

# Metallo-Supramolecular Self-Assembly of a Multicomponent Ditrigon Based on Complementary Terpyridine Ligand Pairing

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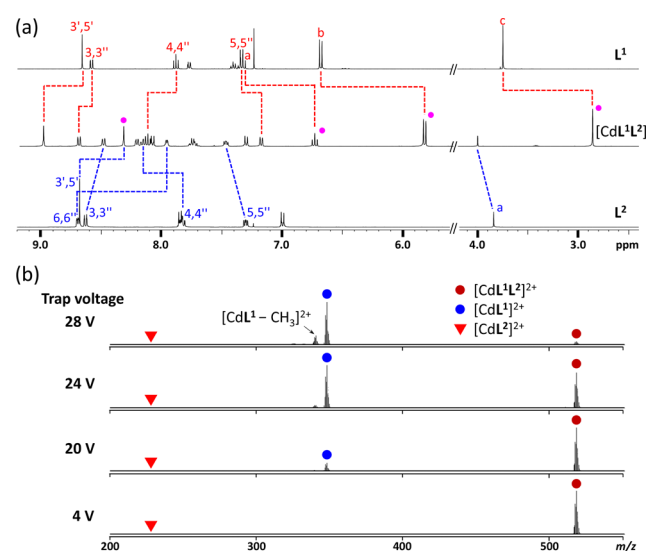
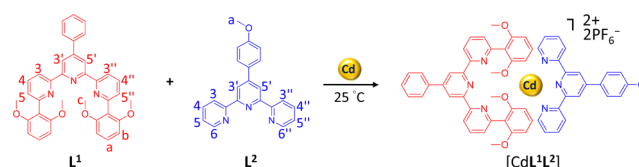
**S** Supporting Information

**ABSTRACT:** Predesigned complementary complexation of two 2,2':6',2''-terpyridine-based ligands was established by installing 2,6-dimethoxyphenyl substituents at the terpyridyl 6,6''-positions, which provided ancillary ion-dipole interactions in the coordination process and extra  $\pi$ -stacking stabilization in the resultant heteroleptic complex. The high-fidelity self-recognition ligation afforded facile access to the quantitative self-assembly of multicomponent triangle  $[\text{Cd}_6\text{L}^3_3\text{L}^4_3]$  and ditrigon  $[\text{Cd}_{15}\text{L}^3_6\text{L}^5_3]$  (that is, a hexagon with six  $120^\circ$  angles and two alternating edge lengths). It was found that the linear 6,6''-substituted ditopic motif ( $\text{L}^3$ ) would be directed by the ligand geometry of  $\text{L}^5$  to selectively incorporate into the parallel homoleptic connections in the bilayered framework.

Inspired by precise biological self-assembly processes,<sup>1</sup> many chemists have devoted their efforts to manipulation of intermolecular noncovalent interactions, in order to create intricate assemblies with desired functions.<sup>2</sup> In artificial systems, metal coordination-driven self-assembly<sup>3</sup> indeed provides facile access to the preparation of predetermined well-defined architectures, but which mostly are composed of less than three kinds of organic ligands. To the best of our knowledge, only a few examples of three or more ligands have been documented.<sup>4</sup> This limitation is mainly due to the increased number of competing pathways leading to unwanted products.<sup>5</sup> Several strategies have been developed to reduce the possibility of irreversible misconnections in a multicomponent system, such as ligand geometry-directed assembly,<sup>6</sup> template-guided organization,<sup>5c,7</sup> complementary complexation,<sup>8</sup> coordination geometry preferences,<sup>9</sup> hierarchical stepwise assembly,<sup>10</sup> and orthogonal self-assembly.<sup>11</sup> However, it remains a formidable challenge to accurately introduce molecular functionality into specific positions in a supramolecular framework, especially via a one-pot thermodynamically driven assembly. For this purpose, a more delicate ligand design might be anticipated.

