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Self-assembled Amphiphilic Janus Double Metallacycle

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Abstract

A double metallacycle was prepared via the size-selective integrative self-sorting of four different building blocks driven by a reversible metal-ligand coordination interaction. A hydrophobic dendron was placed on a metallacycle and a hydrophilic dendron was attached to the other metallacycle, producing a two-faced Janus-type supramolecule with two distinct functionalities. In aqueous media, hierarchical self-assembly of the supramolecular system was induced by the combination of coordination interactions and hydrophobic-hydrophilic interactions resulting in the formation of micrometer-sized fiber-like structures, a morphology distinct from metallacycles bearing only one type of functionality. This study provides a versatile approach for the construction of Janus-type molecules and demonstrates that integrative self-sorting of a supramolecular coordination system can be utilized for the preparation of complex supramolecular systems with pre-designed functionalities and morphologies

Graphical Abstract

Coordination-driven self-assembly of Janus double metallacycle by the integrative self-sorting of four different precursors. A hydrophobic dendron was placed on a metallacycle and a hydrophilic dendron was attached to the other metallacycle, producing a two-faced Janus-type supramolecule with two distinct functionalities. Further self-assembly of the metallacycle in aqueous media lead to the formation of a large fiber-like morphology.

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Supporting Information

Detailed materials and methods. Synthesis and characterization of building blocks and metallacycles. The Supporting Information is available free of charge on the ACS Publications website.

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Coordination-driven self-assembly is a powerful methodology for the rational design and synthesis of various discrete supramolecular systems using small and simple molecular building blocks.¹ With the development of synthetic and topological aspects of the self-assembled systems, the functions of the supramolecules have received increasing interest, and applications in separation,² catalysis,³ polymer synthesis,⁴ biomedicine,⁵ etc.⁶ These self-assembled systems are mostly constructed via the combination of complementary pairs of two highly symmetric building blocks, thus ensuring the exclusive formation of a single product. As a result, the number of functionalities of these supramolecular systems is often limited.

In order to introduce multiple functionalities to a supramolecular system to achieve the same high-level functional complexity observed in various biomolecules, self-sorting of complex systems is often employed. Self-sorting can be defined as high fidelity recognition between molecules (and ions) within complex mixtures.⁷ The precise control over the self-sorting process of a complex supramolecular system could lead to the formation of products with a greater structural and functional complexity than simple self-assembled systems.⁸ For supramolecular systems based on coordination-driven interactions, the heteroligation of metal ions may enable the formation of multicomponent cages via integrative self-sorting,⁹ yet the functional groups attached to the ligands may influence the self-sorting outcomes.^{9d} In contrast, the self-sorting organoplatinum(II)-based systems are mainly directed by the size and shape of the constituent building blocks.¹⁰ These studies focused on non-integrative (narcissistic) systems to establish the principle of self-sorting,¹⁰⁻¹¹ whereas integrative systems remained unexplored but have the potential for singular, multifunctional assemblies.

Janus molecules are molecules bearing two chemically distinct functionalities, resulting in different chemical or physical properties localized at distinct parts of the same molecule.¹² Janus molecules have great potential as building blocks for self-assembly due to their asymmetric structure and functionalization, and has inspired widespread applications in biotechnology¹³ and materials science.¹⁴ The synthesis of Janus molecules relies on covalent bond formation that often involves tedious multistep syntheses and challenging separation that limit the expansion of Janus molecules libraries for the further understanding of structure-property relationships of these molecules.

Herein, an amphiphilic Janus supramolecule was prepared via the self-sorting of an organoplatinum (II)-based coordination system. An asymmetric, tetrapyridyl ligand **1** was

prepared by connecting two dipyriddy ligands with different sizes as the bridging motif for the double metallacycle. Size-selective integrative self-sorting of ligand **1** with dipyriddy ligands bearing distinct sizes and functionalities (a hydrophobic, octyloxy chain-containing dendron for **2** or a hydrophilic, tri(ethylene oxide)-containing dendron for **3**) and complementary organoplatinum(II) building block **4** in a 1:1:1:4 ratio lead to the formation of a double metallacycle **5** bearing two dendrons with distinct properties attached to opposite sides of the metallacycle core (Scheme 1). Metallacycles bearing only hydrophobic dendrons (**6**) or hydrophilic dendrons (**7**) were prepared via the 2+2 coordination-driven self-assembly between the dipyriddy ligand **2** or **3** with **4** (Figures S14-S21) as reference compounds for examining the fidelity of the size-selective self-sorting process.

To confirm that the size of the building blocks was the determining factor during the self-sorting process of the supramolecular system, building blocks **2**, **3**, and **4** were mixed in a 2:2:4 ratio. The ^1H NMR spectra of the reaction mixture exhibited peaks corresponding to metallacycles **6** and **7** under the same conditions, with no broad peaks and unassignable signals (Figure 1a). Similarly, two peaks corresponding to metallacycles **6** and **7** at 14.90 ppm and 14.72 ppm, respectively, were observed in the ^{31}P NMR spectra of the reaction mixture (Figure S22). These results indicate the formation of **6** and **7** as the predominant products in the solution via the size-selective, narcissistic self-sorting of the supramolecular system.

