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One-Pot Self-Assembly of Stellated Metallo-Supramolecules from Multivalent and Complementary Terpyridine-Based Ligands

Jun-Hao Fu, Shih-Yu Wang, Yu-Sheng Chen, Soumyakanta Prusty, and Yi-Tsu Chan*

Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan

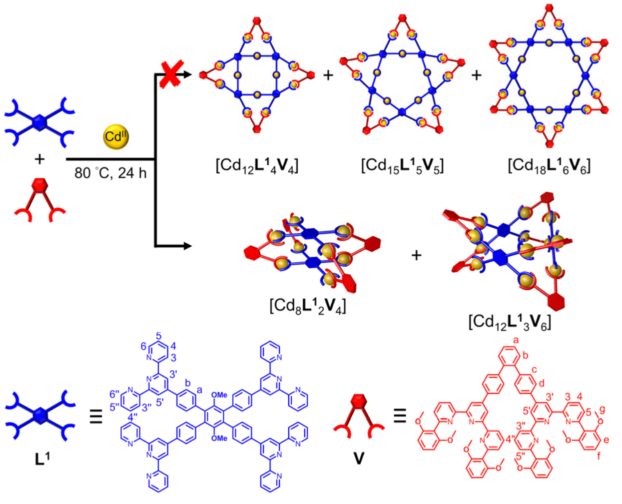
Supporting Information Placeholder

ABSTRACT: A series of stellated metallo-supramolecular architectures has been assembled through three-component integrative self-sorting. Building on the complementary ligand pairing, the initial attempts to synthesize the hexagram complex from a combination of X-shaped *tetrakis*- and V-shaped *bis*-terpyridine ligands, and Cd^{II} ions, resulted in an unprecedented mixture of stellated octanuclear and dodecanuclear metallocages, which were further isolated by column chromatography. To overcome the unexpected obstacle, the multivalent ligand design along with spontaneous heteroleptic complexation was applied to realization of the one-pot synthesis of the intricate topology. A centrally situated triangle served as a prop for quantitative formation of the six-pointed stellated complex. Notably, in the absence of the triangular prop, a four-pointed star was produced.

Metal-mediated self-assembly continues to spark the vibrant field of supramolecular chemistry, owing to its ability to deliver molecular architectures of aesthetic appeal.[1] Over the last few years, more intricate coordination-driven self-assembled structures, such as sphere-in-sphere polyhedrons,[2] multilayer polygons,[2b,3] and multicavity cages,[4] have been documented. Concurrently, such molecules possess diverse potential functions in host-guest chemistry,[5] catalysis,[6] drug delivery,[7] stabilizing media,[8] etc. To achieve greater complexity and functionality of such molecules, chemists seek to incorporate more than one type of ligands through integrative self-sorting process. Although such self-organizing events are ubiquitous in biological systems,[9] it still remains an arduous challenge to rational construction of artificial supramolecules of great intricacy, due to lack of efficient self-assembly strategies. Few approaches, such as topological control,[10] maximum site occupancy,[11] steric control strategies,[1b,12] and charge separation,[10,13] have been developed for spontaneous preparation of heteroleptic complexes.

Tridentate 2,2':6',2"-terpyridine (tpy) ligands garnered immense attention in construction of supramolecular assemblies due to its coordinating ability towards a wide range of transition metal ions.[1g,14] Metalloligands bearing robust <tpy-M^{II}-tpy> junctures are often chosen as primary components for construction of tpy-based heteroleptic supramolecular architectures.[1g,15] However, multistep synthesis and difficulties in purification cannot be avoided. Aiming for more efficient self-assembly processes, recently we emphasized the importance of ligand multivalency[3b,16] and developed complementary ligand pairing for one-pot synthesis of tpy-based multicomponent metallo-supramoleular architectures.[12d,12f] As compared with regular polygons and polyhedrons, construction of stellated metallo-supramolecules[15a,17] is more challenging because precise manipulation of non-covalent interactions between molecular subunits is needed for such high level self-assembly. Herein, we report rational construction of a series of tpy-based stellated architectures, including two stellated metallocages, $[Cd_8\mathbf{L}^1_2\mathbf{V}_4]$ and $[Cd_{12}\mathbf{L}^1_3\mathbf{V}_6]$, a four-pointed star, $[Cd_{12}\mathbf{L}^2_2\mathbf{V}_4]$, and a six-pointed star, $[Cd_{21}\mathbf{L}^3_3\mathbf{V}_6]$, based on multivalent ligand design and spontaneous heteroleptic complexation.

Scheme 1. Self-Assembly of Stellated Metallocages $[Cd_8L^1_2V_4]$ and $[Cd_{12}L^1_3V_6]$



Towards the construction of star polygons, X-shaped ligand $\mathbf{L}^1$ and 60°-bent *bis*-tpy ligand $\mathbf{V}$ were chosen to complex with Cd^{II} ions in a stoichiometric ratio of 1:1:3 (Scheme 1). The tetratopic ligand $\mathbf{L}^1$ was synthesized through the Suzuki-Miyaura coupling reaction (Scheme S1), whereas ligand $\mathbf{V}$ was obtained from the modified Kröhnke protocol and the subsequent Suzuki-Miyaura coupling reaction.[12f] 2,6-Dimethoxyphenyl groups were installed at terpyridyl 6,6"-positions of ligand $\mathbf{V}$ to meet the requirements for complementary ligand pairing.[12d] Nevertheless, the possible formation of $[Cd_{12}\mathbf{L}^1_4\mathbf{V}_4]$, $[Cd_{15}\mathbf{L}^1_5\mathbf{V}_5]$, and $[Cd_{18}\mathbf{L}^1_6\mathbf{V}_6]$ (Scheme 1) was not observed from the above mentioned combination. ESI-MS analysis revealed the unpredictable formation of a mixture of complexes $[Cd_8\mathbf{L}^1_2\mathbf{V}_4]$ and $[Cd_{12}\mathbf{L}^1_3\mathbf{V}_6]$ (Figure S27) and no signals of the expected complexes with a general formula, $[Cd_{3n}\mathbf{L}^1_n\mathbf{V}_n]$, were found. The mixture of $[Cd_8\mathbf{L}^1_2\mathbf{V}_4]$ and $[Cd_{12}\mathbf{L}^1_3\mathbf{V}_6]$ were again prepared from the required stoichiometric ratio of 1:2:4 ($\mathbf{L}^1$:$\mathbf{V}$:Cd). Both the complexes were found to remain in a concentration-dependent equilibrium with $[Cd_{12}\mathbf{L}^1_3\mathbf{V}_6]$ as a major product (Figure S13). Furthermore, the diffusion-