2,2':6',2''-Terpyridine (tpy) derivatives have been widely utilized in the construction of metallo-supramolecular architectures.<sup>12</sup> Asymmetric bis(tpy) complexes can be prepared by stepwise procedures,<sup>13</sup> but a one-step methodology to generate asymmetric connections is highly demanded for building versatile structures. Here we design and synthesize a complementary pair of tpy-based ligands that could readily undergo selective complexation with  $\text{Cd}^{\text{II}}$  ions to yield a single heteroleptic complex under ambient conditions. Based on our developed toolkit, the

## Scheme 1. Coordination of $\text{L}^1$ and $\text{L}^2$ with $\text{Cd}^{\text{II}}$ Ions



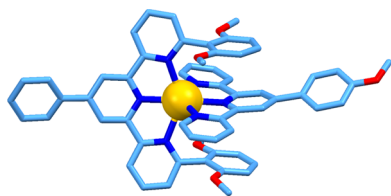
**Figure 1.** (a)  $^1\text{H}$  NMR spectra of  $\text{L}^1$ ,  $[\text{CdL}^1\text{L}^2]$ , and  $\text{L}^2$ . (b) Tandem mass spectra for  $[\text{CdL}^1\text{L}^2]^{2+}$  at trap voltages varied from 4 to 28 V.

construction of two multicomponent self-assemblies, i.e., an enlarged triangle and a bilayered ditrigon, is successfully achieved.

Ligand  $\text{L}^1$ , bearing 2,6-dimethoxyphenyl groups at 6,6''-positions of 4'-phenyl-tpy, was synthesized via the Suzuki–Miyaura coupling reaction of the 6,6''-dibromo-tpy precursor with 2,6-dimethoxyphenylboronic acid in good yield (Scheme S1), and its structure was established by NMR spectroscopy (Figure S2) and mass spectrometry (Figure S5). Ligand  $\text{L}^2$  was prepared following the previously reported procedure.<sup>14</sup> When a 1:1 mixture of  $\text{L}^1$  and  $\text{L}^2$  was treated with 1 equiv of  $\text{Cd}^{\text{II}}$  ions at  $25^\circ\text{C}$  (Scheme 1), the  $^1\text{H}$  NMR spectrum (Figure 1a) exhibited four sharp singlets at  $\delta = 8.99$  ( $3',5'$ -tpy H's of  $\text{L}^1$ ),  $8.33$  ( $3',5'$ -tpy H's of  $\text{L}^2$ ),  $4.00$  ( $\text{OCH}_3$  of  $\text{L}^2$ ), and  $2.86$  ( $\text{OCH}_3$  of  $\text{L}^1$ ) ppm, suggesting the formation of heteroleptic  $[\text{CdL}^1\text{L}^2]$ . The complete assignments were further confirmed by 2D COSY and NOESY

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**Figure 2.** X-ray crystal structure of complex  $[\text{CdL}^1\text{L}^2]$  (cyan, carbon; blue, nitrogen; red, oxygen; yellow, cadmium). Hydrogen atoms,  $\text{PF}_6^-$  ions, and solvent molecules are omitted for clarity.

