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Reinforced Topological Nano-assemblies: 2D Hexagon-Fused Wheel to 3D Prismatic Metallo-lamellar Structure with Molecular Weight of 119K Daltons

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Self-Assembly • Synthetic metallo-Wheel and Prism • Terpyridine • Topological Molecule

ABSTRACT: By the precisely metallo-ligand design, the advanced coordination-driven self-assembly could succeed the preparation of giant molecular weight of the metallo-architectures. However, the synthesis of single discrete high-molecular-weight (>100K Da) structure has not been demonstrated since the insurmountable synthetic challenge. Herein we present a two-dimensional wheel structure (**W1**) and a gigantic three-dimensional dodecagonal prism-like architecture (**P1**) which were generated by multicomponent self-assembly of two similar metallo-organic ligands and a core ligand with metal ions, respectively. The giant 2D-supra-structure **W1** with six hexagonal metallacycles that fused to the central spoke-wheel was first achieved in nearly quantitative yield, then directed by introducing a meta-substituted coordination site into the key ligand, the supercharged (36 Ru²⁺ and 48 Cd²⁺ ions) double-decker prismatic structure **P1** with two wheel structures **W1** serve as the surfaces and twelve <Tpy-Cd²⁺⁻Tpy> connectivities serve as the edges, which possesses a molecular weight up to 119498.18 Da was accomplished. The expected molecular composition and size morphology was unequivocally characterized by nuclear magnetic resonance, mass spectrometry and transmission electron microscopy investigations. The introduction of wheel structure is able to add considerable stability and complexity to the final architecture. These well-defined scaffolds were expected to play an important role in the functional materials fields, such as molecular encapsulation and medicine sustained-release.

INTRODUCTION

Self-assembly is universal in nature to lead gigantic biological systems with high-level gracefulness and functionality.¹⁻² Chemists in various fields are often pushed forward to think on the artificial synthesis of novel nanoscale-molecular objects, including nanoparticle assemblies,³⁻⁴ self-assembled nanocages, 5-14 mechanomolecules, 15-19 two-dimensional ensembles,²⁰⁻²⁵ and so on.²⁶⁻²⁸ More importantly, these entities have been employed extensively in the area of nanoelectronics, sensors, catalysis, supramolecular gels, biology etc.²⁹⁻³⁴ Of particular interest in synthetic chemistry is the discrete two-dimensional (2D) and three-dimensional (3D) rigid structures, which are accessed by covalent-directed synthesis³⁵⁻³⁶ and coordination-driven self-assembly³⁷⁻³⁸ via predesigned rigid precursors. Large molecular spoked wheels as reinforced macrocycles, which are much more rigid and stable than the macrocyclic structures, have received significant attention in the materials field.³⁹⁻⁴¹ On the other hand, inspired by the function of proteins often intimately rely on their sophisticated tertiary spatial structures, various 3D architectures with different cavity sizes and shapes are recognized as a promising simulator have been widely investigated.⁴²⁻⁴⁶ However, synthesis of reinforced 2D spoke-wheel macromolecules and gigantic 3D molecular mimics still remains immensely challenging, especially the covalent methodology has its own synthetic limitation in the field of reinforced topological architectures.⁴⁷

Coordination-driven self-assembly, which utilizes the spontaneous ordering of precursor components into higher order architectures through the metal-ligand coordination has proven to be a versatile method for constructing discrete rigid structures.⁴⁸⁻⁵² In stark contrast to the multistep construction process of covalent approaches, wheel-based two-dimensional and three-dimensional supramolecules have been achieved in a one-pot reaction in nearly quantitative yield via supramolecular coordination-driven self-assembly.⁵³⁻⁵⁵ Nonetheless, when supramolecular wheels reach to the next generation, the precise control over their shape and size faces severe limitations in many instances, especially for the shape-persistent architectures with size more than 10 nm. By effectively employing linear terpyridine-metal-terpyridine (tpy-M(II)-tpy) coordination as a dynamic linker, a multitude of higher-order supramolecular

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Figure 1. (A) Illustration of the supramolecularly reinforced architectures: from a rigid spoked wheel to reinforced wheel scaffold (W1) and further to 3D double-decker dodecagonal prism-like architecture (P1); Structures of (B) W1 and (C) P1.

structures could been achieved by multivalent terpyridine ligands with various transition metals.⁵⁶⁻⁵⁹