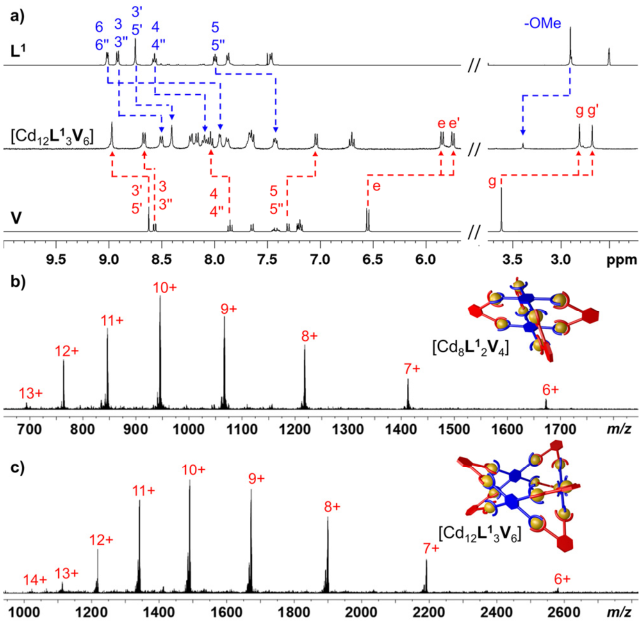


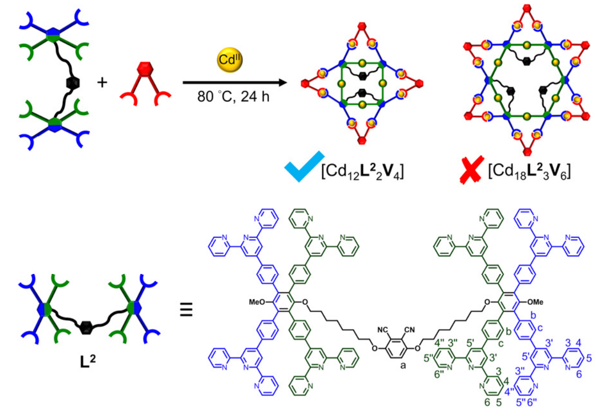
Figure 1. a) ^{1}H NMR spectra of **L**^{1}, **V**, and $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$. ESI-MS spectra of b) $[\mathrm{Cd}_8\mathbf{L}^1_2\mathbf{V}_4]$ and c) $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$.

ordered spectroscopy (DOSY) NMR experiment (Figure S14) confirmed the existence of two species with distinct diffusion coefficients in solution.

It is worth noting that the separation of $[\mathrm{Cd}_8\mathbf{L}^1_2\mathbf{V}_4]$ and $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$ was successfully achieved by column chromatography (Figures 1 and S15), which was mainly benefited from the relatively stable heteroleptic <tpy-Cd$^{\mathrm{II}}$-tpy'> connectivity,[12d,18] and their chemical formulas were further identified by ESI-MS (Figures 1b and 1c). The signals of $[\mathrm{Cd}_8\mathbf{L}^1_2\mathbf{V}_4]$ and $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$ in the ^{1}H NMR spectra were properly assigned with the assistance of COSY and ROESY spectral data (Figures S17-S18 and S21-S22). The two distinct sets of terpyridyl ^{1}H NMR signals strongly support the formation of heteroleptic complexes. The peaks corresponding to protons e and g of ligand **V** in $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$ were split into two signals with equal intensity (Figure 1a). The variable-temperature NMR (Figure S24) indicated the splitting for proton g becomes smaller at higher temperatures. Eventually, the ^{1}H-^{1}H exchange spectroscopy (EXSY) spectrum (Figure S25) verified that the peak splitting stems from a slow exchange rate of the methoxy groups, presumably due to the ion-dipole interactions between Cd$^{\mathrm{II}}$ and methoxy groups. The exchange rate (k_{ex}) was estimated to be 0.039 s^{-1} at 25 °C by varying mixing time (Figure S26).[19] As expected, a single peak in the ^{113}Cd NMR spectrum of $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$ corroborated the presence of one type of metal centers (Figure S23).

Based on NMR analysis, the formation of possible isomers of $[\mathrm{Cd}_8\mathbf{L}^1_2\mathbf{V}_4]$ and $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$ cannot be completely excluded. To clarify this issue, the computational and experimental results are discussed as follows. By rotating the ligand **L**^{1} by 90° in $[\mathrm{Cd}_8\mathbf{L}^1_2\mathbf{V}_4]$, two possible isomers can be generated, i.e., eclipsed and staggered (Figure S30), and it was realized that the eclipsed isomer has a lower total energy after geometry optimization. Similarly, $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$ has two possible isomers consisting of two different kinds of cyclic tetramers as subunits. The subunit for isomer **1** is a puckered tetramer composed of four 60°-bent *bis*-tpy ligands, and that for isomer **2** is a rhombus composed of two 120°-bent and two 60°-bent *bis*-tpy ligands (Scheme S5). The computational calculation suggested isomer **1** of $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$ is lower in total energy (Figure S31). In addition, by comparing the ^{1}H NMR spectra of $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$ and two subunits,[12f] it revealed that the signals from ligand **V** are much closer to those in the puckered tetrameric subunit (Figure S32), again supporting the formation of the proposed structure of $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$. Furthermore, electrospray ionization-traveling wave ion-mobility spectrometry-mass spectrometry (ESI-TWIM-MS)[18,20] was used to gain more structural insights into stellated metallocages $[\mathrm{Cd}_8\mathbf{L}^1_2\mathbf{V}_4]$ and $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$. The narrow drift time distributions (Figures S45 and S46) were indicative of the absence of isomers, and the theoretical and experimental collision cross-sections (CCSs) were in accord with each other for both cases (Tables S1 and S2).

