Giant, Hollow 2D Metalloarchitecture: Stepwise Self-Assembly of a Hexagonal Supramolecular Nut

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Ⓢ *Supporting Information*

ABSTRACT: A polyterpyridinyl building block-based nutlike hexagonal bismetallo architecture with a central hollow Star of David was assembled by a stepwise strategy. This nanoarchitecture can be viewed as a recursive mathematical form that possesses a supramolecular corner-connected cyclic structure, i.e., a triangle or rhombus at various levels of scale or detail. The key metallo-organic ligand (MOL) with four uncomplexed free terpyridines was obtained by a final Suzuki cross-coupling reaction with a tetrabromoterpyridine Ru dimer. The molecular metallorhombus was prepared by reacting the MOL with a 60° bis-terpyridine and Fe^{2+}. The giant hollow hexagonal nut with a diameter of more than 11 nm and a molecular weight of ca. 33 kDa was obtained in near-quantitative yield by mixing the two types of multi-terpyridine ligands with Fe^{2+}. The supramolecular architecture was characterized by NMR (^{1}H and ^{13}C), 2D NMR (COSY and ROESY), and DOSY spectroscopies, high-resolution electrospray ionization mass spectrometry, traveling-wave ion mobility mass spectrometry, and transmission electron microscopy.
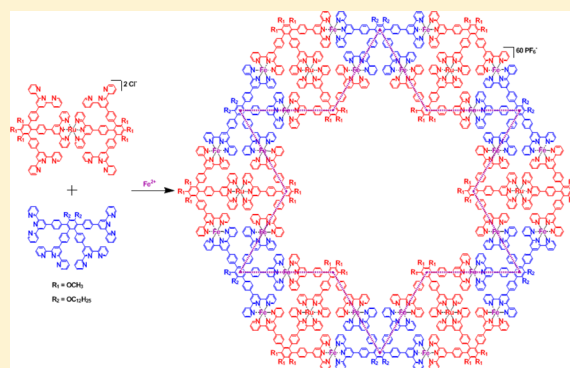
INTRODUCTION

Self-assembly of various organic molecules with metal ions is prevalent in nature. Although the metal complexes occupy only a trace of the weight of an organism, their presence is crucial for cellular function and survival in living beings. Inspired by the structural precision and functional diversity of biology, many efforts have been dedicated to the creation of metallo-organic supramolecules in the past decades to study the coordination between organic molecules and metal ions in the field of supramolecular chemistry.[1] Mono- and polypyridines, porphyrin, and other organic molecules have been utilized to coordinate with Fe, Zn, Cu, Pd, Pt, Ru, and many other metal ions to construct supramolecules such as rings,[2] rotaxanes,[3] knots,[4] cages,[5] and so on.[6]

Among the self-assemblies based on polypyridines, 2,2′:6′,2″-terpyridine (tpy) and its analogues have attracted wide interest because of their excellent ability to strongly coordinate with various transition-metal ions. Numerous supramolecular architectures employing these tridentate ligands have been reported, such as rings,[7] fractals,[8] catenanes,[9] polyhedra,[10] etc. Especially, a stepwise procedure utilizing ⟨tpy−Ru^{2+}−tpy⟩ connectivity was recently used in some multicomponent systems to assemble highly ordered di- and multimetallic supramolecules,[11] which are hard to access by other systems. Furthermore, the ⟨tpy−Ru^{2+}−tpy⟩ connectivity is strong

enough to participate in Suzuki coupling reactions to achieve symmetric and asymmetric metallo-organic ligands (MOLs) with high complexity.[12]

Herein we report the synthesis of a bismetallo rhombus and a giant nutlike hollow hexagonal supramolecule that is constituted by six rhombuses linked nose to tail with 120° direction to form a hollow Star of David in the center. This giant architecture with high symmetry[13] can be viewed as a recursive mathematical form that possesses a self-similar structure, i.e., a triangle or rhombus at various levels of scale or detail. These constructions were achieved via a stepwise strategy instead of direct self-assembly. The key MOL [**T₂Ru**] was prepared by a fourfold Suzuki coupling reaction on a tetrabromo-substituted Ru^{2+} complex in better yield (55%) than ever reported before (see the Supporting Information (SI)). [**T₂Ru**] and Fe^{2+} were treated with **V** and **K**, respectively, to generate the monorhombus and the hexarhombic hollow nut. The monometallo rhombus structure or recursive unit could also obtained by a single-step reaction.[14] In our initial attempt, tris-terpyridine **T** and tetrakis-terpyridine **K** were assembled with Fe^{2+} directly; however, the expected monometallo hexagonal structure (Scheme 1) was not obtained, although the geometric