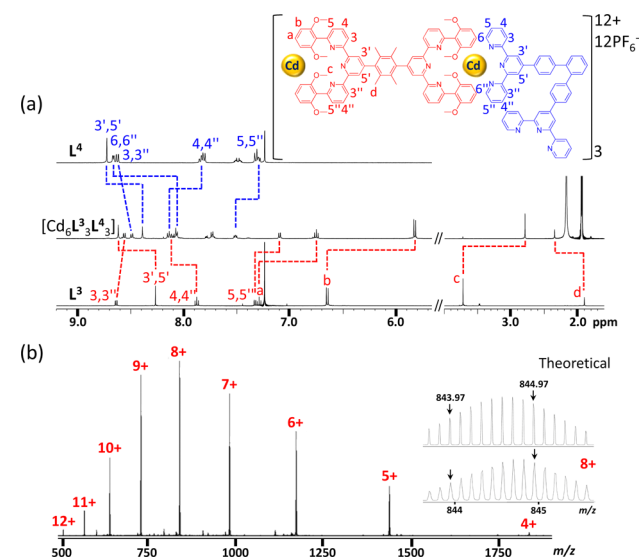
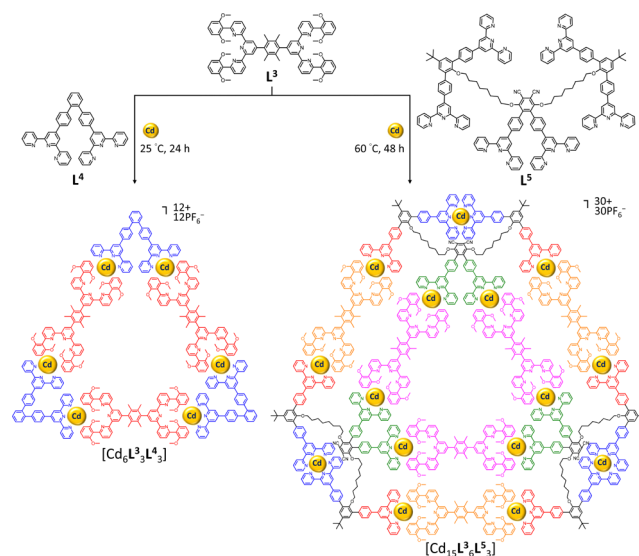
NMR experiments (Figures S10 and S11). Moreover, in comparison with uncoordinated  $\text{L}^1$  and  $\text{L}^2$ , four significant upfield shifts (Figure 1a, pink circles) for the dimethoxyphenyl protons of  $\text{L}^1$  and the 3',5'-tpy protons of  $\text{L}^2$  were clearly observed. This shielding effect is most likely caused by  $\pi$ -stacking between the tpy moiety and the dimethoxyphenyl substituents, which is consistent with the observation in the solid state (Figure 2).<sup>15</sup> Eventually, the existence of  $[\text{CdL}^1\text{L}^2]$  was unequivocally corroborated by the ESI-MS peak at  $m/z = 517.0842$  corresponding to  $[\text{CdL}^1\text{L}^2]^{2+}$  (Figure 1b) and its single-crystal X-ray structure (Figure 2).

Tandem mass spectrometry ( $\text{MS}^2$ ) was utilized to further understand the assembly mechanism for the self-selective coordination. In the experiment, the  $[\text{CdL}^1\text{L}^2]^{2+}$  ions were selected by a quadrupole mass filter and subjected to collision-induced dissociation (CID) in the ion trap cell.<sup>16</sup> When the potential applied to the trap cell was gradually increased from 4 to 28 V, the major fragment attributed to  $[\text{CdL}^1]^{2+}$  was observed, but no detectable signal coming from  $[\text{CdL}^2]^{2+}$  was found (Figure 1b), indicating that  $\text{L}^1$  has a higher binding affinity to the  $\text{Cd}^{\text{II}}$  ion. Notably, at elevated trap voltages,  $[\text{CdL}^1]^{2+}$  further fragmented to  $[\text{CdL}^1 - \text{CH}_3]^{2+}$  ions (Figures 1b and S28), which presumably were stabilized by the  $\text{Cd}\cdots\text{O}$  interaction.<sup>17</sup> Accordingly, it is conjectured that the auxiliary ion-dipole interactions between the methoxy groups and the  $\text{Cd}^{\text{II}}$  center make  $\text{L}^1$  serve as a pseudo-pentadentate ligand to facilitate the heteroleptic complexation. A similar phenomenon was observed in Schmittl's phenanthroline self-sorting systems.<sup>4b,18</sup> In addition, upon treatment of  $\text{L}^1$  with an equimolar amount of  $\text{Cd}(\text{NO}_3)_2$ , only the  $[\text{CdL}^1]$  adduct was produced, which was subsequently titrated with  $\text{L}^2$  and monitored by  $^1\text{H}$  NMR (Figure S22). The  $[\text{CdL}^1\text{L}^2]$  production was increased proportionally to the added  $\text{L}^2$  until reaching the stoichiometric point ( $[\text{L}^1]/[\text{L}^2] = 1$ ), implying that the  $\text{Cd}^{\text{II}}$  ion would not shuttle between  $\text{L}^1$  and  $\text{L}^2$ ; thus, the formation of homodimer  $[\text{CdL}^2_2]$  was inhibited.