Scheme 2. Self-Assembly of Four-Pointed Star $[\mathrm{Cd}_{12}\mathbf{L}^2_2\mathbf{V}_4]$



The formation of the mixture of complexes $[\mathrm{Cd}_8\mathbf{L}^1_2\mathbf{V}_4]$ and $[\mathrm{Cd}_{12}\mathbf{L}^1_3\mathbf{V}_6]$ from X- and V-shaped ligands in combination with Cd$^{\mathrm{II}}$ prefers over the expected series of $[\mathrm{Cd}_{3n}\mathbf{L}^1_n\mathbf{V}_n]$, possibly due to entropic reasons. Hence, to avoid such unpredictable smaller structures, ligand **L**^{2} was designed for the construction of stellated polygons (Scheme 2), with expectation that the intramolecular complexation[3b] between two X-shaped ligands could prevent the formation of undesired $[\mathrm{Cd}_8\mathbf{L}^1_2\mathbf{V}_4]$-type cages. Ligand **L**^{2}

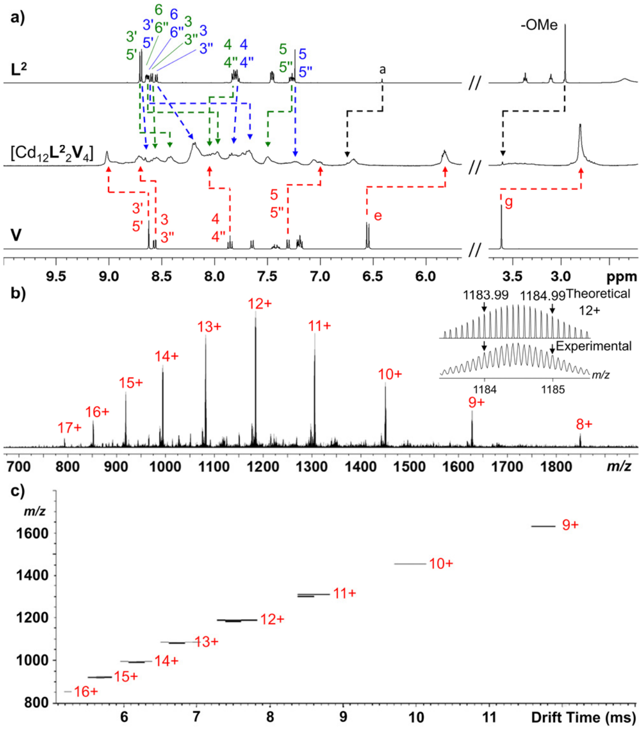
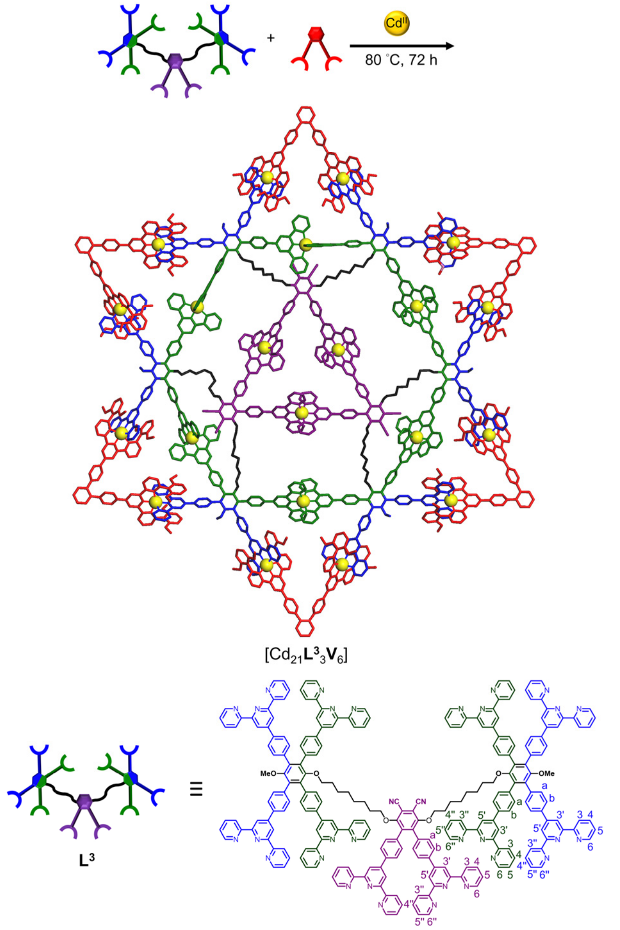


Figure 2. a) ^{1}H NMR spectra of **L**^{2}, **V**, and $[\mathrm{Cd}_{12}\mathbf{L}^2_2\mathbf{V}_4]$. b) ESI-MS spectrum and c) ESI-TWIM-MS plot of $[\mathrm{Cd}_{12}\mathbf{L}^2_2\mathbf{V}_4]$.