Scheme 1. Different Attempts To Achieve the Giant Hollow Hexagon

T **K** **[T₂Ru]**

T₁₂K₆Fe₃₀ **[T₂Ru]₆K₆Fe₂₄**

R₁=OMe R₂=OC₁₂H₂₅ ●=Ru ○=Fe
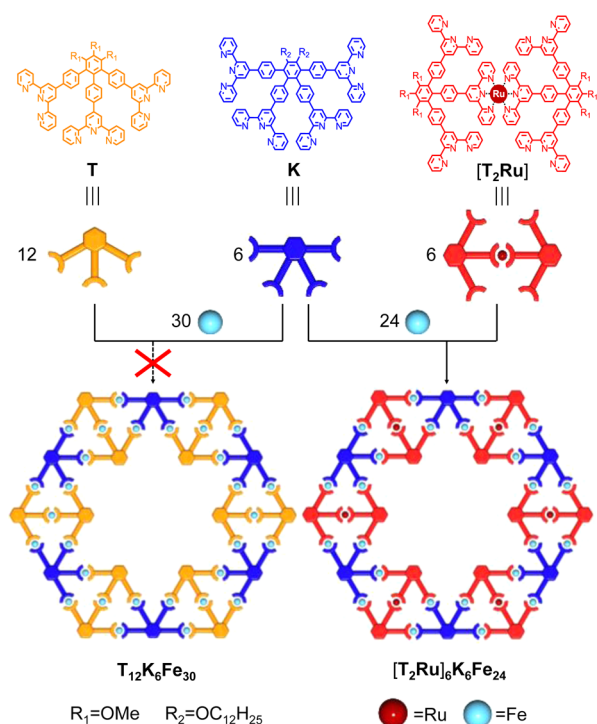
prediction was theoretically achievable. Therefore, we explored stepwise self-assembly as an alternative route to this higher-order superstructure (Scheme 2).

■ RESULTS AND DISCUSSION

For ligand preparation, bis-terpyridine ligand **V** was synthesized according to a known procedure.[15] Since tris-terpyridine **T** owns two kinds of tpy arms and Ru^{2+} has no selectivity between them, the key MOL [**T₂Ru**] could not be obtained by a typical one-step method.[16] A newly designed pathway for the C_2-symmetric ligand [**T₂Ru**] with one ⟨tpy−Ru^{2+}−tpy⟩ connector and four inward free terpyridines was synthesized in four steps (see the SI). The final step was conducted by a fourfold Suzuki coupling reaction with a tetrabromo-substituted Ru dimer and 4-terpyridinyl-B(OH)₂ using Pd^0 as the catalyst. Isolation was performed by column chromatography (Al_2O_3), eluting with CH_2Cl_2/MeOH. The ^1H NMR spectrum of [**T₂Ru**] showed two representative singlets at 8.90 and 8.68 ppm in a 1:2 ratio attributed to the two kinds of tpyH$^{3',5'}$, two complexed tpyH$^{3',5'}$ and four free ones, respectively (Figure 1C). The methoxy signals of [**T₂Ru**] were observed at 4.14 and 3.76 ppm with an exact ratio of 1:2. All of the ^1H NMR peak assignments were confirmed by two-dimensional (2D) rotating-frame Overhauser effect NMR spectroscopy (ROESY) (Figure S22).

