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Alanine-Based Chiral Metallogels via Supramolecular Coordination Complex Platforms: Metallogelation Induced Chirality Transfer

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Abstract

Chiral self-assemblies constantly attract great interest because of their potential to provide insight into biological systems and materials science. Herein we report on the efficient preparation of alanine-based chiral metal-lacycles, rhomboids **1^D** and **1^L** and hexagons **2^D** and **2^L** using a Pt(II) ← Pyridyl directional bonding approach. The metallacycles are subsequently assembled into nanospheres at low concentration, that generate chiral metallogels at high concentration driven by hydrogen bonding, hydrophobic and π – π interactions. The gels consists of microscopic chiral nanofibers with well-defined helicity, as confirmed by circular dichroism (CD), scanning (SEM) and transmission electron (TEM) microscopies. Given these results, we expect this technique will not only unlock interesting new approaches to understand homochirality in nature but also allow the design of versatile soft materials containing chiral supramolecular cores.

Graphical abstract

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ASSOCIATED CONTENT

Supporting Information

Syntheses and characterization data of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.

INTRODUCTION

Chiral self-assembly plays vital roles in biological systems, such as the storage of genetic information in nucleic acids, and the transcription of nuclei in cells.^{1, 2} In living organisms, these self-assemblies are customarily arranged from chiral building blocks via non-covalent interactions, whereby the molecular chirality of the building blocks is spontaneously organized to determine the microscopic supramolecular chirality of the nanostructures. One classic example is the secondary structures of proteins, which can exhibit various conformations such as α -helix, β -sheet, and random coil structure with different supramolecular chirality.³ In-depth studies of chirality at a supramolecular level will contribute to a better understanding of self-assembly in biological systems, and may also be beneficial for the development new medicines and smart materials.^{4, 5} Given that, chemists have started using small organic chiral molecules to investigate supramolecular self-assembly.^{6–8} For example, Ajaygosh and coworkers reported the gelation-induced helix transition to a higher-order supramolecular self-assembly of a rigid π -conjugated system.^{8e} Although some progress has been made, there still remain some fundamental questions related to supramolecular chiral architectures, especially regarding the formation of large, finite assemblies with well-defined structures.

Coordination-driven self-assembly provides a good platform to investigate supramolecular chirality because this process imparts high directionality and accurate positioning to form metallacycles and metallacages through the amalgamation of metal acceptors and organic donors.^{9–12} During the past few decades, various functional moieties have been appended either on the periphery or at the vertices of a number of discrete supramolecular assemblies.^{13–15} Recently, our group reported the efficient preparation of chiral metallacycles and chiral metallacages via the introduction of chiral binaphthyl-derived dicarboxylate units.¹³ Fujita and co-workers used diaminocyclohexane as a chiral building block to construct a chiral tetrahedron.¹⁴ These results prompted us to design a new chiral precursor to further study supramolecular chirality of Pt(II)–Pyridyl based supramolecular coordination complexes (SCCs). Herein, we report on the design and synthesis of an alanine-based chiral precursor¹⁸ compliant with coordination-driven self-assembly, and forms chiral organoplatinum(II) metallacycles rhomboids **1^D/1^L** and hexagons **2^D/2^L**. These metallacycles subsequently self-assemble to form uniform, well-defined nanospheres in methanol. Under appropriate conditions, these metallacycles can further interact via hydrogen bonding, hydrophobic and

π – π interactions to generate metallogels that display supramolecular chirality via the formation of helices (Scheme 1).

RESULTS AND DISCUSSION

Design and Synthesis of Chiral Metallacycles

According to the principle of directional bonding, the directionality and angularity of each component involved in coordination-driven self-assembly dictate the final architectural outcome, allowing discrete SCCs with well-defined shape and size to be easily prepared with high efficiency.^{19, 20} The rhomboids **1^D**/**1^L** and hexagons **2^D**/**2^L** were furnished by reacting a 120° (d/l)-alanine-based dipyrindyl ligand **3^D**/**3^L** and a Pt(II) acceptor, **4** or **5**, respectively, in a 1:1 molar ratio (Scheme 1). The chiral precursor **3^D** or **3^L** was readily synthesized by a Pd-catalyzed cross-coupling reaction (Scheme S1).

