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A supramolecular oligo[2]rotaxane constructed by orthogonal platinum(II) metallacycle and pillar[5]arene-based host–guest interactions

Bingbing Shi*, Yuchun Wang, Yi Zhou, Xing-Xing Zhao, Yizhou Li, Nuoqian Yan, Wen-Juan Qu, Qi Lin, Tai-Bao Wei

Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

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ABSTRACT

Oligo[*n*]rotaxanes are one of the most extensively studied categories of mechanically bonded macromolecules. In this study, a supramolecular oligo[2]rotaxane is successfully constructed driven by platinum(II) metallacycle and pillar[5]arene-based host–guest interactions in an orthogonal way. The supramolecular oligo[2]rotaxane is further applied in fabricating a light harvesting system.

Mechanically interlocked molecules (MIMs), including rotaxanes and catenanes, have attracted considerable attention in the development of mechanically bonded molecular machines, such as switches, shuttles, muscles [1–3]. Specifically, oligo[*n*]rotaxanes, as one of the most extensively studied mechanically bonded macromolecules [4,5], were widely studied by scientists during the past decades. Up to now, a large number of oligo[*n*]rotaxanes have been prepared by taking advantage of macrocyclic hosts-based host–guest interactions, such as crown ethers [6], tetracationic cyclophanes [7], pillararenes [8,9]. These macrocycle-based oligo[*n*]rotaxanes were widely used as drug delivery vehicles, hydrogels, insulated polymers, light-harvesting systems, molecular tubes, and stimuli-responsive molecular shuttles [10]. Therefore, the preparation of oligo[*n*]rotaxanes with unique structures and functions is in great demand for the development of supramolecular chemistry and materials chemistry.

Platinum(II) metallacycles are a class of discrete macrocyclic hosts which were constructed by forming metal–ligand bonds with predictable coordination geometries and moderate bond energies [11,12]. Platinum(II) metallacycles with functionalized exterior vertices have been actively applied in the construction of various supramolecular systems, such as supramolecular polymers, transmembrane channels, sensors, nanostructures [13,14]. Moreover, platinum metallacycles were used to effectively fabricate mechanically interlocked molecules by taking advantage of the reversible Pt coordination bonding and metallacycle-based host–guest interactions [15]. However, to the best of our knowledge, oligo[*n*]rotaxanes constructed by platinum metallacycle-based host–guest interactions have rarely been reported.

In the previous report, our group demonstrated the host–guest complexation between a [2 + 2] platinum(II) metallacycle and an alkylated derivatized naphthalene [15]. On the other side, the neutral guest bearing a cyano site is an effective guest for pillar[5]arene in the case of an alkylated derivative [16–20]. In view of this and as a part of our research effort devoted to supramolecular oligo[*n*]rotaxanes, we report a novel supramolecular oligo[2]rotaxane constructed by an alkylated derivatized naphthalene guest for [2 + 2] platinum(II) metallacycle cavity and a neutral guest possessing two cyano binding sites for pillar[5]arene cavity. As shown in Scheme 1, by taking advantage of metallacycle-based host–guest interactions and the dynamic covalent chemistry in the formation of reversible Pt coordination bonds, a [2]rotaxane **1·2** was first prepared by employing a template-directed clipping procedure [21]. The [2]rotaxane **1·2** was thought of as a homoditopic AA-type monomer. A ditopic connector **3** containing two cyano binding sites was used as a BB-type monomer to interact with **1·2**, resulting the forma-

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* Corresponding author.
E-mail address: bingbingshi@nwnu.edu.cn (B. Shi).

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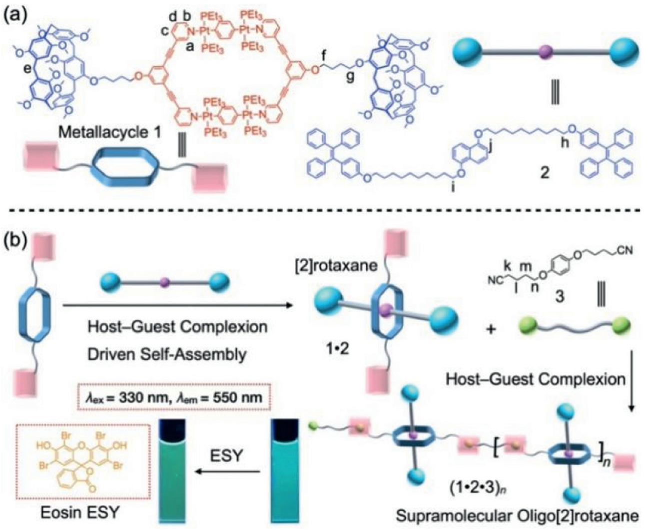