Herein, we present a supramolecularly reinforced 2D hexagon-fused macromolecule W1 and a 3D supercharged prismatic lamellar structure **P1** that been prepared by multicomponent self-assembly of two similar metallo-organic ligands (LA and LB, respectively) and a core ligand (LH) with metal ions (Scheme 1). In reinforced wheel W1, it is self-evident that six hexagonal metallacycles are fused to the central spoke-wheel in two-dimensional plane. The double-decker structure P1 exhibits two reinforced wheel W1 in the layers and twelve <Tpy-Cd2+-Tpy> connectivities in the edges which could lead to a dodecagonal prism-like architecture (Figure 1). Overall, the giant structure with 168 anions contains 36 Ru²⁺ and 48 Cd²⁺ ions with a molecular weight up to 119498.18 Da. Still more interesting is the fact that the discrete supermolecule with such a huge skeleton and high molecular weight has not, to the best of our knowledge, been specifically documented.⁶⁰ The supercharged entity would be expected to give researchers an insight into complicated intermolecular interactions and the reinforcement strategy affords elegant way to next generation supramolecules and materials.

RESULTS AND DISCUSSION

Conventionally, giant terpyridine-based architectures have been self-assembled by combination of single multivalent ligand or multiple components with transition metals. No matter which approach is taken, the ligand design is extremely crucial. For instance, Li et al. employed terpyridine and pyrylium salts to prepare octo-topic ligand with difference in arm length, underwent self-assembly to generate a ring-in-ring-in-ring metal complex with molecular weight 38,352 Da.⁶¹ To create desirable supramolecularly reinforced large shape-persistent structures, we designed two intricate wing-like metalloorganic ligands LA and LB that consist of three different starting components connected by metal Ru²⁺ chelation (Scheme 1). We overcome the challenge by introducing "Trident" component into the building block for the first time, which can be perfectly reacted together with organic ligand LH to generate the anticipated core wheel, and it is worth mentioning that LH has been used to build the first generation of spoked wheel.⁵³ Moreover, the introduction of meta-substituted coordination site in the key metallo-organic ligand LB could ensure non-planar directionality.62

Self-Assembly and Characterization of the Rigid Scaffold Spoked Wheel W1. In our synthetic design, the

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Scheme 1. (A) Synthesis of Metallo-organic Ligands LA and LB; (B) Self-Assembly of Hexagon-Fused Wheel W1; (C) Self-Assembly of Prismatic Lamellar Structure P1^a



^aReagents and conditions: (i) N-ethyl morpholine, CH₃OH:CHCl₃ (1:1, v:v), reflux, 1d; (ii, iii) N-ethyl morpholine, CH₃OH:CHCl₃ (1:1, v:v), reflux, 1d; (iv, v) Pd(PPh₃)₄, K₂CO₃, CH₃CN:CH₃OH (5:1, v:v), reflux, 5d or 7d; (vi, vii) CH₃CN/CHCl₃/CH₃OH (2:1:1, v:v:v), reflux, 1d.

organic ligands 2, 6, LH were synthesized by known procedures^{27,54} and the Ru^{III}-terpyridine mono-complexes **1** and **4** were obtained by a multi-step reaction (Scheme S1 and S3). The key complex **3** was synthesized by reacting **1** with **2** with an isolating process. It is worth noting that **1** is a newtype promising building block for a diversity of reinforced wheel structures. The metalloorganic ligand LA was obtained in three steps from **1**. In the final step, a five-fold Suzuki coupling reaction of the pentabromo-substituted trinuclear Ru(II) complex 5 with 4'-(4-boronophenyl)terpyridine 6 (Scheme 1) was conducted. After refluxing for 5 days under nitrogen at 85 °C, the crude product was purified by method of flash column chromatography (Al_2O_3), and eluting with CH₂Cl₂ and CH₃OH to give metallo-organic ligand LA. Full experimental details were available in the supplementary information.

The ¹H NMR spectrum of metalloorganic ligand **LA** was complicated owing to the presence of seven chemical environments (terpyridine in different environments have been labeled by letter assignments A to G in order to distinguish their difference, Figure 2). Fortunately, the ¹H NMR spectrum exhibited clear sharpening peaks in the expected ratio, suggesting that the ligand **LA** was synthesized correctly (Figure 2A). All the peak assignments of metalloorganic ligand **LA** were further confirmed according to 2D COSY and 2D NOESY NMR (Figures S26 and S27). In addition, the highresolution ESI-MS analysis was done to confirm the formation of ligand **LA** (Figure S62), which displayed peaks at m/z 682.71, 875.87, 1164.80, and 1646.68, in accordance with the charge states of 6+ to 3+ due to the loss of the corresponding number of NTf_{2}^{-} units.