We recently reported that Fe^{2+} would be a proper metal to use in self-assembly to obtain the thermodynamic product while at higher temperature.[17] By a similar procedure, the self-assembly of the bismetallo rhombus [**T₂Ru**]V₂Fe₄ was achieved by treating **V**, [**T₂Ru**], and Fe^{2+} in a stoichiometric ratio (2:1:4) as a model system (Scheme 1). Excess KPF_6 was used to exchange the counterion to give the complex [**T₂Ru**]V₂Fe₄ as a violet precipitate after filtration and washing with water and MeOH. The ^1H NMR spectrum of [**T₂Ru**]V₂Fe₄ showed a very sharp pattern, and the three representative singlets exhibited with an integration ratio of 2:2:1 were attributed to the tpyH$^{3',5'}$'s (Figure 1B). Two downfield shifts at 9.22 and 9.20 ppm were assigned to the tpyH$^{3',5'}$'s complexed with Fe^{2+}, and the singlet at 8.80 ppm is due to the tpyH$^{3',5'}$'s coordinated with Ru^{2+}. The methoxy protons of [**T₂Ru**]V₂Fe₄ were observed at 4.22, 4.08, and 3.93 ppm with a precise 1:2:2 ratio. The singlet at 4.08 ppm was attributed to the methoxy installed on **V**, and the other two singlets were assigned to the methoxy protons on

Scheme 2. Self-Assembly of the Molecular Rhombus [T₂Ru]V₂Fe₄ and the Giant Hollow Hexagonal Nut [T₂Ru]₆K₆Fe₂₄

2 Cl⁻

[T₂Ru]

