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Vertical Assembly of Giant Double- and Triple-Decker Spoked Wheel Supramolecular Structures

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Conflict of interest

The authors declare no conflict of interest.

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Abstract

The double- or triple-decker 3D metallo-hexagons were obtained by self-assembly of multitopic tris-terpyridines with Cd^{2+} ions in near-quantitative yield. Comprising up to 72 ionic pairs, the multiple spoked wheels display characteristic reversible gelation properties under thermodynamic conditions. The supramolecular metallo-nanoarchitectures were characterized by ^1H NMR, 2D NMR (COSY and NOESY), and diffusion-ordered spectroscopy (DOSY) and HR-ESI-MS, traveling-wave ion mobility mass spectrometry (TWIM-MS), TEM, and AFM. For the first time, the self-assembly of 45 units at once was demonstrated to yield exceptional giant triple-decker hexagons of up to circa 42000 Da.

Keywords

coordination; gelation; molecular spoked wheels; self-assembly; terpyridine

As an important part of supramolecular chemistry, coordination-driven self-assembly has attracted considerable attention owing to its promising applications in diverse fields, such as host–guest chemistry,^[1] catalysis,^[2,3] sensing,^[4,5] biology,^[6] and optical materials.^[7] A series of high molecular-weight supramolecular architectures with precise shapes and sizes, from two-dimensional (2D) metallo-macrocycles^[2,4,8] to three dimensional (3D) cages,^[2,8a,9] polyhedra^[10] and intricate molecular knots,^[11] have been extensively reported. For the purpose of mimicking the complexity and functionality of biological systems, more elegant and complex molecules based on coordination-driven assembly have long been pursued by chemists. Among these, the self-assembly of huge discrete highly ordered supramolecular structures ($MW > 30000$ Da) is full of challenges in terms of their ligand design and architectural construction, which need precise control over the geometric angles and connectivity of multiple ligands and metal ions. Moreover, such motifs were desired for their potential applications in diverse fields.^[12]

Tridentate 2,2':6',2''-terpyridine (tpy) and its analogues are common building blocks for constructing coordination-driven metallo-structures owing to their intrinsic ability to coordinate with different transition metal ions and excellent photoelectrical properties.^[13] Much effort has also been devoted to construct complicated higher-order motifs through terpyridinyl ligand–metal coordination interactions. For example, Newkome and co-workers reported the self-assembly of the first generation Sierpinski triangle fractal and hexagonal gasket.^[14] Li and co-workers prepared two species of concentric hexagons using tetratopic

pyridine and terpyridine ligands coordinating with metal ions.^[15] Furthermore, a well-defined spiderweb-like ring-in-ring-in-ring superstructure was successfully synthesized through self-assembly of the multivalent terpyridine ligands with metal ions by Chan et al.^[16] It is worth noting that the above-mentioned super-structures were constructed by extending the structure in a 2D plane, just like the concentric ring system (Figure 1a). Herein, we introduce the 3D double- or triple-decker hexagon system by vertically extending the plane spoked wheels^[17] into 3D space (Figure 1b).

Initially, double tris-terpyridine compounds **L**¹⁻³ were synthesized through a multi-fold Suzuki cross-coupling reaction of hexakis-Br-substituted **1a-1c** with 4'-boronatophenyl-2,2':6',2''-terpyridine using [Pd(PPh₃)₄] as the catalyst. Isolation was achieved by column chromatography (Al₂O₃) and recrystallization with CHCl₃ and CH₃OH. The structure of **L**¹⁻³ was characterized by NMR spectroscopy and ESI-MS (Figure 2 and the Supporting Information).

Self-assembly of **S**¹ was performed by mixing a stoichiometric ratio (3:1:12) of **L**¹, **T**, and Cd(NO₃)₂·4H₂O in CHCl₃/CH₃OH at 65°C for 12 h. After adding excess NH₄PF₆, a pale-yellow precipitate was obtained followed by a thorough washing with CH₃OH. Then **S**¹ was generated as a faint yellow solid in 96% yield. **S**² and **S**³ were synthesized in 95% and 98% yields, respectively, by a similar procedure as **S**¹ (Scheme 1). ¹H NMR spectra of ligands **L**² and **T** and complex **S**² are shown in Figure 2a. In the aromatic region of the NMR spectrum of ligand **L**², two distinguishable sets of tpy resonances represented by two characteristic singlets at 8.71 and 8.60 ppm are observed, which were assigned to tpyH^{2',5'} peaks; in the non-aromatic region, one triplet and one singlet appeared at 4.28 and 3.74 ppm in a 1:3 integration ratio, which were attributed to methylene and methoxy groups. For the complex **S**², the ¹H NMR spectrum exhibited broad resonance peaks presumably owing to the low tumbling motion on the NMR time scale for the large supramolecular architecture.^[18] Three characteristic singlets corresponding to tpyH^{2',5'} protons were observed at 8.89, 8.78, and 8.60 ppm with downfield shifts, along with the upfield shifts of tpyH^{6,6''} protons compared to **L**² and **T**. Additionally, the methylene and methoxy protons at 4.44 and 3.88 ppm also exhibited down-field shifts, agreeing with the expected structure. Assignments of other protons were confirmed by 2D COSY and NOESY NMR experiments. In contrast to the slight downfield shifts in most of tpy-based supramolecular structures, the tpyH^{4,4''} and tpyH^{5,5''} protons in **S**² exhibited distinct upfield shifts, especially for the tpy^{5,5''} protons of hexakis-terpyridine **T** (δ = 6.56 ppm, δ = 0.67 ppm). This could be ascribed to the highly shielded environment from the proximity of two < tpy-Cd²⁺-tpy > connections and such a result strongly supported the stacking hexagon formation.^[16,19] Similarly, the ¹H NMR spectra of **S**¹ and **S**³ showed distinct patterns and all of the peaks were fully assigned (see the Supporting Information).