The above assemblies were characterized by multinuclear NMR analysis. The ³¹P{¹H} NMR spectra of **1^D** and **2^D** exhibited sharp singlets (ca. 12.90 ppm for **1^D**, 16.71 ppm for **2^D**) with concomitant ¹⁹⁵Pt satellites corresponding to a single phosphorus environment (Figure 1A and 1B). These peaks showed an upfield shift compared with those of the relevant starting Pt(II) acceptors **4** and **5** by approximately 7.70 and 5.78 ppm, respectively. This change as well as the decrease in coupling of the flanking ¹⁹⁵Pt satellites (ca. $J = -26.42$ Hz for **1^D**, $J = -38.88$ Hz for **2^D**) is consistent with the electron backdonation from the platinum centers. As shown in the ¹H NMR spectrum of rhomboid **1^D** (Figure 1D), the signals corresponding to the H_{1a-d} protons of the pyridine and phenyl rings are downfield shifted as compared to those of the free alanine ligand **3^D** (Figure 1C), which is caused by the decrease in electron density that occurs upon Pt–N bond formation. Moreover, the metal coordination caused the H_{1a} protons of the pyridine rings to split into two sets of two doublets. As for hexagonal metallacycle **2^D**, downfield shifts of the H_{1a-d} protons on the pyridine and phenyl rings relative to those of ligand **3^D** were also observed (Figure 1E). The characterization of the other configurations (**1^L** and **2^L**) are included in the supporting information (Figure S15, S16, S23, and S24). The well-defined signals in both the ³¹P{¹H} and ¹H NMR spectra support the formation of discrete assemblies.

Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) was used to determine the stoichiometry of multi-charged supramolecular structures.¹⁹ The mass spectrum of **1^D** contained two peaks consistent with the formation of a [2+2] assembly. These peaks corresponded to an intact entity with charge states arising from the loss of counterions trifluoromethanesulfonate (OTf) [$m/z = 1131.58$ for $[M - 3OTf]^{3+}$ and $m/z = 811.37$ for $[M - 4OTf]^{4+}$] (Figure 2A). For **2^D**, three peaks were identified for the assembly, supporting the formation of a [3+3] assembly (Figure 2B), e.g., $m/z = 1216.64$ corresponding to $[M - 4OTf]^{4+}$, $m/z = 943.44$ for $[M - 5OTf]^{5+}$, and $m/z = 761.34$ for $[M - 6OTf]^{6+}$. The detailed ESI-TOF-MS analysis of **1^L** and **2^L** can be found in the supporting information (Figure S17 and S25). All the assigned peaks were isotopically resolved and in good agreement with their calculated theoretical distributions, further supporting the structures as shown in Scheme 1.

Circular dichroism (CD) experiments were performed to confirm the chirality of the metallacycles. As depicted in Figure 3, the CD spectra of the enantiomeric self-assemblies, e.g., rhomboids **1^D** and **1^L** and hexagons **2^D** and **2^L**, exhibited mirrored responses. The CD spectra of the rhomboids displayed a major single band at ca. 186 nm, while those of the hexagons have two bands at ca. 187 and ca. 198 nm, corresponding to the transitions of the alanine units.²¹ Compared with the free ligands, all assemblies exhibited a slight red shift due to the metal-to-ligand charge-transfer effect (Figure S26). These data showed that enantiomerically pure chiral metallacycles were successfully prepared via directional bonding approach.

Further Self-Assembly of the Chiral Metallacycles

Scanning electron microscopy (SEM) revealed the further self-assembly behavior of these complexes in methanol. SEM samples were prepared by depositing solutions of chiral metallacycles onto SiO₂/Si substrates followed by slow evaporation in air at room temperature. Both rhomboids and hexagons formed almost uniform, highly ordered nanosphere structures upon exposure to methanol at a low concentration (6×10^{-6} M). The diameters of these nanospheres were within the range of 60–100 nm (Figure 4A and 4B). The observed diameters of the nanospheres were much larger than the molecular dimensions of the single rhomboids and hexagons, indicating that the metallacycles further self-assemble to form the nanospheres (Figure S27). Transmission electron microscopy (TEM) was also used to visualize these aggregates (Figure 4C, 4D, and S28), suggesting that all these nanospheres were solid inside.

