Supramolecular Nanoarrays by the Self-assembly of Terpyridine-Based Monomers with Transition Metal Ions

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Supramolecular Arrays by the Self-assembly of Terpyridine-Based Monomers with Transition Metal Ions

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Hierarchical construction of a highly ordered supramolecular array has been, in general, a challenge due to the complexation of building blocks and the hard-to-control weak interactions. Herein, we present a type of well-ordered nanoribbon, which was self-assembled *via* shape complimentary and hydrophobic effects from the bowl-shaped supramolecular components, which were synthesized by combining designer terpyridine-based monomers and two different metal ions (Ru^{2+}, Zn^{2+}). Interestingly, switching counter ions or changing monomer concentrations, a transformation between a uniform nanosphere and nanoribbon occurred. It opens a door to fabricate readily tailorable, large-scale, supramacromolecular materials.

Introduction

To better understand and mimic biological systems, it is necessary to simplify the complicated natural structures and build upon simple but yet effective models.[1,2] Supramolecular chemistry has provided a powerful platform to investigate the mechanisms as well as dynamic processes of such assembles.[3,4] The hierarchical fabrication of supramacromolecules has recently received considerable attention, due to the wide applications in optoelectronic and biomedical-related materials.[5-10] In contrast to typical covalent connectivity, supramolecular chemistry possesses advantages, such as minimizing side reactions and higher yields, due to reversible, non-covalent assembly, to provide error checking for monomer positioning as the assembly progress toward its low energy thermodynamic state. Among weak non-covalent interactions, hydrophobic effects, electrostatic interactions, and complementary shape designs have been widely utilized due to their important roles in the formation of abiological structures and dynamic processes.[11] Numerous metallo-supramolecular assembles obtained by weak interactions, such as micelles and spheres, have been reported;[12,13] however, fine-tuning the assembly processes and an understanding of formational mechanisms can be challenging due to these weak interactions, which generally limits directionality so crucial for the rational design and construction of large scale assembles.

Tailored terpyridine derivatives have been shown to afford directional monomers, which have generated a wide-range of 2D and 3D supramolecular architectures[14] upon coordination with transition metal ions,[6,14,15,16,25,26] such as: Zn^{2+}, Cd^{2+}, Fe^{2+}, or Ru^{2+}. Recently, utilizing terpyridine-based monomers and different step-wise assembly processes, a powerful toolbox has generated diverse routes to kinetically stable assembles that can overcome entropic effects, as shown in a series of homo- and hetero-nuclear metallomacrocycles.[17-19]

Taking advantage of a step-wise assembly strategy, we herein report a giant, terpyridine-based, triangle-in-*tris*triangle nanobowl **8**, which has a tailor-made macrocyclic core connected with <tpy-Zn^{2+}-tpy> linkages and three exterior thermodynamically stable triangles comprised of <tpy-Ru^{2+}-tpy> bonds. The core is derived from tetra*kis*terpyridinyl-dihydroanthracene, which provides the desired bending angle to form a nonplanar complex. The edge of this nanobowl is decorated with long hydrophobic C_{22} chains enhancing its overall solubility. The bowl-like core provides the polar and hydrophilic component, while the hydrophobic side-chains help tune the stack-ability of a bowl-in-bowl assembly. The bowl-shape of **8** leads to directional self-assembly due to the effect of their complementary shapes;[20-22] moreover, these long alkyl chains give rise to van der Waals interactions to assist in the intermolecular self-assembly process.[23] Predicated

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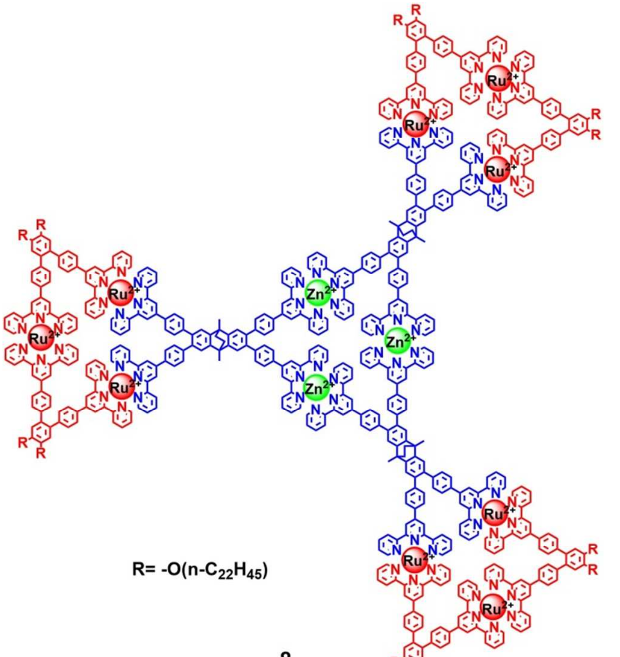
Electronic Supplementary Information (ESI) available: [Experimental procedures and characterization data including COSY and NOESY NMR, ESI- and TWIM-MS.]. See DOI: 10.1039/x0xx00000x on these interactions, nanoribbon and nanosphere assembles were obtained utilizing these nanobowls, as the stackable monomers.