K

V

60 PF₆⁻

R₁=OCH₃
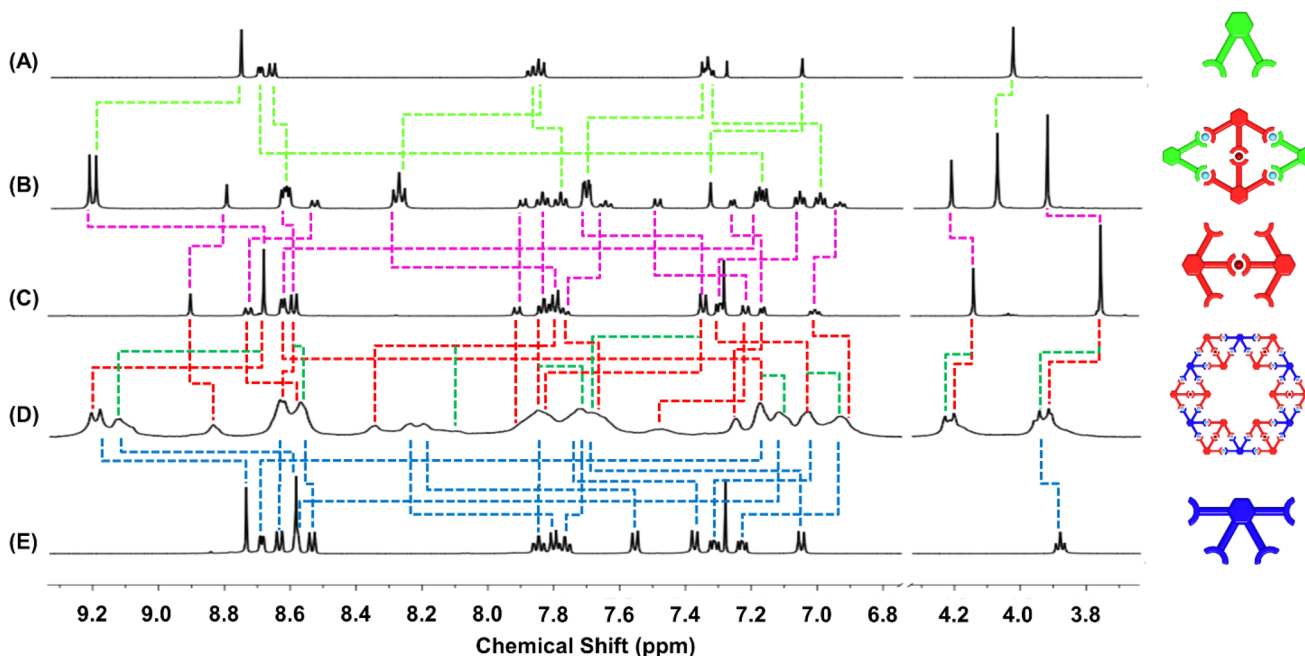R₂=OC₁₂H₂₅

12 PF₆⁻

[T₂Ru]V₂Fe₄
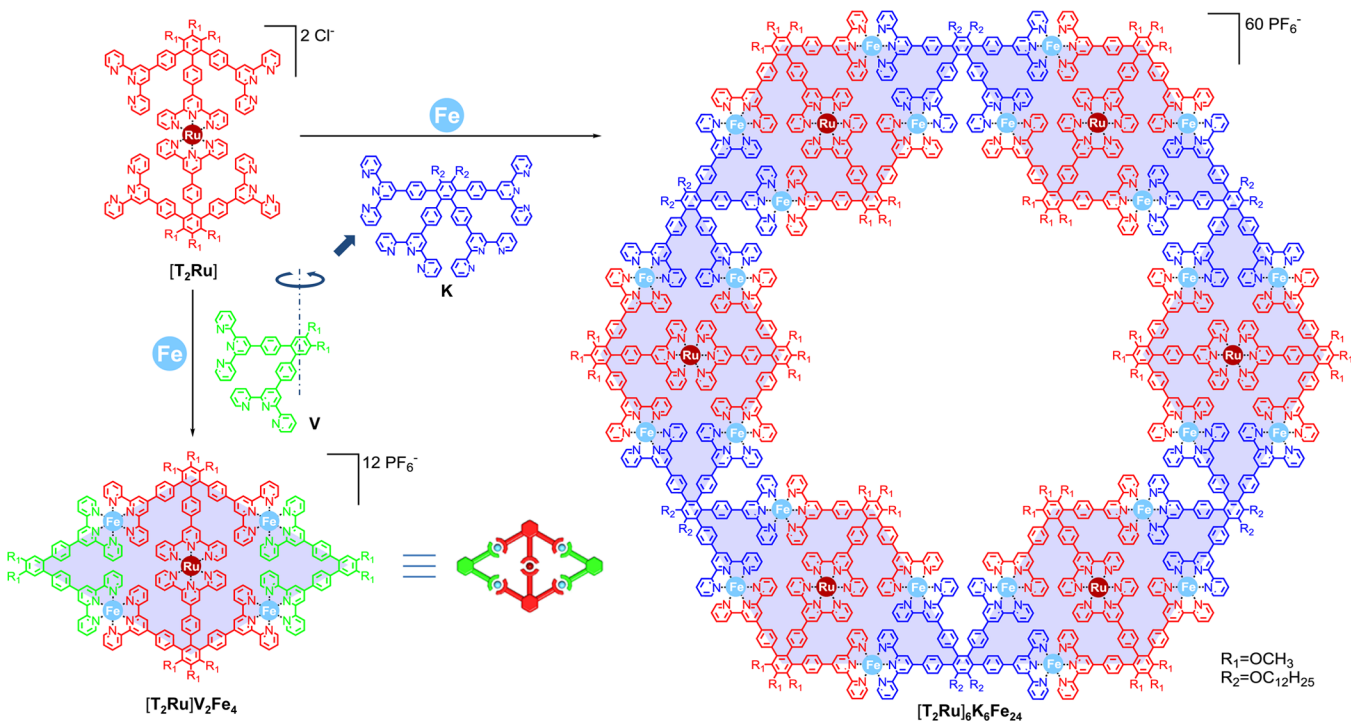
[T₂Ru]₆K₆Fe₂₄

Figure 1. ^{1}H NMR spectra (500 MHz) of (A) ligand **V** in CDCl$_3$, (B) rhombus $[\mathbf{T_2Ru}]\mathbf{V_2Fe_4}$ in CD$_3$CN, (C) metallo-organic ligand $[\mathbf{T_2Ru}]$ in CDCl$_3$, (D) hollow hexagon $[\mathbf{T_2Ru}]_6\mathbf{K_6Fe_{24}}$ in CD$_3$CN, and (E) tetrakis-terpyridine ligand **K** in CDCl$_3$.

$[\mathbf{T_2Ru}]$. All of the assignments were readily confirmed by the 2D ROESY spectrum (Figure S7). The diffusion-ordered NMR spectroscopy (DOSY) spectrum showed a narrow band near a diffusion coefficient of 3.24×10^{-10} m^2 s^{-1}, suggesting the formation of a discrete rhombus structure (Figure 2A).