X-ray crystallographic analysis of  $[\text{CdL}^1\text{L}^2]$  (Figure 2) showed that the  $\text{Cd}^{\text{II}}$  ion was in a pseudo-octahedral environment, and the two dimethoxyphenyl substituents and the central pyridine unit of  $\text{L}^2$  were parallel to each other, with an average centroid-centroid distance of 3.6 Å, which is comparable to common  $\pi$ - $\pi$  stacking distances in pyridine-containing metal complexes.<sup>19</sup> As compared to homoleptic  $[\text{CdL}^2_2]$ , this donor-acceptor-donor stacking provided the additional thermodynamic stabilization for the heteroleptic structure.

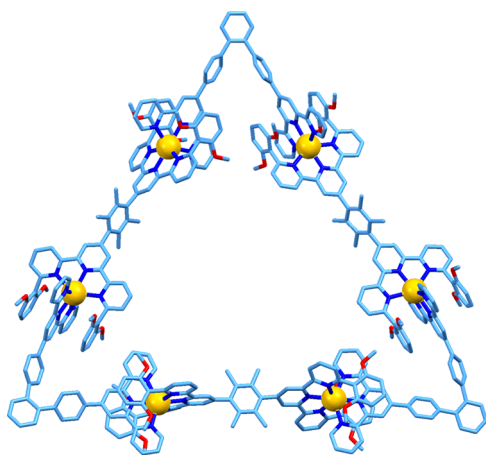
Building on our predesigned complementary ligand pair, the ditopic ligands  $\text{L}^3$  and  $\text{L}^4$  were synthesized (Scheme S2) and used as an edge and a vertex, respectively, for the self-assembly of the multicomponent triangle (Scheme 2). After an equimolar mixture of  $\text{L}^3$  and  $\text{L}^4$  was reacted with 2 molar equivalents of  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{PF}_6$  was utilized to precipitate the counterion-exchanged complex ( $\text{PF}_6^-$ ), which was subsequently dissolved in  $\text{CD}_3\text{CN}$ . The self-assembly process at 25 °C was monitored by  $^1\text{H}$  NMR.

## Scheme 2. Self-Assembly of Triangle $[\text{Cd}_6\text{L}^3_3\text{L}^4_3]$ and Ditrigon $[\text{Cd}_{15}\text{L}^3_6\text{L}^5_3]$



**Figure 3.** (a)  $^1\text{H}$  NMR spectra of  $\text{L}^4$ ,  $[\text{Cd}_6\text{L}^3\text{L}^4_3]$ , and  $\text{L}^3$ . (b) ESI-MS spectrum of  $[\text{Cd}_6\text{L}^3\text{L}^4_3]$  and isotope pattern of  $[\text{M} - 8\text{PF}_6]^{8+}$ .