Scheme 1. (a) Chemical structures and cartoon representation of metallacycle **1** and guest molecule **2**. (b) Schematic representation of the formation of supramolecular oligo[2]rotaxane.

tion of a supramolecular oligo[2]rotaxane $(\mathbf{1{\cdot}2{\cdot}3})_n$. Moreover, the supramolecular oligo[2]rotaxane $(\mathbf{1{\cdot}2{\cdot}3})_n$ showed aggregation induced emission (AIE) [22] property in solution and was used to fabricate a light harvesting system with high energy conversion efficiency.

Metallacycle **1** with two pillar[5]arene motifs at its exterior vertices was designed and obtained by stirring a mixture of organic ligand **5** and 180° organic di-platinum(II) acceptor **4** in 1:1 ratio in acetone at 25 °C for 2 h (Scheme S1 in Supporting information). Multinuclear (^{1}H and ^{31}P) NMR spectroscopy was performed to investigate the self-assembled metallacycle with highly symmetrical structure. As shown in Fig. 1a, compared with those of the free organic ligand **5**, the ^{1}H NMR signals corresponding to the protons of the pyridyl groups (H_a–H_d) on metallacycle **1** showed downfield shifts, indicating the coordination of the nitrogen atoms to the platinum centers. Upon the formation of the metallacycle, the ^{31}P{^{1}H} NMR spectrum of **1** shifted upfield from that of the starting 180° Pt(II) acceptor **4** and contained a lone sharp singlet, indicating a single phosphorus environment (Fig. 1b). Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) was conducted to further confirm the structure of metallacycle **1**. Three isotopically resolved peaks corresponding to the intact metallacycle with the loss of tri-fluoromethanesulfonate (OTf) anions were found at *m/z* 2174.7475 [**1**–2OTf]$^{2+}$, 1400.1810 [**1**–3OTf]$^{3+}$, and 1012.8936 [**1**–4OTf]$^{4+}$, respectively (Fig. 1c). The isotopic spacings of the peaks corresponded well with their theoretical distributions, supporting the formation of the desired metallacycle **1**.

A [2]rotaxane **1·2** was *in situ* obtained by simply mixing the dumbbell template **2** (1.00 mmol/L) and metallacycle **1** (1.00 mmol/L) in 1:1 molar ratio in acetone. The formation of the [2]rotaxane was confirmed by ^{1}H NMR spectroscopy, ^{31}P NMR spectroscopy and ESI-TOF-MS analyses. As shown in Fig. S4 (Supporting information), compared with the signals of free dumbbell **2**, the peaks related the protons H_j on the [2]rotaxane **1·2** showed down field shift. The ^{31}P{^{1}H} NMR signal of the [2]rotaxane **1·2** shifted upfield from that of metallacycle **1** and contained a lone sharp singlet (Fig. 2a). These results demonstrated the formation of the corresponding [2]rotaxane **1·2**. Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) was performed to further confirmed the structure of **1·2**. As shown in Fig. 2b, two isotopically resolved peaks relating to **1·2** with the loss of OTf anions were found at *m/z* 1778.0596 [**1·2**–3OTf]$^{3+}$ and 1296.3049 [**1·2**–4OTf]$^{4+}$, which corresponded well with their theoretical distributions.