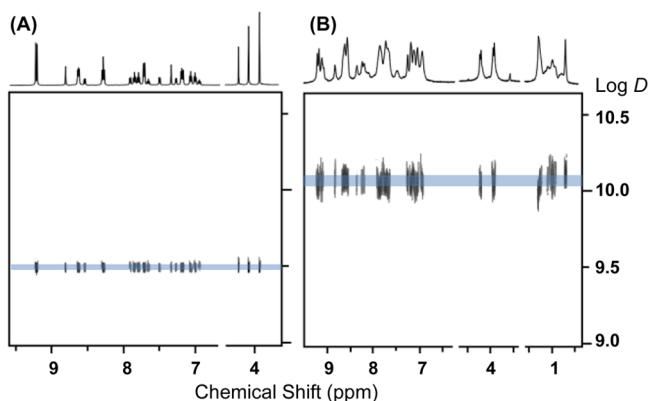**Figure 2.** DOSY spectra of (A) the rhombus $[\mathbf{T_2Ru}]\mathbf{V_2Fe_4}$ and (B) the hexagonal nut $[\mathbf{T_2Ru}]_6\mathbf{K_6Fe_{24}}$.

Electrospray ionization mass spectrometry (ESI-MS) of $[\mathbf{T_2Ru}]\mathbf{V_2Fe_4}$ (Figure 3A) revealed a series of peaks with charge states from 3+ to 9+ derived by the loss of PF$_6^-$ units. The experimental isotope pattern of each charge state agreed well with the corresponding simulated one based on the molecular weight of $[\mathbf{T_2Ru}]\mathbf{V_2Fe_4}$ (5458.7 Da). The narrow drift time distribution in the ESI traveling-wave ion mobility mass spectrometry (ESI-TWIM-MS)[18] plots further indicated that no other structural conformers or isomers were present (Figure 3B).

Inspired by our success with the bismetallo rhombus, we designed and synthesized a giant hollow 2D supramolecular nut using tetra-terpyridine **K** in place of bis-terpyridine **V** during the self-assembly with $[\mathbf{T_2Ru}]$ and Fe^{2+}. **K** was obtained from a
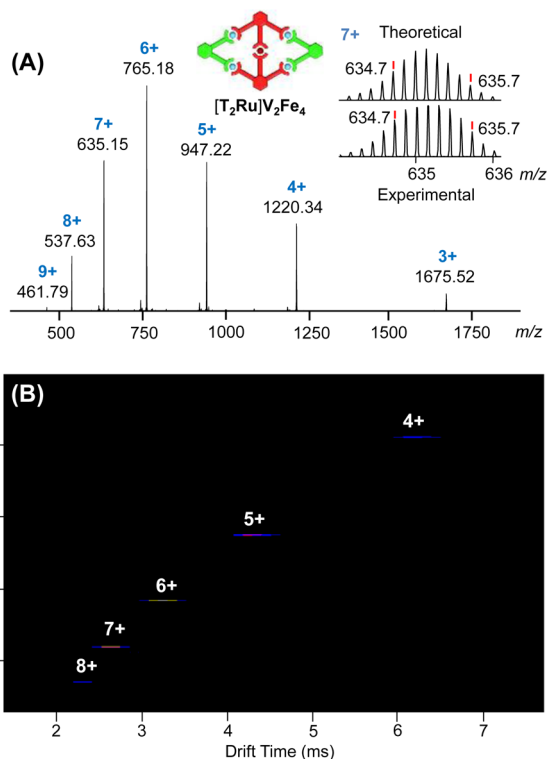

Figure 3. (A) ESI-MS spectrum and (B) 2D ESI-TWIM-MS plot (m/z vs drift time) for the rhombus $[\mathbf{T_2Ru}]\mathbf{V_2Fe_4}$. The charge states of intact assemblies are marked.

tetrabromobenzene derivative and 4′-boronatophenyl-2,2′:6′,2″-terpyridine (tpy-B(OH)$_2$) by a Suzuki cross-coupling reaction using Pd(PPh$_3$)$_2$Cl$_2$ as the catalyst in a mixed solvent (3:3:1 toluene/H$_2$O/t-BuOH) according to a reported method.[17,19]

The ^{1}H NMR spectrum of **K** (Figure 1E) displayed characteristic methylene signals at 3.88 ppm, and two singlets

at 8.74 and 8.59 ppm in a ratio of 1:1 were observed as the tpyH$^{3',5'}$'s of terpyridines in different chemical environments. The assignment of tpyHs and all of the other expected resonances were confirmed by the 2D ROESY spectrum (Figure S25).