Scheme 3. Self-Assembly of Six-Pointed Star $[\mathrm{Cd}_{21}\mathbf{L}^{3}_{3}\mathbf{V}_{6}]$



composed of two X-shaped tetravalent terpyridyl moieties connected through C8 alkyl linkers was synthesized via the Mitsunobu reaction of the corresponding hydroquinone precursor and the subsequent Suzuki-Miyaura coupling reactions of 4'-(4-boronophenyl)-tpy with eight aryl-bromo positions (Scheme S2). However, a mixture of **L**^{2}, **V**, and Cd^{II} ions in a molar ratio of 1:2:6 led to the formation of four-pointed star complex $[\mathrm{Cd}_{12}\mathbf{L}^{2}_{2}\mathbf{V}_{4}]$ (Scheme 2). ESI-MS analysis revealed the peaks corresponding to 8+ to 17+ charge states for $[\mathrm{Cd}_{12}\mathbf{L}^{2}_{2}\mathbf{V}_{4}]$ and no signals resulting from the expected hexagram $[\mathrm{Cd}_{18}\mathbf{L}^{2}_{3}\mathbf{V}_{6}]$ were found (Figure 2b). The broad ^{1}H NMR signals in the aromatic region of $[\mathrm{Cd}_{12}\mathbf{L}^{2}_{2}\mathbf{V}_{4}]$ could be attributed to the overlapping of signals for six different types of terpyridyl entities (Figures 2a and S33), and all the signals were carefully assigned with the help of COSY and ROESY spectra (Figures S35 and S36). Besides, the DOSY NMR experiment (Figure S34) indicated that all the relevant signals have the same diffusion coefficient ($D = 1.6 \times 10^{-10}$ m^{2}s^{-1}), implying the exclusive formation of $[\mathrm{Cd}_{12}\mathbf{L}^{2}_{2}\mathbf{V}_{4}]$. As expected, the ^{113}Cd NMR spectrum showed four distinct Cd^{II} environments (Figure S37), where two signals at δ 262.9 and 265.6 ppm are corresponding to homoleptic <tpy-Cd^{II}-tpy> moieties and two overlapped signals at δ 246.3 and 246.5 ppm are derived from heteroleptic <tpy-Cd^{II}-tpy'> connections. Moreover, the ESI-TWIM-MS structural analysis of $[\mathrm{Cd}_{12}\mathbf{L}^{2}_{2}\mathbf{V}_{4}]$ exhibited an average experimental CCS of 1864.8±32.3 Å^2, which is in good agreement with the theoretical values (Figure 2c and Table S3).

Building on the self-assembly result of four-pointed star $[\mathrm{Cd}_{12}\mathbf{L}^{2}_{2}\mathbf{V}_{4}]$, it was conceived that the presence of a centrally located stable triangle might lead to formation of the target hexagram-type architecture. Therefore, the ligand **L**^{2} was further modified by attaching a 60°-bent V-shaped *bis*-tpy moiety as the precursor for the central triangle. A mixture of **L**^{3}, **V**, and Cd(NO$_3$)$_2$ in a stoichiometric ratio of 1:2:7 was heated at 80 °C for 72 h in CHCl$_3$/MeOH (1:1, v/v), and then excess NH$_4$PF$_6$ was added to exchange counterions from NO$_3^-$ to PF$_6^-$ (Scheme 3). The ^{1}H NMR of the resultant complex in CD$_3$CN revealed seven sets of terpyridyl signals, a preliminary indication towards the formation of the expected complex $[\mathrm{Cd}_{21}\mathbf{L}^{3}_{3}\mathbf{V}_{6}]$ (Figures 3a and S39). Notably, the characteristic resonances from ligand **V** were split into two signals after complexation, strongly supporting the formation of two kinds of heteroleptic coordination bonds in the periphery. The DOSY NMR experiment (Figure S40) depicted the existence of a single species with a diffusion coefficient of 1.4 × 10^{-10} m^{2}s^{-1} in CD$_3$CN. All the ^{1}H NMR signals of the complex were carefully assigned according to the COSY and ROESY spectra (Figures S41 and S42). Furthermore, the ^{113}Cd NMR spectrum of the complex (Figure S43) showed five signals affirming the construction of $[\mathrm{Cd}_{21}\mathbf{L}^{3}_{3}\mathbf{V}_{6}]$. The three downfield signals located at δ 268.2, 269.2 and 269.6 ppm originated from the central ring-in-ring part of $[\mathrm{Cd}_{21}\mathbf{L}^{3}_{3}\mathbf{V}_{6}]$, belonging to homoleptic <tpy-Cd^{II}-tpy> units. On the other hand, the upfield signals situated at δ 242.3 and 244.2 ppm are assigned to the heteroleptic <tpy-Cd^{II}-tpy'> connections in the peripheral stellated part of $[\mathrm{Cd}_{21}\mathbf{L}^{3}_{3}\mathbf{V}_{6}]$. Eventually, the ESI-MS spectrum of the complex unequivocally confirmed the chemical composition of six-pointed star $[\mathrm{Cd}_{21}\mathbf{L}^{3}_{3}\mathbf{V}_{6}]$ showing twelve major peaks with the charge states from 11+ to 22+ ions (Figure 3b), which were isotopically resolved and found to be consistent with the calculated isotopic distributions (Figure S44). The narrow drift time distributions for the 14+ to 22+ species observed in the ESI-TWIM-MS plot (Figure 3c) verified the absence of other isomers. The average CCS of 3056.2±39.2 Å^2 derived from the corresponding drift times is consistent with the theoretical values obtained from the annealing simulation (Table S4). Moreover, the AFM and TEM images of $[\mathrm{Cd}_{21}\mathbf{L}^{3}_{3}\mathbf{V}_{6}]$ (Figures S49 and S50) displayed an average height of