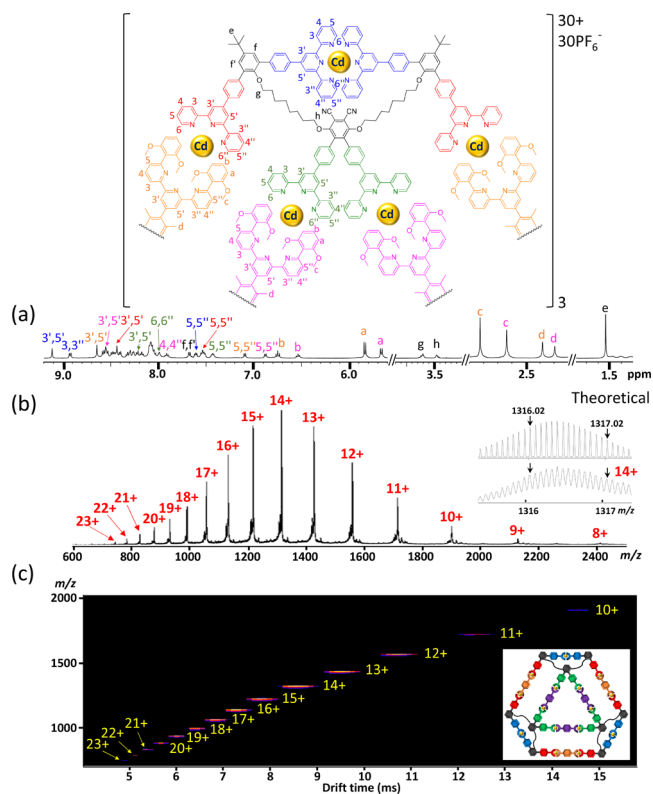
The result indicated that the time required to generate a single assembly was 1 day, and its cyclic structure was supported by the two distinct sets of tpy signals and four characteristic singlets at  $\delta = 8.62$  (3',5'-tpy  $H$ 's of  $\text{L}^3$ ), 8.39 (3',5'-tpy  $H$ 's of  $\text{L}^4$ ), 2.79 ( $\text{OCH}_3$  of  $\text{L}^3$ ), and 2.35 ( $\text{CH}_3$  of  $\text{L}^3$ ) ppm in the  $^1\text{H}$  NMR spectrum (Figure 3a) as well as a  $^{113}\text{Cd}$  NMR singlet at  $\delta = 242.09$  ppm (Figure S19). The DOSY spectrum (Figure S20) revealed that all the related peaks have the same diffusion coefficient ( $D = 2.71 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) in  $\text{CD}_3\text{CN}$ . The composition of  $[\text{Cd}_6\text{L}^3\text{L}^4_3]$  was further verified by ESI-MS, with the nine main peaks resulting from the 4+ to 12+ ions and their corresponding isotope distributions (Figures 3b and S29). Besides, the ESI-TWIM-MS structural analysis<sup>20</sup> of  $[\text{Cd}_6\text{L}^3\text{L}^4_3]$  showed an average collision cross-section (CCS) of  $983.8 \pm 20.7 \text{ \AA}^2$ , in good accord with the theoretical values (Figure S31 and Table S2). It is noteworthy that the preformed triangular  $[\text{Cd}_3\text{L}^4_3]$ <sup>21</sup> could be completely transformed into  $[\text{Cd}_6\text{L}^3\text{L}^4_3]$  in the presence of  $\text{L}^3$  and  $\text{Cd}^{\text{II}}$  ions at 60 °C after 6 days (Figure S27).



**Figure 4.** Crystal structure of  $[\text{Cd}_6\text{L}^3\text{L}^4_3]$  (cyan, carbon; blue, nitrogen; red, oxygen; yellow, cadmium). Hydrogen atoms,  $\text{PF}_6^-$  ions, and solvent molecules are omitted for clarity.

