Spontaneous Supramolecular Polymerization Driven by Discrete Platinum Metallacycle-Based Host-Guest Complexation

Bingbing Shi,^{*,†,‡}[®] Zhixuan Zhou,[‡][®] Ryan T. Vanderlinden,[‡] Jian-Hong Tang,[‡][®] Guocan Yu,^{*,§} Koushik Acharyya,[‡] Hajar Sepehrpour,[‡][®] and Peter J. Stang^{*,‡}[®]

[†]Key Laboratory of Eco-Functional Polymer Materials of the Ministry of Education, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, P. R. China

[‡]Department of Chemistry, University of Utah, 315 South 1400 East, Room 2020, Salt Lake City, Utah 84112, United States [§]Laboratory of Molecular Imaging and Nanomedicine, National Institute of Biomedical Imaging and Bioengineering, National Institutes of Health, Bethesda, Maryland 20892, United States

Supporting Information

ABSTRACT: Considerable progress in platinum metallacycle-based supramolecular polymerization has promoted the fabrication and application of supramolecular materials. However, despite recent advances, supramolecular polymers constructed through platinum metallacycle-based host-guest complexation remain rare because of the dynamics of platinum metallacycles. Here, we achieve linear supramolecular polymerization via platinum metallacycle-based host-guest complexation by following the design rule of suppressing the dynamics of the metallacycles. The establishment of the platinum metallacycle-based host-guest system and the realization of this type of supramolecular polymerization are expected to open opportunities for platinum metallacycle-based functional materials.

N oncovalent interactions are ubiquitous in multifunctional architectures in natural systems, which remain an ongoing inspiration for chemists to explore new methods to obtain multicomponent artificial materials.¹ Supramolecular polymers are an important class of supramolecular materials that are constructed from monomeric units connected by reversible and directional noncovalent interactions.² The intriguing functions and properties that originate from the dynamic behavior of supramolecular polymers make them promising materials for applications in various fields, including tissue engineering, pharmaceuticals, diagnostics, nanoelectronics, biosensors, and catalysis.³ However, many fundamental principles that govern the formation of supramolecular polymers remain unresolved.⁴ Therefore, it is important to develop efficient and viable strategies to form supramolecular polymers to promote their future applications. Host-guest systems, which form through the cooperative effect of various noncovalent interactions, play an important role in the development of supramolecular materials because of their high efficiency, good selectivity, and rich responsiveness.⁵ In macrocycle-based host-guest systems, guest molecules can be encapsulated inside the cavities of the macrocyclic hosts driven by the complementary shape and size as well as noncovalent interactions between the host and guest

molecules.⁶ Macrocyclic hosts are currently the most commonly used building blocks to fabricate supramolecular polymers through host-guest complexation.

Platinum(II)-based self-assembled metallacycles, which are constructed through coordination interactions, are a class of discrete macrocyclic hosts initiated by Fujita's and Stang's groups in the early 1990s.⁸ Metallacycles with functionalized exterior vertices have been widely used as building blocks to construct functional supramolecular polymers.⁹ Supramolecular polymers constructed by platinum(II) metallacycle-based host-guest complexation are rare. In our recently reported work,¹⁰ with a view to suppress the dynamics of a platinum(II) metallacycle and enhance its stability by hostguest complexation between metallacycle host and guest molecules, a cross-linked supramolecular polymerization strategy was achieved. Linear supramolecular polymers are powerful structural motifs in natural systems.¹¹ The design principles, directionality, dynamics, and functionality of linear supramolecular polymers have recently attracted great interest.¹² Herein we report that linear supramolecular polymerization is achieved via platinum(II) metallacyclebased host-guest complexation in the solid state as well as in solution.

The linear supramolecular polymerization strategy presented in this work is controlled by the molecular design of the monomer. As shown in Scheme 1, monomer 1, which contains two naphthalene moieties at its vertices, was designed and expected to self-assemble into a linear supramolecular polymer through the host-guest interactions between the cavity of the metallacycle and the naphthalene groups. Using palladiumcatalyzed coupling and subsequent etherification reactions, organic ligand 2 with a naphthalene group was synthesized (Scheme S1). The desired metallacycle 1 was then obtained by stirring a 1:1 ratio of organic ligand 2 and 180° organic diplatinum(II) acceptor 3 in acetone at 30 °C for 2 h (Scheme S2). Multinuclear (¹H and ³¹P) NMR spectroscopy demonstrated a self-assembled, highly symmetrical metallacycle. As shown in Figure 1a, compared with those of the free organic ligand 2, the signals corresponding to the protons of the

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Scheme 1. (a) Cartoon Representation and Chemical Structure of Metallacycle 1 with Two Naphthalene Moieties; (b) Top and Side Views of the Solid-State Structure of Metallacycle 1^a



^aHydrogen atoms are omitted for clarity.