With this metalloorganic ligand **LA** in hand, we utilized it as an outer rim, by mixing it with the core ligand **LH** and Zn(II) ions at a precise stoichiometric ratio of 6:1:18 for 12 h. Addition of excess bistrifluoromethanesulfonimide lithium salt (LiNTf₂) as counterion to change NO₃⁻ anion to NTf₂⁻ anion, a red precipitate was obtained in nearly quantitative yield (94%). This assembled product still showed good solubility in acetonitrile, N,N-Dimethylformamide and other solvents. Using acetonitrile as solvent, NMR and electrospray ionization mass spectrometry (ESI-MS) were conducted to determine the molecular composition of the formed complex.

Figure 2 shows the comparison of ¹H NMR spectra of ligands **LA**, **LH** and assembled product, all distinguishable peaks showing that a discrete structure is formed. The broadening of the peaks is due to the eight different chemical environments of terpyridine units, and the slow tumbling motion on the NMR time scale supporting the formation of a very large complex.⁶³ The evidence for the reaction among ligands and metal ions is that the uncomplexed terpyridine units in ligands **LA** and **LH** witnessed significant upfield shifts ($\Delta \delta > 1.00$ ppm). In addition, in the nonaromatic region, only a singlet peak at 3.36 ppm for –OCH₃ was observed, which indicated that a single and symmetrical complex was generated (Figure 2B). The other NMR peak



Figure 2. NMR study of the hexagon-fused wheel **W1**. ¹H NMR spectra (500 MHz, 298 K) of (A) Metallo-organic ligand **LA** in CD₃CN; (B) Macromolecule **W1** in CD₃CN; (C) Organic ligand **LH** in CDCl₃. Methoxy region was assigned to indicated the single -OCH₃; (D) DOSY NMR spectra of reinforced wheel **W1** in CD₃CN at 25 °C. (Terpyridine in different chemical environments were labeled by letter assignments A-H in order to distinguish their difference)



Figure 3. (A) ESI-MS spectrum and (B) 2D ESI-TWIM-MS plot of hexagon-fused wheel W1; (C) TEM image and the magnified image of a single W1.

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assignments are confirmed on the basis of the 2D COSY and 2D NOESY NMR spectra. 2D NMR diffusion-ordered NMR spectroscopy (DOSY) was also performed to verify the purity and size of the macromolecules. There only exists a single band corresponding to the ¹H NMR signal peaks, suggesting that only one species exists in the solution (Figure 2D). Furthermore, the experimental diffusion coefficient (D) was determined to be 8.31×10^{-11} m²s⁻¹ in CD₃CN at 298 K. Calculated by a modified Stokes-Einstein equation based on flat structures, the radius (r) of the hexagon-fused wheel macromolecules was roughly estimated (Supporting Information), which exhibiting a relatively smaller size possibly caused by the broad NMR signal, but confirming that only one species exist in the solution.

13 Electrosprav ionization mass spectrometry (ESI-MS) ex-14 periments combined with traveling wave ion mobility mass 15 spectrometry (TWIM-MS) were performed to further inves-16 tigate the composition and purity of accepted supra-17 molecule.64 After directly conducting electrospray ionization mass spectrometry (ESI-MS), no peaks of zig-zag 1D ol-18 19 igomer which might generate from metalloorganic ligand LA or organic ligand LH were found, which provided evi-20 dence of the quantitative formation of hexagon-fused wheel 21 W1. The ESI-MS spectrum of W1 exhibiting a series of peaks 22 derived from the 21+ to 36+ ions (Figure 3A), which was 23 due to the loss of the corresponding number of NTf₂⁻ units 24 in the ionization process, and their m/z values were con-25 sistent with the theoretically calculated values of W1. The 26 ESI-TWIM-MS spectrum of W1 showed one narrow drift 27 time distribution ranging from 26+ to 38+ charge states 28 (Figure 3B), indicating that the desired product possesses 29 high structural rigidity, as well no isomers exists. Moreover, 30 when the concentration increases from 0.3 to 5 mg mL⁻¹, the 31 ESI-MS spectrum revealed that a new series of prominent 32 peaks appeared near the previous peaks corresponding to [W1+(CH₃CN)_n] (n=4, 8, 12), which result from the incorpo-33 ration of CH₃CN solvent molecules on its surface or coordi-34 nation sites⁶⁵⁻⁶⁶ (Figure S70). 35