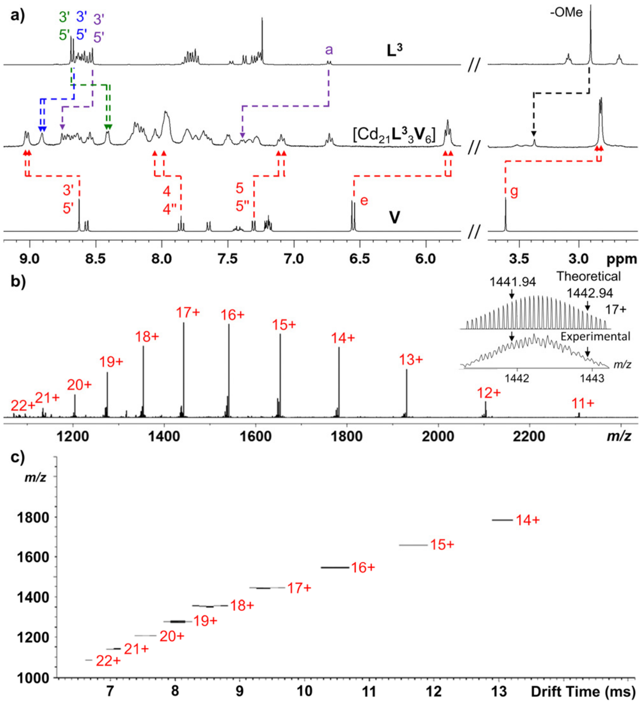


Figure 3. a) ^{1}H NMR spectra of **L**^{3}, **V**, and $[\mathrm{Cd}_{21}\mathbf{L}^{3}_{3}\mathbf{V}_{6}]$. b) ESI-MS spectrum and c) ESI-TWIM-MS plot of $[\mathrm{Cd}_{21}\mathbf{L}^{3}_{3}\mathbf{V}_{6}]$.

1.34±0.06 nm and an average diameter of 6.00±0.11 nm, respectively, which agree well with the dimensions of the molecular model (Figure S48).

In summary, the quantitative self-assembly of the stellated metallo-supramolecular architectures, four-pointed star $[Cd_{12}\mathbf{L}^2{}_2\mathbf{V}_4]$ and six-pointed star $[Cd_{21}\mathbf{L}^3{}_3\mathbf{V}_6]$, were successfully accomplished through multivalent ligand design and complementary ligand pairing in a one-pot manner. The centrally situated 60°-bent *bis*-tpy in ligand $\mathbf{L}^3$ was found to be the fundamental unit that controls and stabilizes the hexagram-type architecture, by providing rigidity through the formation of an inner triangle. The intricate metallo-supramolecular architectures were characterized thoroughly by ^{1}H NMR, ^{113}Cd NMR, DOSY, ESI-MS, TWIM-MS, AFM, and TEM. Additionally, the high stability of heteroleptic <tpy-Cd^{II}-tpy'> allowed the separation of stellated metallocages $[Cd_8\mathbf{L}^1{}_2\mathbf{V}_4]$ and $[Cd_{12}\mathbf{L}^1{}_3\mathbf{V}_6]$ by column chromatography from their mixture. The presented self-assembly methodology is expected to provide access to rational construction of metallo-supramolecules with enhanced topological diversity and complexity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
Experimental details and characterization data (PDF)

AUTHOR INFORMATION

Corresponding Author

*ytchan@ntu.edu.tw

Notes

The authors declare no competing financial interest.

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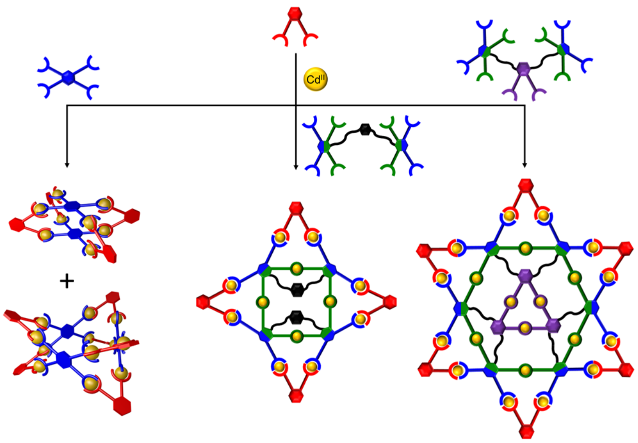
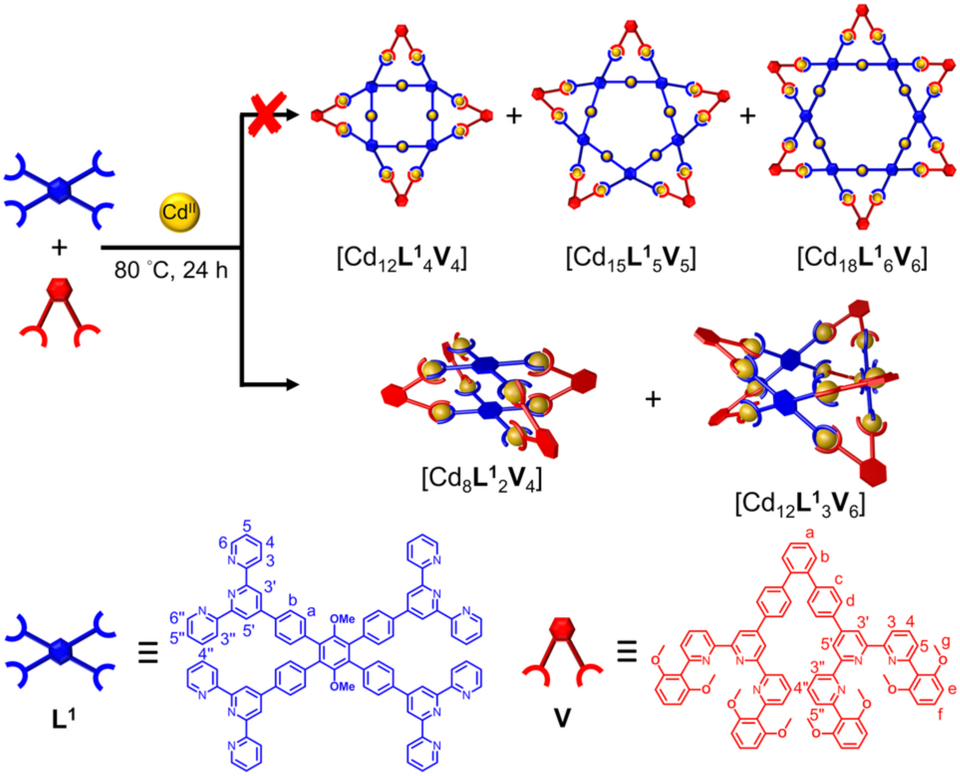
Table of Contents Artwork