Metallogelation

As **1^D/1^L** and **2^D/2^L** (Scheme 1) contain amide bonds, robust cores, and long alkyl chains, higher-order self-assembled structures may be formed via hydrogen-bonding, hydrophobic and π – π stacking interactions. These characteristics prompted us to explore the metallogelation of these chiral metallacycles. We used the traditional “inversion test tube” approach to study the metallogelation behavior of the complexes in various solvents. Specifically, the sample tube containing the metallacycles and solvents were heated to thoroughly dissolve the metallacycles. The solutions were cooled to room temperature over a period of two hours, and then the sample tubes were inverted to check the flow of the solution (Further details are given in the experimental section). A metallogelation experiment (Tables S2 and S3) indicated that these chiral metallacycles could only immobilize in strongly polar solvents; such as, methanol and ethanol; whereas they were insoluble on most low-polarity solvents and were soluble in medium-polarity solvents such as dichloromethane and ethyl acetate. The critical metallogelation concentration (CGC) of rhomboids **1^D** was larger than that of hexagons **2^D** under identical conditions.

Compared with traditional organogels based on small molecules, the CGC of these metallogels were higher. For instance, the CGC of **2^D** in methanol was 3.2 mM. As these metallacycles have large molecular weight (for example, **2^D** = 5461 Da), the CGC values of metallogelation are reasonable. In order to characterize the properties of metallogels, rheology and differential scanning calorimetry studies were performed (Figure S29 and S30). Rheological data were collected to characterize metallogels **1^D** and **1^L**, **2^D** and **2^L**. In

each case, the storage modulus (G') is much larger than the loss modulus (G''), and the storage modulus G' is independent of the angular frequency, thus indicating a viscoelastic behavior of the metallogels. The metallogels formed from the rhomboids and hexagons fully dissolved to give a transparent solution when the sample tubes were heated to approximately 45–48 °C. The non-viscous solution states could be reversibly returned to the metallogels when the solutions were cooled to room temperature. These experiments indicate that the metallogels can be transformed between the sol state and gel state using temperature as the external stimulus.

Morphological studies

During the metallogelation process, higher order self-assembled nanostructures formed, depending upon the structure of the metallacycles as well as their hydrogen-bonding interactions. The morphologies of the metallogels **1^D/1^L** and **2^D/2^L** at their CGC values were explored by SEM and TEM, which revealed that all assemblies formed interconnected fibers (Figure 5A and S32), with well-defined helicity. These fiber structures have lengths of several micrometers with a diameter of about 100 nm for the rhomboids and about 200 nm for the hexagons. In particular, metallacycle enantiomers e.g. **1^D** and **1^L** or **2^D** and **2^L** assembled in clockwise and counter-clockwise arrangements, yielding self-assembled aggregates with right-handed and left-handed helical configurations, respectively. TEM was used to further examine the morphologies of the microscopic chiral species. The nanofibers are composed of ribbons with helical morphologies (Insert images in Figure 5C, 5D, and S31). Mirror images of the helices were found to be transferred by the enantiomer of rhomboids and hexagons, further indicating that the molecular chirality of the metallacycles could be transferred to the microscopic level.

Supramolecular chirality

To further understand the microscopic assembly structure of the metallogels, we measured CD spectra (Figure 6).^{22, 23} As depicted in Figure 3, the rhomboids and hexagons did not display CD signals in the range of 230–400 nm, while upon the formation of metallogels, strong CD signals were obtained in that range. In the case of metallogel of **1^D**, a positive band at about 277 nm and a negative Cotton effect at about 341 nm with a crossover at 301 nm were observed. Likewise, for hexagons **2^D**, a negative Cotton effect at about 317 nm and a positive band at about 278 nm with a crossover at 294 nm were observed. For the metallogels of **1^L** and **2^L**, the mirror images of the CD profiles of **1^D** and **2^D**, respectively, were obtained. The results are consistent with the UV absorptions of the metallogels (Figure S33). The strong CD signals with negligible linear dichroism (LD) artefacts were also confirmed by the LD spectrum (Figure S34). All the above data indicate that the local chirality of the metallacycles was transferred to the large nanostructure as supramolecular chirality upon the formation of metallogels. Additionally, the absence of CD signals at ca. 300 nm in dichloromethane suggests that the molecular chirality of the metallacycles could not be transferred to the microscopic level in dichloromethane due to the absence of gel formation.