Figure 1. (a) Partial ¹H NMR spectra (500 MHz, acetone- d_6 , 298 K) of metallacycle **1** and organic ligand **2**. (b) ³¹P{¹H} NMR spectra (202.3 MHz, acetone- d_6 , 298 K) of platinum(II) metallacycle **1** and 180° organic diplatinum(II) acceptor **3**.

pyridyl groups showed downfield shifts ($\Delta \delta = -0.45, -0.44,$ -0.35, and -0.45 ppm for H_a, H_b, H_c, and H_d, respectively), confirming the coordination of the nitrogen atoms to the platinum centers. Upon the formation of the metallacycle, the ³¹P{¹H} NMR spectrum of **1** shifted considerably upfield from that of the starting 180° Pt(II) acceptor 3 by 5.24 ppm and contained a lone sharp singlet at 12.89 ppm with concomitant ¹⁹⁵Pt satellites (J_{Pt-P} = 3406.73 Hz), which was consistent with a single phosphorus environment (Figure 1b). The ¹H and ³¹P{¹H} NMR results demonstrated the formation of a discrete structure as the sole isolated assembly product. Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) confirmed the formation of metallacycle 1. One isotopically resolved peak corresponding to the intact metallacycle with the loss of three trifluoromethanesulfonate (OTf) anions was found at m/z 1004.99 [M - 30Tf]³⁺ (Figure S10). The isotopic spacings of the peak corresponded well with its theoretical distribution, supporting the formation of the desired metallacycle.

The linear supramolecular polymer was characterized both in the solid state and in solution. Colorless rhombohedral prism single crystals of metallacycle 1 were prepared by a slow diffusion method. The structure of metallacycle 1 was unambiguously confirmed by X-ray diffraction study (Scheme 1b). In the crystal structure, the naphthalene groups of monomers 1 were encapsulated in the cavities of the adjacent metallacycles to form host-guest complexes (Figures S11 and 2). A linear supramolecular polymer formed spontaneously via



Figure 2. (a, b) Two views of the solid-state structure constructed through host-guest complexation of monomer 1. (c) Cartoon representation of the host-guest complexation between the cavity and the naphthalene groups of the metallacycle. Hydrogen atoms are omitted for clarity.

host-guest interactions of monomer **1** in the solid state (Figure 3). The crystal structure of the linear supramolecular



Figure 3. (a, b) Two views of the solid-state structure of the linear supramolecular polymer constructed through host-guest complexation of monomer 1. (c) Schematic representation of the construction of the linear supramolecular polymer through host-guest complexation of monomer 1. Hydrogen atoms are omitted for clarity.

polymer revealed that host 1 possessed six hydrogen atoms, with C–H··· π distances of 2.894–2.895 Å, which indicated that the naphthalene guests were included into the cavity of the platinum(II) metallacycle, driven by C–H··· π interactions. The host–guest complexation suppressed the dynamics of the metallacycle (i.e., stabilized the metallacycle), which contributed to the construction of the linear supramolecular polymer in the solid state.

The host-guest complexation motif between the cavity of metallacycle **1** and naphthalene and the spontaneous formation of the linear supramolecular polymer in the solid state encouraged us to further investigate the supramolecular polymerization behavior of monomer **1** in solution. The host-guest complexation between the cavity of metallacycle **1** and naphthalene was first investigated by 2D NOESY NMR spectroscopy in acetone (Figure S12). NOE correlation signals between the protons of the naphthalene groups and protons of the ethyl groups on metallacycle **1** were observed, indicating that the electron-rich naphthalene groups were encapsulated in

the cavity of cyclic monomer 1, resulting in the host-guest complexation in acetone.

The linear supramolecular polymerization behavior of monomer 1 was then investigated by a combination of various techniques, including ¹H and 2D DOSY NMR, viscosity, dynamic light scattering (DLS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Figure 4a reveals that the ¹H NMR spectra of monomer 1 were



Figure 4. (a) Partial ¹H NMR spectra (400 MHz, acetone- d_6 , 298 K) of monomer 1 at various concentrations. (b) Concentration dependence of the weight-average diffusion coefficient (D) of monomer 1 (500 MHz, acetone- d_6 , 298 K). (c) Double-logarithmic plot of specific viscosity of monomer 1 versus its concentration in acetone.

concentration-dependent. With increasing the monomer concentration from 1.00 to 90.0 mM, all the signals of the protons of monomer 1 became broad. 2D DOSY NMR spectroscopy, shown in Figure 4b, indicated fast exchange between different aggregates on the DOSY time scale. As the monomer concentration increased from 1.00 to 90.0 mM, the measured weight-average diffusion coefficients decreased considerably from 5.46×10^{-10} to 1.52×10^{-10} m² s⁻¹, reflecting the concentration dependence of the linear supramolecular polymerization of monomer 1. According to previous reports,¹³ a sharp decrease in the diffusion coefficient is expected to be observed when repeating units self-assemble into high-molecular-weight supramolecular polymers.