Notably, these two types of assembles can be tuned by simply changing component concentrations and/or counter ions, as will be demonstrated.

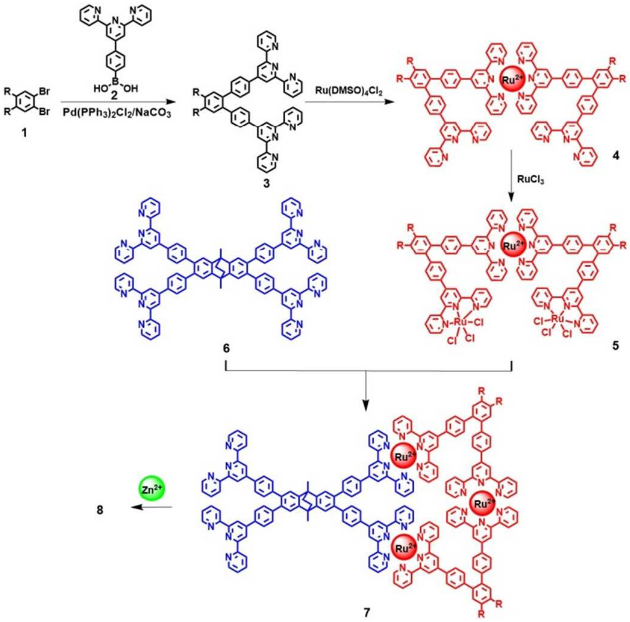


8

Figure 1. The structure of dodecametallo-complex, nanobowl **8**.

Results and Discussion

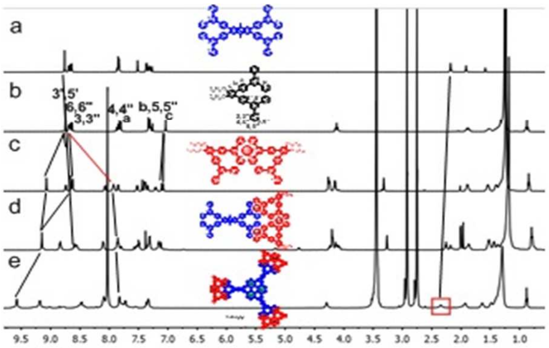
The *bis*terpyridinyl ligand **3** and dimer **4** were prepared using the Suzuki coupling reaction by reported procedures.[24] The Ru adduct **5** was synthesized (98%) from dimer **4** with 2 equivalents of $RuCl_3$ by refluxing this mixture in EtOH. Then treatment of adduct **5** with ligand **6** in a precise (1:1) ratio in refluxing mixture of MeOH and $CHCl_3$ (1:1, v/v) with a catalytic amount *N*-ethylmorpholine gave a red powder, which was column chromatographed (Al_2O_3) eluding with a solvent mixture of MeOH/$CHCl_3$ (1:20, v/v) to give (45%) the desired all Ru, stable intermediate **7**, possessing the *tris*macrocycle and two uncoordinated terpyridinyl moieties. All new compounds were characterized by ^{1}H NMR, MALDI-TOF or ESI-TOF mass spectroscopies. The proton NMR peaks were assigned *via* their COSY or NOESY spectra. Interestingly, the proton signals of **7** (Figure S9) assigned to the terpyridine moieties coordinated with Ru^{2+} ions were expected to appear as three types of NMR peaks. But their proton signals showed only one set of sharp peaks (coordinated tpy$H^{3',5'}$) at 9.21 ppm, as a singlet, indicating that the dihydroanthracene connections between the uncoordinated terpyridine and coordination triangle are insulators thus effectively blocking electronic interactions in contrast to a fully aromatic connector. As well, the singlet at 8.65 ppm was assigned to the uncoordinated tpy$H^{3',5'}$s.



Scheme 1. The synthesis of nanobowl **8**.

