mL MeOH was added. After refluxing for 10 hours at 70 \square . After cooling to room temperature, the expectant product was deposited by NH₄PF₆ (20 times) which was filtered and washed with MeOH $(3 \times 20 \text{ mL})$ and water thoroughly to give a grey solid (12.9 mg, 95%). ¹H NMR (400 MHz, CD₃CN) δ (ppm): 9.05 (s, 10H), 9.03 (s, 18H), 8.82 (m, 28H), 8.66 (s, 5H), 8.62 (s, 9H), 8.36 (m, 28H), 8.24 (t, 28H), 8.16 (m, 38H), 8.08 (m, 28H), 7.88 (d, 18H), 7.53 (t, 28H) (Fig. S2). ESI/MS (m/z): Found For: 566.1246 [L2₃Cd₃- $^{-14}$ $5PF_6^{-1}^{5+}$ (Calcd. For: 566.3015), 743.8853 $[L2_3Cd_3-4PF_6^{-1}]^{2+}$ \tilde{S}_{+} (Calcd. (Calcd. For: 744.1067), 1040.1736 $[L2_3Cd_3-3PF_6]^{3+1}$ For: 1040.5017), respectively and Found For: 645.1247 [L2₄Cd₄- $6PF_6^{-}]^{6+}$ (Calcd. For: 645.3037), 1140.1736 $[\mathbf{L2}_4\mathbf{Cd}_4-4PF_6^{-}]^4$ (Calcd. For: 1040.4026), respectively.

4.10. Synthesis and characterizations of L3₃Cd₃

L3 (9.98 mg, 0.0125 mmol) was dissolved in a mixed solvent of $CHCl_3$ and CH_3OH at the ratio of 1:1 in 20 mL, $Cd(NO_3)_2$.

4H₂O (3.86 mg, 0.0125 mmol) in 20 mL MeOH was added. M_23NUS After refluxing for 10 hours at 70 □. After cooling to room temperature, the expectant product was deposited by NH₄PF₆ (20 times) which was filtered and washed with MeOH (3 × 20 mL) 24. and water thoroughly to give a solid (12.7 mg, 92%). ¹H NMR (400 MHz, CD₃CN) δ (ppm): 9.04 (s, 12H), 8.92 (s, 6H), 8.82 (d, 12H), 8.36 (d, 12H), 8.24 (m, 24H), 8.20 (d, 6H), 8.13 (d, 12H), 8.06(d, 6H), 7.52 (t, 12H) (Fig. S3). ESI/MS (m/z): Found For: 575.8367 [L3₃Cd₃-5PF₆⁻]⁵⁺ (Calcd. For: 575.9001), 756.0364 [L3₃Cd₃-4PF₆⁻]⁴⁺ (Calcd. For: 756.1009), 1056.0194 [L3₃Cd₃-3PF₆⁻]³⁺ (Calcd. For: 1056.1006), respectively. 27.

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