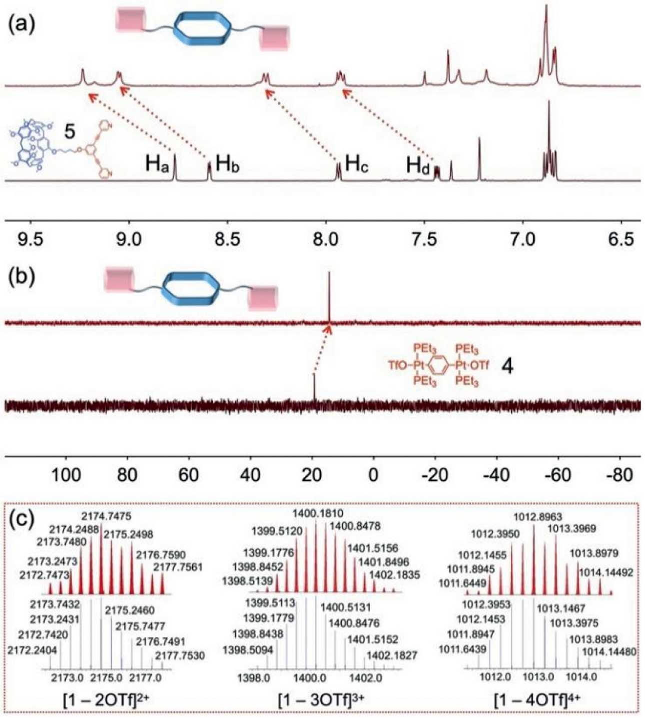

Fig. 1. (a) Partial ^{1}H NMR (400 MHz, acetone-d_6, 298 K) spectra of **1** and ligand **5**. (b) ^{31}P{^{1}H} NMR (97.1 MHz, acetone-d_6, 298 K) spectra of **1** and ligand **4**. (c) Experimental (red) and calculated (blue) electrospray ionization peaks of charge states of **1**.

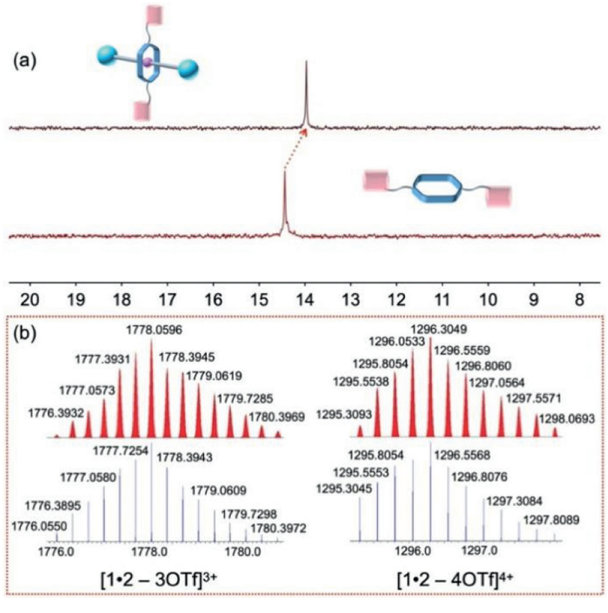

Fig. 2. (a) ^{31}P{^{1}H} NMR (97.1 MHz, acetone-d_6, 298 K) spectra of [2]rotaxane **1·2** (1.00 mmol/L) and **1** (1.00 mmol/L). (b) Experimental (red) and calculated (blue) electrospray ionization peaks of charge states of [2]rotaxane **1·2**.

Then, a supramolecular oligo[2]rotaxane was obtained by simply mixing an equimolar **1·2** (1.00 mmol/L) and ditopic connector **3** (1.00 mmol/L) in acetone. The formation of the supramolecular oligo[2]rotaxane was confirmed by ^{1}H NMR spectra. As shown in Fig. 3, after the addition of 1.00 equiv. of **3** (1.00 mmol/L) into an acetone solution of **1·2** (1.00 mmol/L), the peaks related to pro-