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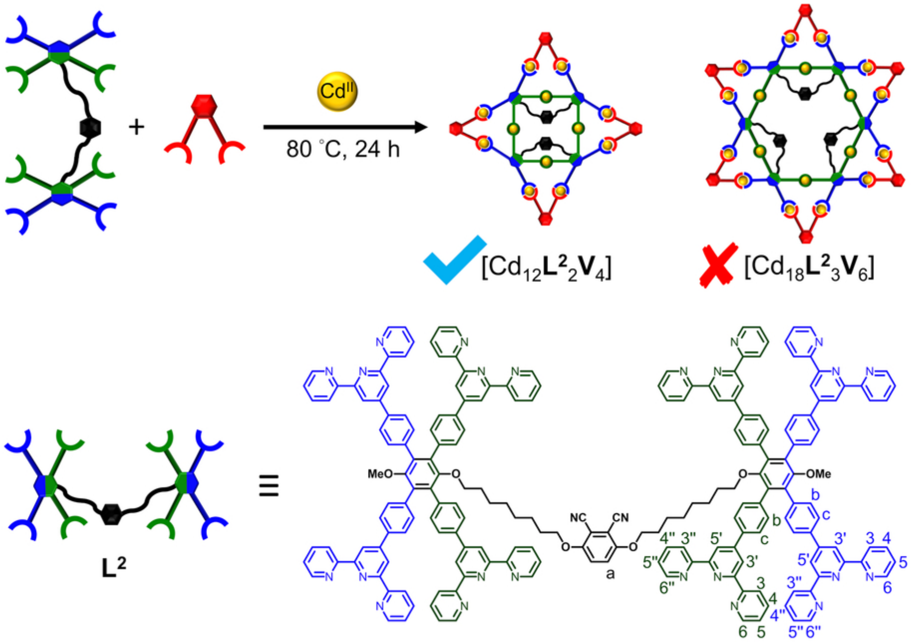

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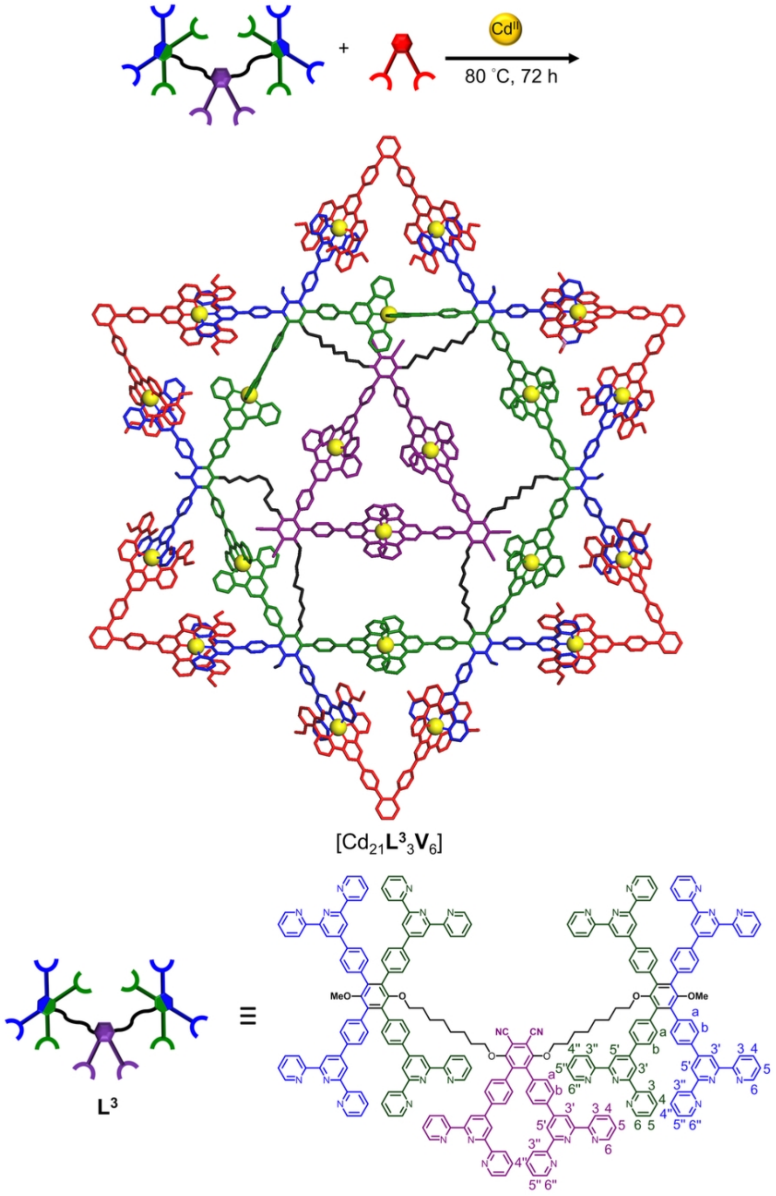