Specific viscosity measurement was performed to probe the macroscopic properties of the supramolecular polymeric assemblies.¹⁴ As presented in Figure 4c, the double-logarithmic plot of specific viscosity versus concentration indicated a viscosity transition of the linear supramolecular polymer constructed from monomer 1. In the low concentration range of monomer 1, the slope was approximately unity, which is characteristic of low-molecular-weight oligomers of uniform size. A sharp increase of viscosity was observed when the concentration of the monomer exceeded the critical polymerization concentration of approximately 50.0 mM.

The size distributions of the assemblies of monomer 1 in acetone were investigated by DLS experiments (Figure S13). The average diameters (D_h) of the assemblies of monomer 1 at different concentrations were determined to be 295 nm (at 1.00 mM) and 1720 nm (at 60.0 mM). The size increase indicated that bulk aggregates formed when the concentration of monomer 1 was higher than the critical polymerization concentration, demonstrated by the formation of a high-molecular-weight linear supramolecular polymer of monomer 1 driven by host–guest complexation between the cavity of metallacycle 1 and naphthalene in solution.

The self-assembly behavior of monomer 1 in acetone was further investigated by SEM and TEM. Figure 5 depicts well-



Figure 5. (a) SEM and (b) TEM images of the nanobelt aggregates of monomer 1. High-magnification (c) SEM and (d) TEM images of the nanobelt aggregates of monomer 1. (e) TEM image of monomer 1 after the addition of tetrabutylammonium bromide in acetone. (f) Cartoon representation of the nanobelt aggregates of monomer 1.

ordered nanobelt structures, which indicated the formation of a linear supramolecular polymer in acetone that became entangled to form the nanobelt structures. The SEM and TEM observations are consistent with the solid-state packing structure of the linear supramolecular polymer (Figure S14). Moreover, rod-like microfibers with different diameters and lengths were drawn from the solution of monomer 1 at 120 mM, which directly evidenced the formation of the linear supramolecular polymer in solution (Figure 6a-c).

Applications of the host-guest complexes and dynamic coordination of metal-ligand bonds have been widely used in the fields of multi-stimuli-responsive functional supramolecular materials.¹⁵ The reversible thermo-induced gel-like polymer and sol transitions of the polymer were visualized macroscopically (Figure 6d). Upon heating, the gel-like polymer easily flowed because the host-guest complexes dissociated at elevated temperature, indicating a transition between a gel-like polymer and sol. This process was completely reversible; the polymer re-formed upon cooling because of the restoration of the host-guest complex. However, the gel-like linear supramolecular polymer also exhibited responsiveness toward bromide anion (Br⁻). After the addition of tetrabutylammonium bromide (TBAB) to the gel-like linear supramolecular polymer, the solution quickly became turbid due to the disruption of the coordination bonds. TEM analysis confirmed the sensitivity of the supramolecular polymer to Br-(Figure 5e). After the addition of TBAB to the solution of the supramolecular polymer, the nanobelt structures of the



Figure 6. (a, b) SEM images of rod-like microfibers drawn from a highly concentrated solution of monomer 1. (c) Cartoon representation of the formation of rod-like microfibers. (d) Photographs showing the phase transitions of the linear supramolecular polymer triggered by external stimuli. (e) Schematic representation of the stimuli responsiveness of the linear supramolecular polymer.

supramolecular polymer were destroyed, and irregular aggregates were observed.

In summary, we demonstrated the preparation of a linear supramolecular polymer, not just in the solid state but also in solution, which was obtained by platinum(II) metallacyclebased host-guest complexation. We prepared metallacycle 1 containing two naphthalene moieties at its vertices, which then spontaneously assembled into an infinite linear supramolecular polymer through host-guest interactions between the cavity of the metallacycle and the naphthalene group both in the solid state and in solution. The host-guest complexation and the formation of the linear supramolecular polymer were confirmed by using various techniques. Furthermore, the supramolecular polymer was responsive to multiple stimuli. The present work established a metallacycle-based host-guest system and overcame the challenge associated with platinum-(II) metallacycle-based host-guest complexation-induced linear supramolecular polymerization in the solid state as well as in solution, which may stimulate the development of new approaches to fabricate functional supramolecular materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b06181.

Experimental details, NMR spectra, crystal data, and other materials, including Figures S1–S14 and Schemes S1 and S2 (PDF)

X-ray crystallographic data for 1 (CIF)

AUTHOR INFORMATION

Corresponding Authors *bingbingshi@nwnu.edu.cn

*guocan.yu@nih.gov

*stang@chem.utah.edu ORCID Bingbing Shi: 0000-0001-9523-5758 Zhixuan Zhou: 0000-0001-8295-5860 Jian-Hong Tang: 0000-0002-3299-5167 Hajar Sepehrpour: 0000-0002-3297-5167 Hajar Sepehrpour: 0000-0002-2307-0576 Notes

The authors declare no competing financial interest.

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