To understand the self-assembly of chiral metallacycles, FT-IR spectra were measured in the different states of the gelators, exhibiting that the N-H stretching frequency of the amide

functionalities shifted to higher wavenumbers upon dilution. This implies that the intermolecular H-bonding interactions play a crucial role in the metallogels formation. Moreover, for metallogel **2^D**, broad signals appeared at 25 °C in the proton NMR spectrum, indicating an extensive aggregation present in the gel state. Upon warming to 45 °C, a solution state was obtained and the signals corresponding to the aromatic and the pyridine protons were sharpened, indicating that these aggregations also play an important role in the gel formation. These observations were further supported by concentration dependent and temperature-dependent CD spectroscopies. For example, in the concentration-dependent CD measurements in methanol, **1^D** and **1^L** showed a signal around 300 nm, at a concentration of 3×10^{-4} M. This indicates that a certain amount of aggregation of metallacycles led to the formation of nanofibers at that concentration. SEM images of rhomboid **1^D** at a concentration of 7×10^{-4} M confirmed the coexistence of fibers and nanospheres. Temperature dependent CD spectra were also measured. This suggests that with an increase of temperature the intensity of the gel signals decreased, and disappeared at 45 °C i.e. at the melting points of the gels, as expected. These control experiments collectively suggest that hydrogen bonding, π - π stacking and hydrophobic interactions are responsible for the metallogel formation.

CONCLUSIONS

Alanine-based chiral metalla-rhomboids and hexagons, were synthesized with high-efficiency using a Pt(II) $\leftarrow$ Pyridyl directional bonding approach. Higher-ordered nanostructures such as nanospheres were obtained in methanol upon further assembly of the metallacycles. Driven by hydrogen bonding, hydrophobic effect, and π - π interactions, gelation of the metallacycles are observed at suitable concentration. As a result, the extended π systems of the SCCs interacted to give one-dimensional ordering to form chiral fibers. Interestingly, the molecular chirality of metallacycles was transferred via the formation of helices at the supramolecular level during the metallogelation process. The results described herein offer a novel approach to develop soft materials with precise control over the dimensionality and chirality of the resultant nanostructures.

EXPERIMENTAL SECTION

Materials and Methods

All reagents were commercially available and used as supplied without further purification. NMR spectra were recorded on a Varian Unity 300 or 400 MHz spectrometer. Mass spectra were recorded on a Synapt G2 ESI-Q-TOF mass spectrometer using electrospray ionization with a MassLynx software suite. The UV-vis experiments were conducted on a JASCO UV-550 spectrometer. SEM experiments were carried out on a Hitachi S-4800 FE-SEM instrument. TEM images were recorded on a Tecnai G2 F30 (FEI Ltd.) (Detailed informations about the materials and methods were exhibited in the supporting information).

Synthesis of **3^D**

To a mixture of 3, 5-bis(pyridine-4-ylethynyl)benzoic acid (324.3 mg, 1.0 mmol) and decyl 2-aminopropanoate (229.4 mg, 1 mmol, D-configuration) in dry DCM (30 mL), 1-(3-

Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (383.4 mg, 2.0 mmol) and 1-Hydroxybenzotriazole (270.2 mg, 2.0 mmol) were added and the reaction mixture was stirred at room temperature for 72 h under nitrogen atmosphere. Then the organic layer is washed with H₂O (3 × 10 mL) and finally concentrated. The pure product **3^D** is obtained by flash chromatography on silica gel (CH₂Cl₂ /CH₃OH = 20 : 1) (257.2 mg, yield: 48 %). ¹H NMR (400 MHz, CD₂Cl₂, 295K): 8.63 (d, *J* = 8.0 Hz, 4H), 8.00 (d, *J* = 4.0 Hz, 2H), 7.99 (t, 1H), 7.43 (t, *J* = 4.0 Hz, 4H), 6.80 (d, *J* = 4.0 Hz, 1H), 4.75 (t, *J* = 4.0 Hz, 1H), 4.20 (m, 2H), 1.69 (t, *J* = 8.0 Hz, 2H), 1.27 (m, 14H), 0.89 (t, *J* = 8.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, 295K): 173.15, 164.80, 149.87, 137.34, 134.99, 130.80, 130.56, 125.50, 123.31, 91.52, 88.30, 65.97, 48.75, 31.83, 29.46, 29.45, 29.24, 29.15, 28.49, 25.77, 22.63, 18.62, 14.06. LRESI-MS: calcd. for [M + H]⁺, 536.28; [M + Na]⁺, 558.27. Found : 536.30; 538.30.