The target nanobowl **8** was self-assembled using an exact 1:1 ratio of monomer **7** with $Zn(NO_3)_2$ in a stirred mixture of MeOH and $CHCl_3$ at 25 °C for 1h, then the reaction mixture was treated with saturated aqueous NH_4PF_6. The ^{1}H NMR spectrum of the resultant complex **8** (Figure 2e) showed four types of signals, which were assigned to the four different terpyridinyl moieties, but due to their very close juxtaposition, only a few of the signals could be assigned, such as the different tpy$H^{3',5'}$ show one singlet at 9.74 ppm, the doublets at 8.68, 8.63, and 8.60 ppm were assigned to the arylH^a. The sharp singlet at 2.11 ppm was assigned to the methyl protons on the dihydroanthracene moieties (Figure S13) suggesting that the supramolecular assemble adopts an all *cis* conformation.

Figure 2. The ^{1}H NMR spectra of a) ligand **6** in $CDCl_3$, b) ligand **3** in $CDCl_3$, c) dimer **4** in $CDCl_3/CD_3OD$ (2:1, v/v), d) complex **7** in $CDCl_3/CD_3OD$ (2:1, v/v), and e) complex **8** (PF_6^-; d_7-DMF).



The ESI-MS (ElectroSpray Ionization-Mass Spectroscopy) spectrum of **8** (Figure 3) further supports formation of the tetra*kis*triangle by the series of dominant peaks at *m/z* 919.3, 990.3, 1071.7, 1165.1, 1274.2, 1403.1, 1558.0, and 1747.1 corresponding to charge states ranging from 16+ to 9+, respectively.

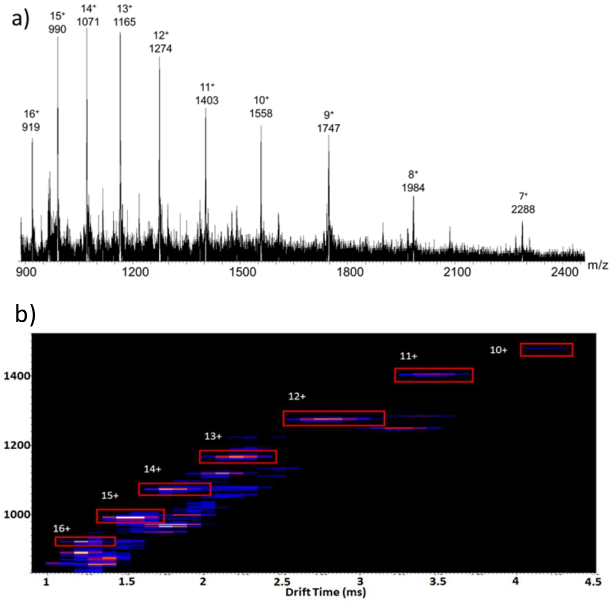


Figure 3. a) ESI-MS spectrum of **8**; b) ESI-TWIM-MS plot with the charge states of intact assemblies marked.

These MS results provide support for the combination of 6 ligand **3**s, 3 ligand **7**s, 9 Ru^{2+}, and 3 Zn^{2+} metal ions along with the experimental *m/z* values for each charge state, which is consistent with the calculated values. Additional support (Figure 3) for **8** was provided by ESI-TWIM-MS experiments [ESI-MS coupled with traveling-wave ion mobility spectrometry (TWIM-MS), a variant of ion mobility spectrometry].[27] The TWIM-MS denotes molecular separation, such as chromatography, separating ions by their charge and shape/size in the TWIM region, followed by *m/z* in the adjoining mass analyzer. This method provides a tool to resolve isomeric ions and determine structural information that serves as a unique complement to more traditional characterization procedures.[28-30] The TWIM-MS spectrum exhibits charge states ranging from 16+ to 10+, derived from **8** with a single, narrow band for each charge state and a narrow drift time distribution for the signals extracted for each band, clearly indicating a single species, supporting the NMR results.

The molecular modeling of **8** further supports its giant, bowl-like structure. A Zn-based triangle is surrounded by three Ru triangles, along with the 12 C_{22} rim appendages. The distance between two adjacent Ru atoms on the rim is 4.7 nm. The dihedral angle between inner triangle and outer triangles is 105°. These results are consistent with the conclusions from the above NMR, ESI-MS, and TEM results.

With the hydrophobic alkyl chains and hydrophilic metal coordination complex moieties, we investigated the self-assembling properties of this supramacromolecule in solvent mixtures; water and DMF were initially chosen as the mixed solvent system. The nanobowl **8** has excellent solubility in DMF and the DMF-water mixture was considered as a good medium to induce the hydrophobic effects. Adjustment of the solvent ratios permitted the fine-tuning of the self-assembly behavior.