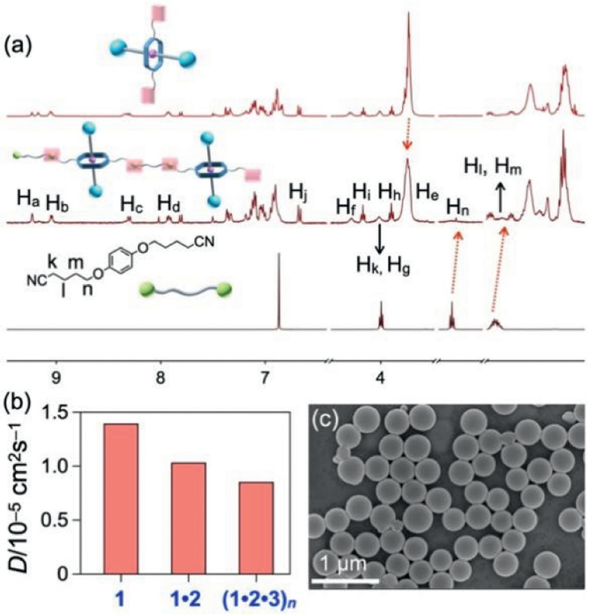

Fig. 3. (a) Partial ^{1}H NMR (400 MHz, acetone-d_6, 298 K) spectra of [2]rotaxane **1·2** (1.00 mmol/L), supramolecular oligo[2]rotaxane $\mathbf{(1{\cdot}2{\cdot}3)_n}$ and guest molecule **3** (1.00 mmol/L). (b) The weight average diffusion coefficient (D) of **1** (1.00 mmol/L), **1·2** (1.00 mmol/L) and $\mathbf{(1{\cdot}2{\cdot}3)_n}$ (1.00 mmol/L) (400 MHz, acetone-d_6, 298 K). (c) SEM image of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ in H_2O/acetone (v:v = 9:1) ($c_1 = c_2 = c_3 = 1.0 \times 10^{-5}$ mol/L).

tons H_k–H_n on **3** showed up field shifts, while the singles of protons H_e on **1·2** showed down field shift. These results indicated that the cyano heads of ditopic connector **3** were threaded into the cavities of the cyclic pillar[5]arene motifs of **1·2** to form a supramolecular oligo[2]rotaxane $\mathbf{(1{\cdot}2{\cdot}3)_n}$. To further study these self-assembly processes, 2D DOSY NMR experiments were performed. Upon the addition of **2** (1.00 mmol/L) into a solution of **1** (1.00 mmol/L), the measured weight-average diffusion D values decreased from 1.39×10^{-5} to 1.03×10^{-5} cm^2/s, indicating the formation of [2]rotaxane **1·2**. The D value further decreased to 0.85×10^{-5} cm^2/s when adding guest **3** (1.00 mmol/L) into the solution of **1** (1.00 mmol/L) and **2** (1.00 mmol/L), proving the evidence for the formation of the supramolecular oligo[2]rotaxane $\mathbf{(1{\cdot}2{\cdot}3)_n}$ (Fig. 3b and Figs. S5–S7 in Supporting information).

Next, we investigated the photophysical property of the obtained supramolecular oligo[2]rotaxane $\mathbf{(1{\cdot}2{\cdot}3)_n}$. As shown in Fig. 4a and Fig. S8b (Supporting information), a substantial enhancement of the fluorescent emission intensity of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ ($c_1 = c_2 = c_3 = 1.0 \times 10^{-5}$ mol/L) was achieved by increasing the water fraction of an acetone solution of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ upon excitation at 330 nm, which was attributed to the aggregation induced emission activity of the tetraphenylethene (TPE) [23,24] groups on $\mathbf{(1{\cdot}2{\cdot}3)_n}$. A highest emission intensity with a fluorescent quantum yield as 29.9% was obtained in a mixture solution of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ (H_2O/acetone, v:v = 9:1) (Fig. S8c in Supporting information). Moreover, the self-assembled behavior of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ in H_2O/acetone (v:v = 9:1) was investigated by scanning electron microscope (SEM). As shown in Fig. 3c, sphere assemblies about 300 nm were observed by SEM, resulting the aggregation induced emission activity of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ in H_2O/acetone (v:v = 9:1). The formation of the [2]rotaxane **1·2** allowed us to easily introduce the TPE groups to the oligo[2]rotaxane $\mathbf{(1{\cdot}2{\cdot}3)_n}$, avoiding the complicated synthesis process. The AIE effect of the supramolecular oligo[2]rotaxane $\mathbf{(1{\cdot}2{\cdot}3)_n}$ endow it a good donor for fabricating an artificial light-harvesting system in solution, which has attracted increasing interests from scientists owing to the efficient solar energy conversion [25–29].