Single crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of diisopropyl ether into an MeCN solution of  $[\text{Cd}_6\text{L}^3\text{L}^4_3]$ . The solid-state structure (Figure 4) showed that the triangle with the expected composition is crystallized in the triclinic space group  $P\bar{1}$ , and each pseudo-octahedral  $\text{Cd}^{\text{II}}$  center is coordinated by two respective tpy units from  $\text{L}^3$  and  $\text{L}^4$ , resulting in an alternating ligand arrangement in the metallomacrocyclic. The six  $\text{Cd}^{\text{II}}$  centers are approximately located in the same plane to form an isogonal hexagon with two types of lateral Cd–Cd lengths (12.2 and 15.8 Å). In addition, the calculated CCS (TM: 1004.4 Å<sup>2</sup>) derived from the crystal structure agreed well with the experimental value (Table S2).<sup>22</sup>

To extend this spontaneous heteroleptic complexation to a more sophisticated assembly, we examined the self-assembly of  $\text{Cd}^{\text{II}}$  ions and ligands  $\text{L}^3$  and  $\text{L}^5$  (Scheme 2), with the expectation that  $\text{L}^3$  would selectively incorporate into the parallel lateral sides of our previously reported ring-in-ring structure,<sup>23</sup> which was constructed from  $\text{L}^5$  via a cooperative coordination of the tetraprotic intermediate. A mixture of  $\text{L}^3$  (6 equiv),  $\text{L}^5$  (3 equiv), and  $\text{Cd}^{\text{II}}$  ions (15 equiv) was heated at 60 °C for 2 days. The <sup>1</sup>H NMR spectrum of the resultant complex exhibited five distinguishable sets of tpy resonances (Figure 5a), which are indicative of the formation of the expected ditricon. The assignments were verified by the 2D ROESY and COSY NMR experiments (Figures S13–S18). The structure of  $[\text{Cd}_{15}\text{L}^3\text{L}^5_3]$  was also strongly supported by the diffusion coefficient of  $2.19 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  in  $\text{CD}_3\text{CN}$  (Figure S21) and three sharp <sup>113</sup>Cd NMR singlets at  $\delta = 266.46, 241.23,$  and  $239.51$  ppm in an integration ratio of 1:2:2 (Figure S19). The assembled composition of  $[\text{Cd}_{15}\text{L}^3\text{L}^5_3]$  was unambiguously confirmed by the 16 ESI-MS peaks generated from the ions with 8+ to 23+ charges (Figure 5b) and their isotope patterns (Figure S30). The experimental average CCS ( $2203.5 \pm 32.0 \text{ Å}^2$ ) derived from the narrow drift time distributions (Figure 5c) was consistent with the modeled ones (Table S2). Furthermore, the individual assemblies on mica imaged by AFM revealed an average height of  $1.1 \pm 0.2 \text{ nm}$  (Figure S32), and the average diameter of  $5.7 \pm 0.4 \text{ nm}$  measured by high-resolution TEM was in good agreement with the dimension of the energy-minimized structure (Figures S33 and S34). These results suggested that the insertion of  $\text{L}^3$  into the intramolecular homoleptic complex (Scheme 2, blue tpy's) was completely suppressed, which is supposedly due to the geometrical constraint imposed by the C8 alkyl spacer.



**Figure 5.** (a) <sup>1</sup>H NMR spectrum, (b) ESI-MS spectrum and isotope pattern of  $[\text{M} - 14\text{PF}_6^-]^{14+}$ , and (c) ESI-TWIM-MS plot of  $[\text{Cd}_{15}\text{L}^3\text{L}^5_3]$ .

In summary, a novel self-selective ligation approach has been developed to construct multicomponent tpy-based supramolecular architectures. The complementary ligand pair allowed us not only to transform a  $[\text{M}_3\text{L}_3]$  triangle into an enlarged analogue, but also to introduce the 6,6''-substituted building blocks into specific positions of the ring-in-ring framework on the basis of the preprogrammed ligand geometry. We believe that this heteroleptic complexation could pave the way for preparation of more elaborate and diverse self-assembled structures.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b01005.

- Experimental details and characterization data (PDF)
- Crystallographic data for  $[\text{CdL}^1\text{L}^2]$  (CIF)
- Crystallographic data for  $[\text{Cd}_6\text{L}^3\text{L}^4_3]$  (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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