Electrospray ionization mass spectrometry (ESI-MS) spectrum of **S**² showed a series of peaks with charge states from 8 + to 19 +, which correspond to the loss of a different number of PF₆⁻ anions (Figure 2b). The experimental isotope patterns were in accord with the corresponding simulated ones in exact agreement with a molecular weight of 27098.8 Da for **S**². The traveling-wave ion mobility-mass spectrometry (TWIM-MS) spectrum (Figure 2c) exactly showed a set of narrow drift time distribution plots for the 10 + to 19 + species,

indicating that no superimposed fragments, isomers, or conformers result from self-assembly. The compositions of **S**¹ and **S**³ were also confirmed by ESI-MS (Supporting Information, Figures S61 and S62, respectively).

Encouraged by the successful self-assembly of the double-stacked hexagonal superstructures, **L**⁴ was synthesized by a multi-fold Suzuki coupling reaction and characterized by NMR spectroscopy and HR-ESI-MS (Figures S37, S38, and S48). The assembly experiment was conducted by mixing with **L**⁴, **T**, and Cd(NO₃)₂·4H₂O in a precise 2:1:12 ratio following a similar procedure (Scheme 2, left). Unfortunately, the resultant assemblies were nearly insoluble in CH₃CN. The NMR spectrum exhibited a complicated and broad pattern, demonstrating no discrete self-assembled structure formed (Figure S83). Likewise, the ESI mass spectrum (Figure S84) showed a big hump with no signals responding to the proposed triple-decker hexagon structure. In order to avoid an anion exchange process, Cd(BF₄)₂ was used for the self-assembly with **L**⁴ in CHCl₃/CH₃CN solution rather than Cd(NO₃)₂. ESI-MS measurements were directly performed for the assemblies, and the spectrum showed a series of successive peaks from 13 + to 23 +, which fitted well with the desired **S**⁴ (Figure S63), demonstrating the expected giant triple-decker spoked wheels **S**⁴ formed in solution.

Based on above results, two modified flexible ligands **L**⁵ and **L**⁶ were further synthesized and fully characterized by NMR spectroscopy and HR-ESI (see Supporting Information). Self-assemblies of **S**⁵⁻⁶ were achieved by treating **L**⁵⁻⁶ and **T** with Cd(NO₃)₂·4H₂O in a precise 2:1:12 ratio (Scheme 2, right). ¹H NMR spectrum of **S**⁵ displayed a complex and broad resonance in the aromatic region, which was attributed to the conformational heterogeneity of the giant supramolecular structure.^[18] Nevertheless, there were two diagnostic triplets at 4.46 and 4.25 ppm (methylene groups) and two sharp singlets at 3.86 and 3.92 ppm (methoxy groups) in the non-aromatic region, suggesting the formation of the expected discrete structure (Figure S59). The ESI mass spectrum of **S**⁶ (Figure 3a) showed eleven distinct peaks with continuous charge states (from 13 + to 23 +) confirming the molecular composition of 6 **L**⁶ units, 3 **T** units, 36 Cd²⁺ ions, and 72 PF₆⁻ units. Just like most high molecular-weight supramolecules, the high-resolution isotope pattern for each charge peak of **S**⁶ could not be obtained owing to the resolution limitation of the mass spectrometer.^[15a] The TWIM-MS spectrum (Figure 3b) clearly showed a set of narrow drift time distribution plots for the 14 + to 21 + species, demonstrating that no superimposed fragments, isomers, or conformers are present in the resultant self-assemblies. After deconvolution, the molecule weight of **S**⁶ was measured to be 42014.3 Da, which is among one of the largest metallo-supramolecules in the field of coordination-driven supramolecular self-assembly.^[10a,20]

To acquire further size information, diffusion-ordered NMR spectroscopy (DOSY) experiments were performed. All spectra displayed a single narrow band, indicating the formation of the discrete structures (see Supporting Information). Using the Stokes–Einstein equation, the dynamic radii were calculated to be 5.9, 6.6, and 7.1 nm for **S**¹⁻³ and 7.2 nm and 8.7 nm for **S**⁵ and **S**⁶, respectively, which agreed well with the sizes obtained by molecular modeling. Further, the TEM images were also obtained, in which widespread individual particles could be clearly observed (Figure 4a and the Supporting Information).