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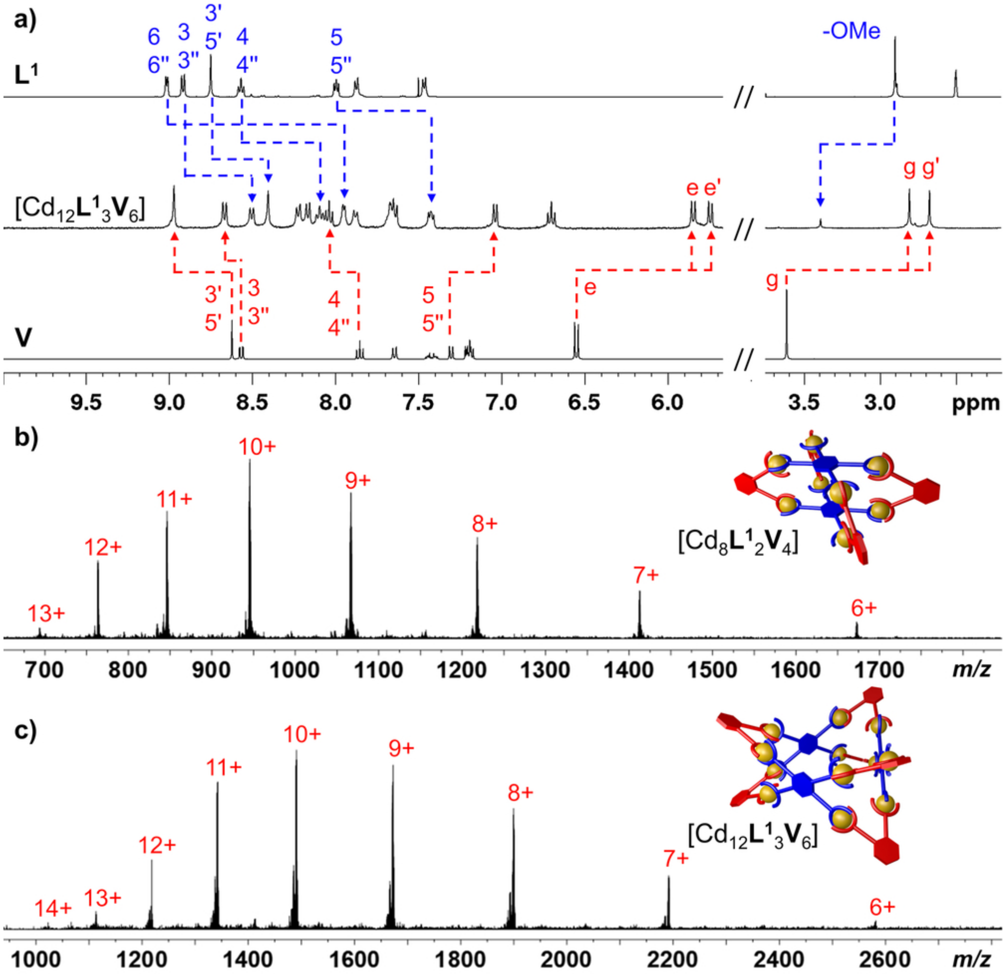

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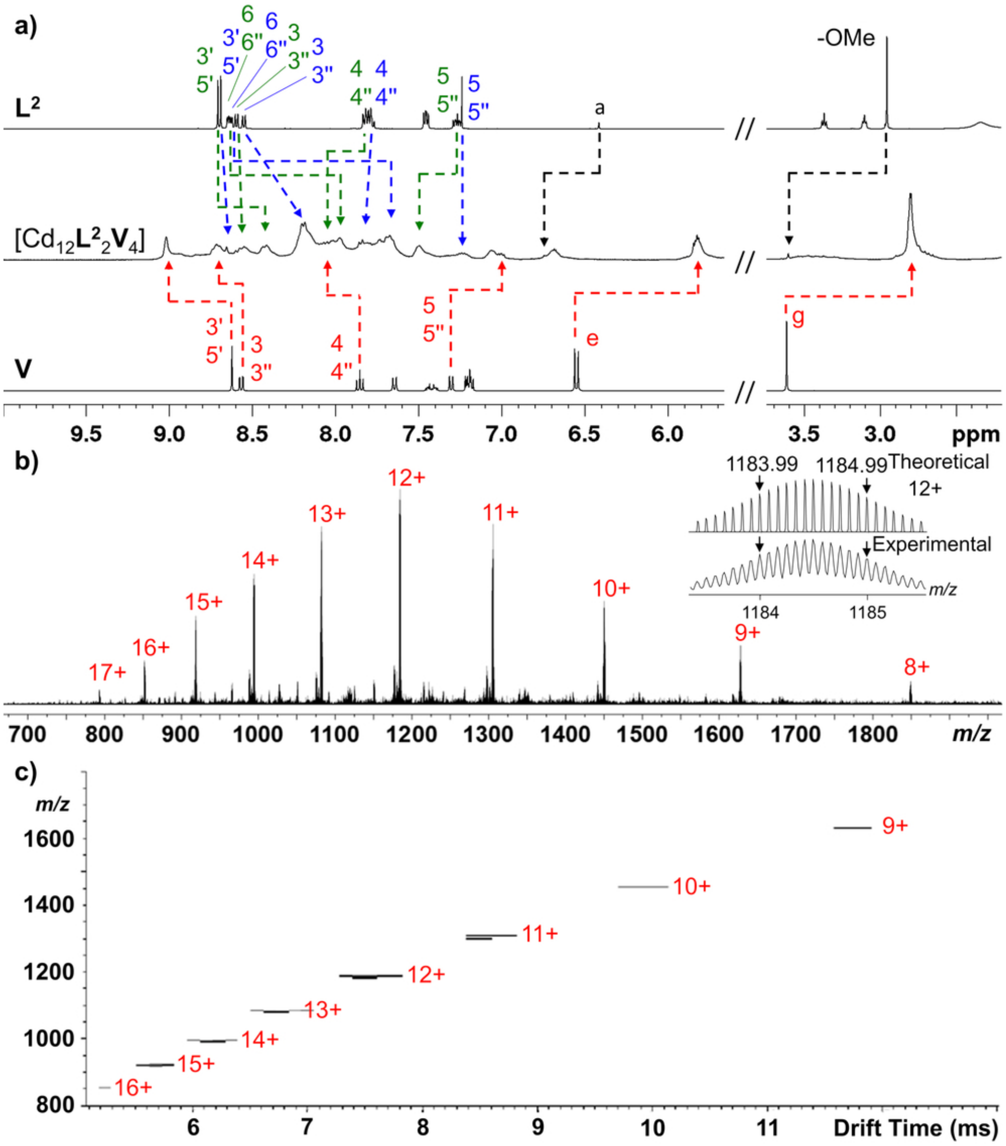