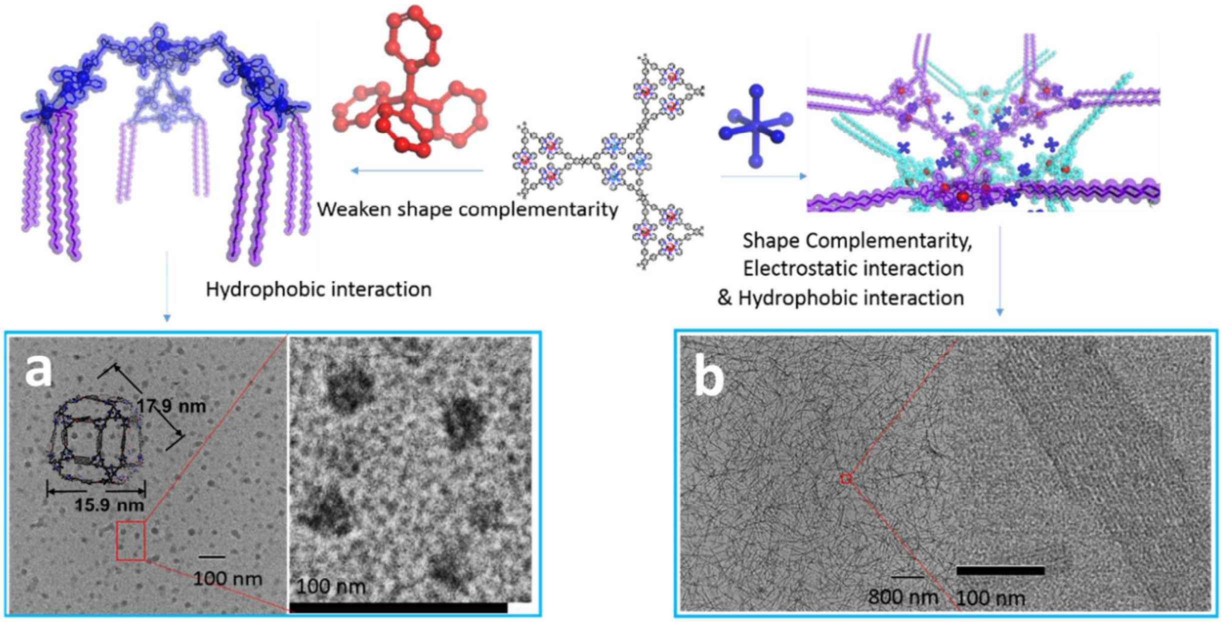


Figure 4. The TEM images of complex **8** with a) BPh_4^- (**9**) (1.4 mg/mL) and b) PF_6^- (1 mg/mL) counter ions.

Dynamic light-scattering (DLS) gave insight to the particle sizes of the nanobowl upon variance of the solution of **8** by the gradual addition of H_2O to DMF (Figure S19). When the ratio of H_2O/DMF (v/v) was greater than 1:20, an overall steady increase in particle size was observed. After the addition of 17% H_2O to the DMF solution, the particle size reached a stable state and the scattering light intensity increased dramatically indicating a narrow distribution, which is symptomatic of forming large assemblies. Although the DLS supported these large assemblies, the solution remained clear, even after 2 weeks. Therefore, we adopted the mixed ratio of H_2O and DMF (1:5 v/v) to probe this self-assembly process.

Transmission electron microscopy (TEM) was then utilized to directly visualize the assembly of nanobowl **8**, as well as to ascertain both the structural size and shape. Deposition on carbon-coated grids was accomplished with a dilute H_2O : DMF (1:5, v/v) with PF_6^- counterions (Cu, 400 mesh, Figure 4b). The TEM images, as shown in Figure 4b, revealed long, well-ordered ribbons in which each nanoribbon measured 80-110 nm and 300-600 nm in width and length, respectively. The ribbons, one-dimensional nanowires, were formed through electrostatic interactions, shape complementarity, and hydrophobic interactions via the hydrophobic interactions derived from the C_{22} alkyl chains effectively linking the supramolecular wires together to generate parallel ribbons. The largest distance between the rigid rims of the nanobowls is *ca*. 5 nm, which agrees well with the average distance of each wire in the nanoribbon.