The measured diameter from the higher magnification image was in good accordance with the theoretical 5.7 nm for **S**^{1–3} and 6.1 nm for **S**^{5–6} calculated by molecular modeling (Figure 4b and the Supporting Information). Furthermore, atomic force microscopy (AFM) images of triple-decker hexagon structure **S**⁶ displayed uniform dots with a larger width than the theoretically predicted diameter owing to the tip broadening effect^[21] (Figure 4c,e). Whereas the height of circa 2.0 nm (Figure 4d), which is slightly less than three times the height of monolayer tpy-complexes,^[14a,22] matched well with the expected structure. Similarly, **S**^{1–3} had nearly twice the height of single tpy-complexes (see the Supporting Information).

After the successful self-assemblies of triple-decker hexagon superstructures **S**^{4–6}, we reasoned that triple-decker structure **S**⁴ was more labile than **S**⁶, because the two bilateral tris(tpy)s moieties of **S**⁴ directly linked to the phenyl group of the middle tris(tpy)s moiety by the aliphatic chain imposed intense strain on the middle tris(tpy)s connection, resulting in a labile stacked structure (Scheme 2, left). Therefore, their stabilities were evaluated by tandem mass spectrometry, in which the other parameters were identical but the voltage of trap cell was gradually changed to increase collision energies (Figures S81 and S82). When the voltage reached 50 V, all peaks of **S**⁴ completely disappeared. However, the peaks of **S**⁶ were present until 70 V, which is higher than **S**⁴, indicating that the triple-decker hexagon **S**⁶ was more stable than **S**⁴. These results will guide the design of more sophisticated 3D architectures in future.

The giant self-assembled double- and triple-decker hexagons could form organometallic gels in DMF. The metallogelation displayed temperature-responsive properties; the formed gel gradually turning into solutions upon heating and subsequently reforming gels after cooling down to room temperature (Figure 5a,d). TEM and scanning electron microscopy (SEM) were conducted to determine the morphologies of the supramolecular gels of **S**¹ and **S**⁵ (Figure 5 and the Supporting Information). All images of two gels showed the bulk networks, which were formed by the intermolecular interaction (i.e., π – π stacking and hydro-phobic interactions),^[15b,23] and sol-gel phase transitions were rationalized by the ability of the organometallic gels based on metal-ligand bonds and noncovalent interactions to dynamically assemble or disassemble by varying temperature.^[24]

In summary, the giant double- (**S**^{1–3}) and triple-decker (**S**^{4–6}) hexagons have been designed and prepared in nearly quantitative yield through a novel multicomponent self-assembly procedure based on < tpy–Cd²⁺–tpy > connectivity. The composition, size, and shape of the self-assembled supramolecules were unambiguously verified by ESI-MS and TWIM-MS, NMR and DOSY NMR spectroscopy, and TEM and AFM imaging. By varying the connecting lengths of alkyl linkers, the portals between the molecular internal and the external space could be adjusted. Thus, these architectures have potential application in molecular recognition and encapsulation for special-sized and special-shaped molecules. Based on these results, the research into giant hollow triple- and quadruple-stacked hexagonal supramolecules and their encapsulation properties is ongoing. The strategy of using the flexible linkers as connections to vertically construct 3D structures provides a new sight for more sophisticated and functional supramolecular architectures.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

a) Cartoon representation of horizontal assembly of 2D metallo-macrocycles to extending ring-in-ring planar structures and b) vertical assembly of 3D double- or triple-decker hexagonal architectures.

Figure 2. a) ^1H NMR spectra (500 MHz) of ligands **L**², **T** in CDCl_3 and double-decker hexagon **S**² in CD_3CN . b) ESI-MS spectrum (Inset: theoretical and experimental isotopic patterns for 12 + moiety) and c) 2D ESI-TWIM-MS plot (m/z vs. drift time) of **S**².

Figure 3.

a) ESI-MS and b) 2D ESI-TWIM-MS plot (m/z vs. drift time) of complex S^6 . The charge states of intact assemblies are marked.

Figure 4.
a) TEM image, b) representative energy-minimized structure from molecular modeling, c) AFM image, d) height histogram from AFM, and e) 3D AFM image of triple-decker hexagon S^6 .

Figure 5.
a,d) Images showing of thermal reversibility of the supramolecular gel, b,e) TEM images
and c,f) SEM images of **S**¹ (up) and **S**⁵ (down) gel in DMF.

Scheme 1.
Synthesis of double tris-terpyridines **L**¹⁻³ and self-assembly of double hexagonal structures **S**¹⁻³.

Scheme 2.
Self-assembly of triple-decker hexagon S^{4-6} .