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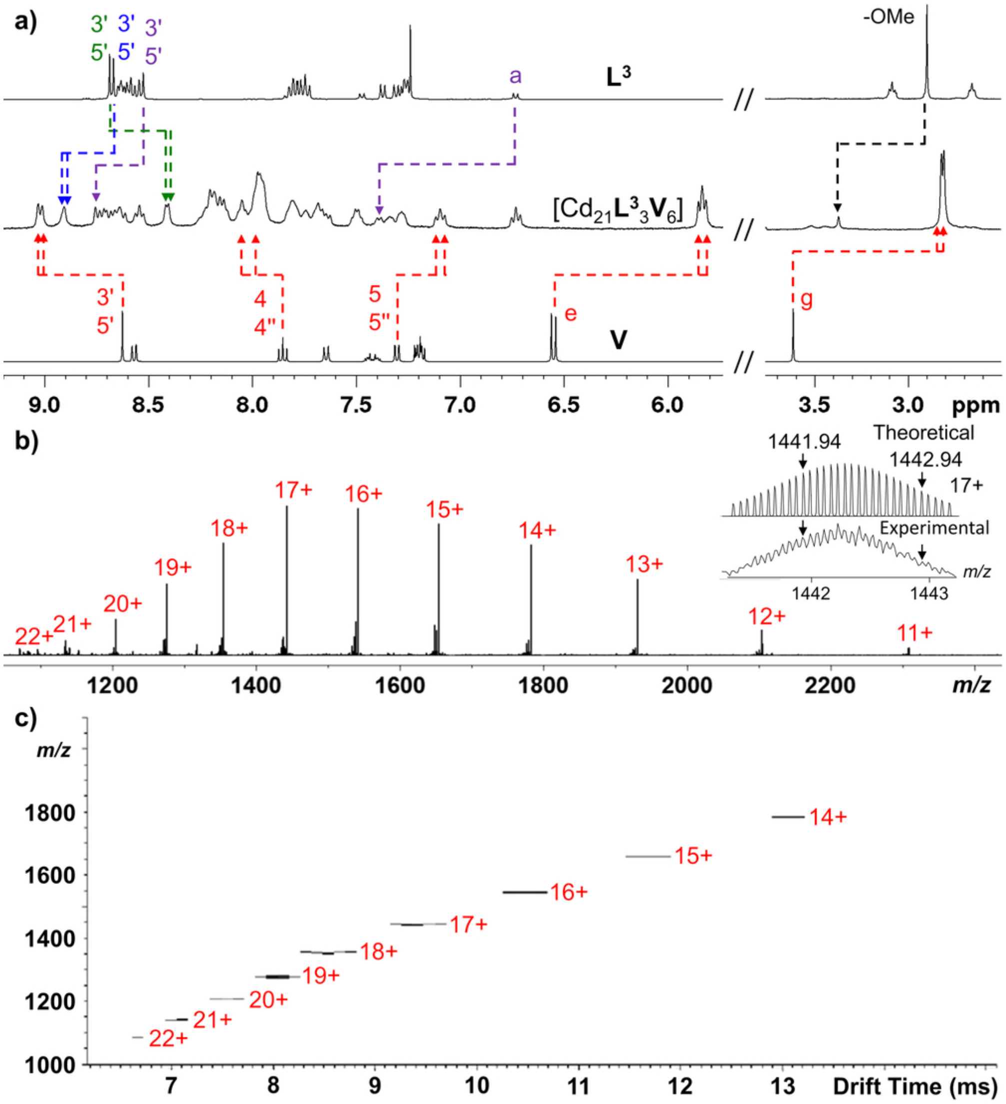

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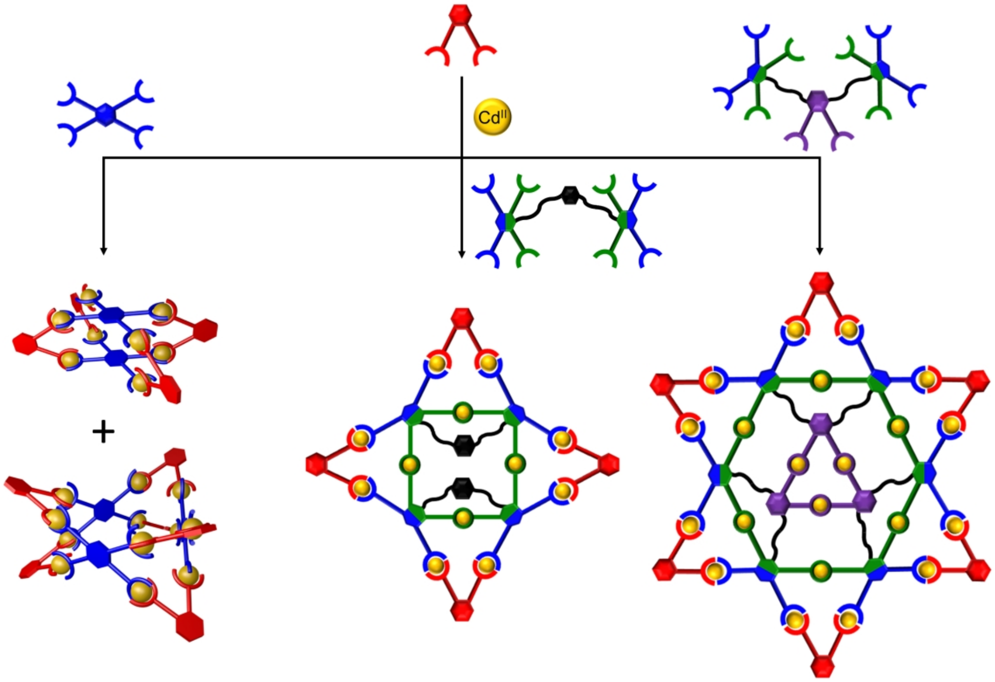

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