Because the asymmetric ligand **1** was used for the synthesis, the ^1H and ^{31}P NMR spectra of the Janus double metallacycle **5** exhibit complicated, broad signals (Figures 1b and S12). Diffusion-ordered NMR spectroscopy (DOSY) study on **5** suggested a single ensemble with a band at the diffusion coefficient of $D = 6.6 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ (Figures 1c and S11). This value is significantly lower compared to that of the 2+2 metallacycles **6** ($D = 1.2 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$) (Figure S15) and **7** ($D = 1.7 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$) (Figure S19), indicating the formation of a larger product relative to the single metallacycles via integrative self-sorting.¹⁵ The composition of **5** was further confirmed using electrospray ionization mass spectrometry (ESI-MS). Prominent peaks corresponding to the intact compound **5** with +4, +5, and +6 charge states were observed due to the loss of the nitrate (ONO_2) counterions at $m/z = 1645.89$, 1304.28, and 1076.52, respectively (Figure 2). These peaks were isotopically resolved and showed good agreement with the theoretical distributions. Peaks that corresponds to fragments of **5** were also observed, likely due to the decomposition and re-assembly of the building blocks in the ESI-MS measurement.

Inspired by the amphiphilic nature of **5**, the aggregation behavior of the metallacycles were studied by conductivity measurements of the aqueous solutions of the metallacycles at different concentrations (Figure 3). The critical aggregation concentration (CAC) of **5** was determined to be $1.11 \times 10^{-6} \text{ M}$. In contrast, the CAC of the hydrophilic dendron-functionalized metallacycle **7** was $5.17 \times 10^{-7} \text{ M}$, which is slightly lower compared to the CAC of **5**. A Tyndall effect was observed for the aqueous solutions of **5** and **7** at concentrations higher than their respective CACs (Figure S23), indicating the existence of aggregates.

Transmission electron microscopy (TEM) was used to visualize the aggregates of metallacycles **5** and **7** at concentrations higher than their respective CACs. Large fiber-like structures with widths of 300 nm and lengths of $\sim 5 \mu\text{m}$ were observed upon self-assembly of **5** (Figure 4a-b). Similar morphology is observed for both metallacycles in scanning electron microscopy (SEM) experiments (Figure S25-S26). A possible mechanism for the formation of the fiber-like morphology involves a bilayer structure formed by the hierarchical self-assembly of the supramolecular system. The first level of organization is the formation of the double metallacycles **5** by metal-ligand coordination that placed the distinct dendrons on opposite sides of the ensemble. Higher level organization originated from the amphiphilic nature of **5** and the stacking interactions between the π systems of the metallacycle core. The hydrophilic-hydrophobic interactions drove the hydrophobic dendrons to the interior of the assembly, whereas the hydrophilic dendrons existed on the exterior of the ensemble, and π - π stacking interactions between the metallacycles provided ordering to form a fiber-like double-sandwich structure (Figure 4e). In contrast, spherical nanoparticles with diameter of ~ 200 nm were observed upon aggregation of **7** in aqueous solution (Figure 4c-d). Dynamic light scattering (DLS) experiment of an aqueous solution of **7** shows an average hydrodynamic diameter of 127.4 ± 8.4 nm (Figure S24), in agreement with the TEM results. With two hydrophilic dendrons located on opposite vertices of its rhomboidal structure, metallacycle **7** is a bola-type amphiphile¹⁶ and the particles were formed via metallacycle ordering and extension of the hydrophilic dendrons from the metallacycle core (Figure 4f). These observations suggest divergent aggregation behavior between **5** and **7** originating from their distinct type and placement of the constituent functional groups.

In summary, utilizing size-selective integrative self-sorting of a four-component supramolecular coordination system, a Janus double metallacycle was prepared with high efficiency. Dendrons with distinct hydrophobicities were placed on opposite vertices of the double metallacycle, endowing the supramolecule with an amphiphilic nature. Hierarchical self-assembly of the supramolecular system was achieved by the synergy of metal-ligand coordination interactions between the pyridyl groups and organoplatinum (II), as well as the hydrophobic-hydrophilic interactions between the dendrons, resulting in the formation of a large fiber-like morphology. In contrast, spherical nanoparticles were observed by hierarchical self-assembly of the metallacycle bearing only one type of dendron. This study represents an alternative approach for building Janus-type molecules, and the modularity of coordination-driven self-assembly may be beneficial for the expansion of Janus-type molecule libraries to improve our understanding of their unique structure-property relationships. Moreover, this study provides a general strategy for the rational design and synthesis of multifunctional supramolecular systems via integrative self-sorting.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(a) Partial ^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$, 298K) of equimolar mixture of metallacycles **6** and **7** ($c = 2.0$ mM). (b) Partial ^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$, 298K) of **5** ($c = 2.0$ mM). (c) Partial ^1H DOSY spectrum (500 MHz, $\text{DMSO}-d_6$, 298K) of **5**.

Figure 2.

(a) ESI-MS spectrum of double metallacycle **5**. (b-d) Expanded experimental (bottom) and theoretical (top) spectra of the 6+ (b), 5+ (c), and 4+ (d) charge states.

Figure 3.
Concentration-dependent conductivity changes of **5** (a) and **7** (b).

Figure 4. (a-d) TEM images of self-assembled structure formed by **5** (a-b) ($c = 1.0 \times 10^{-4}$ M) and **7** (c-d) ($c = 1.0 \times 10^{-4}$ M) in aqueous media. (e-f) Proposed mechanism for hierarchical self-assembly of **5** (e) and **7** (f) in aqueous media.

Scheme 1.

(a) Structure of the Building Blocks Used in Self-Assembly. (b) Size-Selective Narcissistic Self-Sorting of Metallacycles 6 and 7. (c) Integrative Self-Sorting for the Preparation of Janus Metallacycle 5.