The self-assembly of the cyclic hexarhombus $[\mathbf{T_2Ru}]_6\mathbf{K}_6\mathbf{Fe}_{24}$ followed a procedure similar to that for the rhombus $[\mathbf{T_2Ru}]\mathbf{V}_2\mathbf{Fe}_4$ (Scheme 2). The nutlike structure $[\mathbf{T_2Ru}]_6\mathbf{K}_6\mathbf{Fe}_{24}$ was confirmed by ESI-MS and NMR experiments. When regular ESI source conditions (i.e., high ionization temperature and capillary voltage) were applied, the ESI-MS spectrum exhibited a series of peaks with charge states from 17+ to 39+ due to the successive loss of PF_6^- counterions (Figure S31), suggesting the molecular composition of six $\mathbf{K}$, six $[\mathbf{T_2Ru}]$, 24 Fe^{2+} ions, and 60 PF_6^- counterions. For the purpose of clarity, part of the ESI spectrum (from 27+ to 39+) is shown in Figure 4. Because
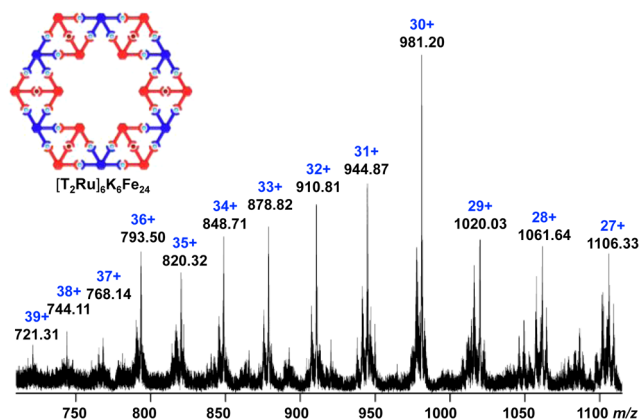

Figure 4. ESI-MS spectrum of the hollow hexagon $[\mathbf{T_2Ru}]_6\mathbf{K}_6\mathbf{Fe}_{24}$ using regular ESI source conditions.

of the high molecular weight (33 773.8 Da) and the complex's multiple counterions (a total of 60 PF_6^- ions), although each experimental isotopic pattern agreed well with the calculated peaks, a perfect well-resolved isotope pattern of the major peaks could not be obtained because of the resolution limitation of the mass spectrometer. For the peaks with charge states from 20+ to 25+, each contained an ion of Cl^- because of the incomplete exchange of counterions from Cl^- to PF_6^-. When mild ESI source conditions were applied, such as low desolvation and source temperatures (Figure S33), low capillary voltage and long accumulation time, a series of peaks ranging from 16+ to 26+ were observed with a high baseline. This was derived from the formation of solvent and/or salt adducts within the supramolecular species.[20]

The ^{1}H NMR spectrum of $[\mathbf{T_2Ru}]_6\mathbf{K}_6\mathbf{Fe}_{24}$ was complicated because of the plentiful peak overlaps caused by the six different groups of terpyridine units in the structure. Moreover, broad peaks were observed because of the slow tumbling motion of this giant structure on the NMR time scale.[21] All of the 6,6″ protons from the uncomplexed tpy units were significantly shifted upfield as a result of electron shielding effects, as is a typical assignment for the inherent pseudo-octahedral connectivity of the ⟨tpy−Fe^{II}−tpy⟩ components. Furthermore, in the non-aromatic region, the two diagnostic OMe signals of $[\mathbf{T_2Ru}]$ at 4.14 and 3.76 ppm split to four singlets at 4.23 and 4.21 ppm and 3.94 and 3.92 ppm, respectively, because of the different chemical environments inside and outside the hollow nut. 2D ROESY was used to interpret the ^{1}H NMR spectrum

of $[\mathbf{T_2Ru}]_6\mathbf{K}_6\mathbf{Fe}_{24}$. The DOSY spectrum unambiguously showed $[\mathbf{T_2Ru}]_6\mathbf{K}_6\mathbf{Fe}_{24}$ as a single component with a diffusion coefficient of 7.59×10^{-11} m^2 s^{-1} at 298 K (Figure 2B), and the experimental hydrodynamic radius (r_H) was consistent with the calculated molecular diameter.[22]