36 According to the giant and rigid two-dimensional plane, 37 transmission electron microscopy (TEM) experiment was performed to visualize the morphology of individual surpa-38 molecules. The reinforced wheel W1 was dissolved in 39 CH₃CN at a concentration of $\sim 10^{-6}$ M and drop-casted on a 40 carbon-coated copper grid (Cu, 400 mesh) surface. In high-41 magnification TEM imaging, the hexagonal-shaped mor-42 phology was observed (Figure 3C). The experimental diam-43 eters were 13.7± 0.4 nm, which correspond to the theoreti-44 cal value of molecular modeling. Moreover, compared with 45 the outer six hollow hexagons, the central wheels were ob-46 served as expected darker dots, the size of those central 47 dark cores was also consistent with the molecular wheel 48 (Figure S74).

49 Self-Assembly and Characterization of the Rigid 3D 50 **Double-Decker Dodecagonal Prism-Like Architecture** 51 P1. Comparison with the metalloorganic ligand LA, the syn-52 thetic routes for metalloorganic ligand LB need more elaborate design. First, Ru^{III}-terpyridine mono-complex 7 53 (Scheme 1) that contains bromine and iodine was rede-54 signed by bringing a phenyl spacer in meta-substituted po-55 sition (Scheme S2). Then, the bromo- and iodo-substituted 56 Ru²⁺-complex 8 was obtained based on the same core 57

complex **3**. Terpyridine boronic acid **9** was redesigned to introduce methyl- group to increase the solubility of the final metalloorganic ligand and assembled product. In the final step, a seven-fold Suzuki coupling reaction of complex **8** with **9** (Scheme 1) was implemented for 7 days using $[Pd(PPh_3)_4]$ as the catalyst, the crude product was purified by method of flash column chromatography (Al₂O₃). Full experimental details were available in the supplementary information.

The ¹H NMR spectrum of metalloorganic ligand LB is presented in Figure 4A. There are eight kinds of terpyridine chemical environments in LB (which have been labeled by letter assignments A to H in Figure S42) leading to several overlapping peaks, nevertheless, the expected ratio of the clear peaks indicates the successful synthesis of ligand **LB**. The nonaromatic region displays three singlets at 3.97, 3.94 and 3.21 ppm with 1:1:1 integration ratio corresponding to the protons of -OCH₃. All other assignments of LB protons were correctly assigned according to 2D COSY and 2D NOESY spectra (Figures S43 and S44). The composition of LB was further confirmed by ESI-MS analysis, which exhibited peaks at m/z 877.69, 1109.17 and 1456.39 corresponding to the charge states of 6+ to 4+ due to the loss of the corresponding number of NTf_{2} units, and the experimental m/z values were completely consistent with the theoretical ones of LB (Figure S67).

Treating metalloorganic ligand **LB** with the core ligand **LH** in the presence of $Cd(NO_3)_2 \cdot 4H_2O$ at a precise stoichiometric ratio of 6:1:24 gave a clear and transparent solution. After the solution cooled at room temperature, excess



Figure 4. NMR study of the double-decker dodecagonal prismlike architecture **P1**. ¹H NMR spectra (500 MHz, 298 K) of (A) Metallo-organic ligand **LB** in DMSO-d₆; (B) Double-decker dodecagonal prism-like architecture **P1** in DMSO-d₆/CD₃CN (1:2); (C) Organic ligand **LH** in CDCl₃; Methoxy region was assigned to indicated the single -OCH₃; (D) DOSY NMR spectra of reinforced wheel **P1** in DMSO-d₆/CD₃CN (1:2) at 25 °C. (Terpyridine labeled by letter assignments A-I is provided in the Supporting Information)



Figure 5. (A) ESI-MS spectrum and (B) 2D ESI-TWIM-MS plot of double-decker dodecagonal prism-like architecture **P1**; (C) TEM image and the magnified image of a single **P1**.