Further insight into the structures of the aggregates for complex **8** was gained by AFM (Figure S18). At concentrations of 100 μg/mL in [H_2O/ DMF (1 : 5)], samples were confirmed to adopt mixed aggregations with either a ribbon-like or a round structure. In the ribbon-like structures the thickness is about 6 nm, which is consistent with the depth of the bowl-shaped complex **8**. In the round structures, the depth is about 9 nm, which indicated the presence of hollow cubic structures flattened under the instrumental conditions.

To explore these weak interactions, we changed the counter ions, from PF_6^- (**8**) to BPh_4^- (**9**). The larger BPh_4^- anion decreases the electrostatic interactions and interferes with shape complementarity. The hydrophilic intermolecular interactions from the alkyl chains thus dominate the aggregation the bowl-shaped supramolecules to give a new cube-like assembly, which, based on molecular modeling, has a nanobowl positioned at each vertex, with the C_{22} chains acting as the linking components. These results were supported by TEM experiments of the nanobowl **9** (BPh_4^-, concentration 1.4 mg/mL), whereby two discrete sizes of assemblies with diameters ranging from 15 to 20 nm were observed (Cu, 400 mesh, Figure 4a). The large scale, uniformed sized particles indicate a self-assembly, based on thermodynamic equilibria; thus, we performed a TEM study of the nanobowl **8** with PF_6^- at different concentrations (Figure 5). At lower concentration [10 μg/mL; H_2O : DMF (1:5, v/v)], the TEM image shows uniform aggregates with 15-20 nm diameters (Figure 5a). Increasing the concentration of the nanobowl solution to 1 mg/mL, the ribbons finally assembled (Figure 5c). Therefore, the nanoribbons are favored at higher concentrations; whereas upon dilution, smaller cube-like aggregation is favored. The number of particles in unit volume decreased correspondingly until entropy[31-33] pushed the self-assembled ribbons into the smaller cubic structure. Beside the weak interactions, it could be concluded that entropy also plays a critical role in this hierarchical self-assembly transmission after either changing the size of counter ions or concentration.

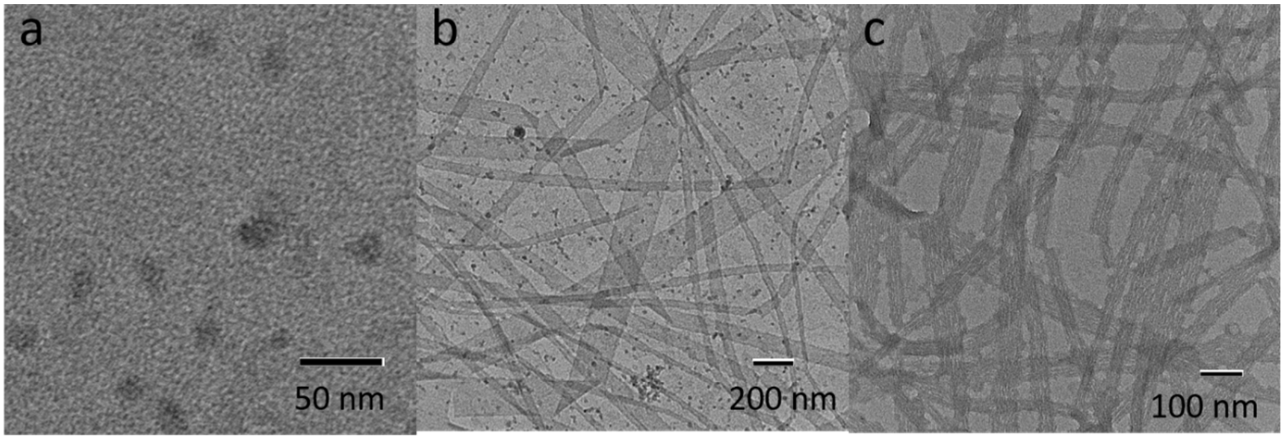


Figure 5. Concentration dependent self-assembly. The TEM images of nanobowl **8** with PF_6^- at concentrations of a) 10 μg/mL, b) 100 μg/mL, and c) 1 mg/mL.

Conclusions

In summary, we have designed and synthesized a novel tetra*kis*triangular supramacromolecule by combining terpyridine-based ligands and transition metal ions by a simple stepwise assembly. The complex and all intermediates have been characterized by NMR and ESI-MS experiments. This metal complex adopts a bowl-like shape and has hydrophobic alkyl chains decorated on the rim, which affords insight into tailoring the self-assemble process to generate nanoribbons and nanoparticles. Interestingly, the nanoribbon and nanoparticle are well-controlled to transfer into each other by simply changing the counter ions or solution concentration, which could lead to a way by which hierarchically construction can be easily transformed to smart materials using simple functional supramacromolecular monomers.

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