For the purpose of comparison, tris-terpyridine $\mathbf{T}$[12] was used to attempt assembly with $\mathbf{K}$ directly (Scheme 1), as mentioned earlier. The assembly with $\mathbf{T}$, $\mathbf{K}$, and Fe^{2+} followed a similar procedure, but the direct self-assembly was unsuccessful, as revealed by NMR and ESI-MS analyses, both of which showed big, complicated overlap patterns. We speculated that $\mathbf{T}$ played multiple roles (inner and outer ones) in the assembly process, resulting in multiple unidentified assemblies and polymeric products.[12]

Compared with $\mathbf{T}$, the introduction of $[\mathbf{T_2Ru}]$ allowed the complex $[\mathbf{T_2Ru}]_6\mathbf{K}_6\mathbf{Fe}_{24}$ to become the unique product of self-assembly because the Ru^{2+}-connected central terpyridine in each $\mathbf{T}$ prevented the generation of the bisrhombus structure.[12] In other words, $[\mathbf{T_2Ru}]$ was employed to prohibit the self-sorting behavior of either $\mathbf{T}$ or $\mathbf{K}$. Furthermore, the use of $[\mathbf{T_2Ru}]$ reduced the chance of forming metallopolymers by simplifying the assembly process. Finally, the self-assembly with $[\mathbf{T_2Ru}]$ and $\mathbf{K}$ is more like a simple chelate approach, which could enhance the stability of complex.

Transmission electron microscopy (TEM) was also performed to confirm the size and shape of the hexagonal 2D supramolecule visually (Figure 5A). The experiment was
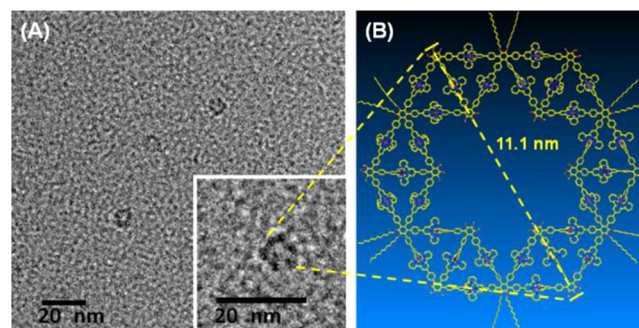

Figure 5. (A) TEM image of hollow hexagonal $[\mathbf{T_2Ru}]_6\mathbf{K}_6\mathbf{Fe}_{24}$. (B) Representative energy-minimized structure from molecular modeling of $[\mathbf{T_2Ru}]_6\mathbf{K}_6\mathbf{Fe}_{24}$.

carried out by deposition of a dilute MeCN solution ($\sim 10^{-6}$ M) of $[\mathbf{T_2Ru}]_6\mathbf{K}_6\mathbf{Fe}_{24}$ on carbon-coated grids (Cu, 400 mesh). The architecture was observed as a dispersion of individual rings with recognizable vertices and edges and the clear hollow structure. The size of the circular pattern correlated well with the size of 11.1 nm calculated by molecular modeling.

■ CONCLUSIONS

We have achieved the self-assembly of a huge nutlike molecular hexamer with high symmetry using ⟨tpy−Ru^{2+}−tpy⟩ and ⟨tpy−Fe^{2+}−tpy⟩ connectivity with a stepwise self-assembly strategy. The synthesis of the key metallo-organic ligand $[\mathbf{T_2Ru}]$ and the high assembly temperature illustrated that the ⟨tpy−Ru^{2+}−tpy⟩ connection is stable enough to participate in the designed functionalization and subsequent self-assembly. Compared with one-pot self-assembly of $\mathbf{T}$ and $\mathbf{K}$, the stepwise procedure showed a highly spontaneous process to produce the supramolecular nut with high complexity in high yield. This work will attract more attention on stepwise self-assembly to

construct highly ordered supramolecules with more structural complexity and eventually to realize functional diversity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06021.

Experimental procedures and characterization data, including ^1H, ^{13}C, COSY, ROESY, and DOSY spectra of the new compounds and ESI-MS spectra of related compounds (PDF)

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Notes
The authors declare no competing financial interest.

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