LiNTf₂ in CH₃OH was added to exchange NO₃⁻ to NTf₂⁻ and obtained a red precipitate. Differing from the reinforced wheel W1, the giant supramolecular dodecagonal prismlike architecture P1 obtained here was shown to be poor solubility in acetonitrile. Especially, when ligands self-assembled with Zn²⁺, the product became insoluble possibly due to the weaker reversibility of Zn-based architecture. Initial analysis on the final assembly was conducted by NMR by using the mixture solvent of dimethyl sulfoxide-d⁶ (DMSO-d⁶) and CD₃CN. Similarly, the broad NMR signals of **P1** suggests the formation of a huge architecture (Figure 4B). It is worth mentioning that the methoxy region shows three singlets at 4.04, 3.99 and 3.33 ppm with a 1:1:1 ratio corresponding to the protons of -OCH₃, and they were similar to those for LB, indicating the obtained assembly was a single and symmetrical complex. All other protons were further assigned based on 2D COSY and NOESY spectra (Figures S53 and S54). In addition, only one single band was found in the 2D DOSY NMR spectrum of P1 (Figure 4D), the diffusion coefficient D= $4.26 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ in CD₃CN/d⁶-DMSO (1:2) at 298 K, and its calculated radius was 7.3 nm also confirming that only one species in the solution (DMSO/CH₃CN).

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Most importantly, it is fortunate that the high accuracy of Waters Synapt G2i Mass Spectrometer is able to provide definitive structural information of such a high molecular weight assembly. The assembly **P1** was dissolved in dimethylformamide (DMF) at a concentration of 1 mg mL⁻¹, its mass spectrometry data is presented in Figure 5A, which display a series of peaks corresponding to the charge states from 34+ to 54+ due to the successive loss of NTf_2^- anions. After calculation and analysis, the experimental mass of **P1** was calculated with average of 119,498.18 Da, accorded with the formula of $[Ru_{36}Cd_{48}C_{4320}H_{3276}N_{360}O_{72}]^{168+}\cdot 168(NTf_{2}^{-})$, and their m/z values were also matched with the theoretically calculated values. Honestly, the molecular weight of the present study is difficult to obtain a clear isotopic pattern owing to the immense molecular weight and the incorporation of DMF solvent molecules on its surface or coordination sites (Figure S71). Furthermore, the TWIM-MS spectrum of **P1** displayed signal ranging from 37+ to 50+ charge states with one narrow drift time distribution, indicating that there was no isomers or conformers exists (Figure 5B).

Transmission electron microscopy experiment was also performed to provide a powerful evidence for the sizes and shapes of **P1**. The TEM image obtained by dissolving **P1** in DMF/CH₃CN (~10⁻⁶ M) and drop-casting onto carboncoated copper grids (400 mesh) is presented in Figure 5C. Eight dots with hexagonal-shaped morphology were observed and the averaged calculated diameters was $13.9 \pm$ 0.4 nm (Figure 5C), agreed well with the diameter of **P1** by modeling (Figure S75).

CONCLUSIONS

In summary, we expanded supramolecular self-assembly strategy toward a reinforced hexagon-fused wheel and a 3D gigantic three-dimensional dodecagonal prism-like architecture with molecular weights up to 47 KDa and 119 KDa,

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respectively, which may be difficult to access by taking advantages of other approaches. By employing stepwise syn-2 thesized metallo-organic ligands that containing trident component replace the simple rim building block, such giant nano-assemblies were obtained by a reinforcement strategy. The high-molecular-weight structures are reminiscent of biological macromolecules such as typical pro-6 teins and protein assemblies.⁶⁷⁻⁶⁸ 1D and 2D NMR, High-res-7 olution MS analysis and TEM investigation were imple-8 mented to unambiguously support the expected molecular 9 composition and size morphology. Like the two-dimen-10 sional covalent organic framework and metal organic 11 framework materials, those stable supramolecular struc-12 tures with well-defined geometries are expected to play an 13 important role in the functional materials fields.⁶⁹⁻⁷⁰ This 14 work exemplifies the potential of coordination assembly to 15 synthesize large and sophisticated architectures and devel-16 ops the reach of supramolecular coordination systems into 17 biomimetic science.

18 ASSOCIATED CONTENT 19

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org at DOI. Experimental procedures and characterization data, including ¹H, ¹³C, COSY, NOESY, and DOSY spectra of the new compounds and ESI-MS spectra of related compounds (PDF)

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#G.W. and M.C. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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Reinforced Topological Nano-assemblies: 2D Hexagon-Fused Wheel to 3D Prismatic Metallo-lamellar Structure with Molecular Weight of 119K Daltons

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