Self-assembly of rhomboids **1^D**

3^D (5.34 mg, 0.01 mmol) and **4** (13.84 mg, 0.01 mmol) were added in CD₂Cl₂ (2 mL) and reacted at room temperature for 10 h. The resulting homogeneous solution was added diethyl ether to precipitate the product, which was isolated, dried under reduced pressure (18.61 mg, 97%). ¹H NMR (400 MHz, CD₂Cl₂, 295K): 9.50 (d, 4H), 8.95 (s, 4H), 8.65 (d, 4H), 8.57 (s, 4H), 8.07 (s, 2H), 7.96 (d, *J* = 4.0 Hz, 2H), 7.92 (d, *J* = 4.0 Hz, 2H), 7.58 (d, 10H), 4.62 (s, 2H), 4.16 (d, *J* = 8.0 Hz, 4H), 1.67 (s, 3H), 1.37 (s, 48H), 1.27 (s, 16H), 1.18–1.10 (m, 72H), 0.88 (s, 6H). ³¹P{¹H} NMR (CD₂Cl₂, room temperature, 121.4 MHz) δ (ppm): 12.90 ppm (s, ¹⁹⁵Pt satellites, ¹*J*_{Pt-P} = 2741.2 Hz). ESI-TOF-MS: *m/z* 811.37 ([M – 4OTf]⁴⁺, 1131.58 ([M – 3OTf]³⁺).

Self-assembly of hexagons **2^D**

3^D (5.34 mg, 0.01 mmol) and **5** (12.84 mg, 0.01 mmol) were added in CD₂Cl₂ (2 mL) and reacted at room temperature for 10 h. The resulting homogeneous solution was added diethyl ether to precipitate the product, which was isolated, dried under reduced pressure (20.3 mg, 96%). ¹H NMR (400 MHz, CD₂Cl₂, 295K): 8.70 (s, 12H), 8.30 (s, 6H), 8.03 (m, 3H), 7.85 (s, 12H), 7.22 (s, 12H), 4.64 (s, 3H), 4.16 (s, 6H), 2.35 (s, 6H), 1.82 (s, 72H), 1.64 (s, 9H), 1.26 (s, 48H), 1.18 (s, 108H), 0.87 (s, 9H). ³¹P{¹H} NMR (CD₃OD, room temperature, 121.4 MHz) δ (ppm): 16.70 ppm (s, ¹⁹⁵Pt satellites, ¹*J*_{Pt-P} = 2301.7 Hz). ESI-TOF-MS: *m/z* 761.34 ([M – 6OTf]⁶⁺, 943.44 ([M – 5OTf]⁵⁺, 1216.64 ([M – 2OTf]⁴⁺).

The Formation of Metallogels

A typical procedure for the metallogels formation in organic solvents is as follows: A suitable amount of metallacycles and 1 mL of organic solvent were mixed in a sealed tube. The metallacycles were dissolved completely upon heating, then the solution was slowly cooled to room temperature, and the metallogels was obtained after 2 h. Metallogelations were confirmed by the absence of flow, as observed by the tube inversion method.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR [CD_2Cl_2] spectra of (A) rhomboids **1^D** and (B) hexagons **2^D**; Partial ^1H NMR [CD_2Cl_2] spectra of (C) chiral ligand **3^D**, (D) rhomboids **1^D**, and (E) hexagons **2^D**.

Figure 2.

(A) Experimental (red) and calculated (blue) ESI-TOF-MS peak of discrete rhomboids 1^D $[M - 3OTf]^{3+}$, $[M - 4OTf]^{4+}$. (B) Experimental (red) and calculated (blue) ESI-TOF-MS peaks of discrete hexagons 2^D $[M - 5OTf]^{5+}$, $[M - 6OTf]^{6+}$.

Figure 3.
CD spectra of the assemblies in methanol ($C = 6 \times 10^{-6}$ M).

Figure 4. SEM images of (A) rhomboids **1^D** and (B) hexagons **2^D** in methanol ($C = 6 \times 10^{-6}$ M); TEM images of (C) rhomboids **1^D** and (D) hexagons **2^D** in methanol ($C = 6 \times 10^{-6}$ M).

Figure 5. SEM images of (A) rhomboids 1^D and (B) rhomboids 1^L in the metallogels state; Enlarge SEM images of (C) rhomboids 1^D and (D) rhomboids 1^L in the metallogel state. The insert TEM images of rhomboids 1^D and rhomboids 1^L in (C) and (D).

Figure 6. CD spectra of (A) metallogels **1^D** and **1^L** (6.6 mM) and (B) metallogels **2^D** and **2^L** (3.2 mM) in methanol and dichloromethane.

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