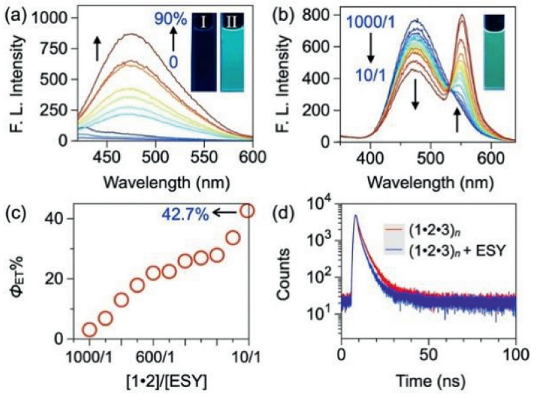

Fig. 4. (a) Fluorescent emission spectra of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ in H_2O/acetone with different water fractions (0–90%) at room temperature, excitation wavelength: 330 nm. Inset: photographs of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ (I) in acetone and (II) in H_2O/acetone (v:v = 9:1) under a UV lamp exited at 365 nm at room temperature. (b) Fluorescent spectra of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ upon the addition of different concentrations of ESY in H_2O/acetone (v:v = 9:1), insert: photo of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ + ESY in H_2O/acetone (v:v = 9:1) under a UV lamp exited at 365 nm. (c) Energy-transfer efficiency of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ + ESY in H_2O/acetone (v:v = 9:1) with different concentrations of ESY. (d) Fluorescence decay profiles of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ and $\mathbf{(1{\cdot}2{\cdot}3)_n}$ + ESY in H_2O/acetone (v:v = 9:1).

A fluorescent dye Eosin Y (ESY) was selected as an energy acceptor due to the overlap between its absorption band and the emission band of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ in H_2O/acetone (v:v = 9:1) (Fig. S8a in Supporting information). As shown in Fig. 4b, with the gradually addition of ESY (0–1.00 × 10^{-6} mol/L) to a solution of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ (H_2O/acetone, v:v = 9:1) ($c_1 = c_2 = c_3 = 1.0 \times 10^{-5}$ mol/L), a decrease of the emission intensity of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ (donor) at 475 nm and an increase of that of ESY (acceptor) at 550 nm were observed, accompanied by a fluorescent color change from blue to green. These phenomena demonstrated the energy transfer from donor to acceptor [30–32].

Fluorescence decay experiments were conducted to further confirm the light-harvesting process. As shown in Fig. 4d, the fluorescent lifetime of $\mathbf{(1{\cdot}2{\cdot}3)}_n$ ($\tau_1 = 0.92$ ns, $\tau_2 = 3.17$ ns) ($c_1 = c_2 = c_3 = 1.0 \times 10^{-5}$ mol/L) was found to be higher than those of the $\mathbf{(1{\cdot}2{\cdot}3)}_n$ + ESY system ($\tau_1 = 0.61$ ns, $\tau_2 = 2.13$ ns) ($c_1 = c_2 = c_3 = 1.0 \times 10^{-5}$ mol/L, $c_{ESY} = 1.0 \times 10^{-6}$ mol/L), indicating that the $\mathbf{(1{\cdot}2{\cdot}3)}_n$ + ESY supramolecular system functioned as an artificial light-harvesting system, in which the energy was transferred from $\mathbf{(1{\cdot}2{\cdot}3)}_n$ to energy acceptor ESY. Furthermore, the energy transfer efficiency was calculated to be 42.7% when the molar ratio of donor:acceptor was 20:1 (Fig. 4c) and the fluorescence quantum yield was seen to be 14.5% (Fig. S8c). Moreover, upon the addition of 0.1 equiv. of ESY to a solution of $\mathbf{(1{\cdot}2{\cdot}3)}_n$ ($c_1 = c_2 = c_3 = 1.0 \times 10^{-5}$ mol/L, $c_{ESY} = 1.0 \times 10^{-6}$ mol/L), spherical assemblies of about 300 nm were also observed by SEM (Fig. S9 in Supporting information), indicating that ESY was entrapped into the obtained sphere assemblies and ensured the efficient energy transfer.

Finally, the solution (H_2O/acetone, v:v = 9:1) of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ and $\mathbf{(1{\cdot}2{\cdot}3)_n}$ + ESY could be used as fluorescent ink. As shown in Figs. 5a and c, fluorescent characters with different colors were obtained by written with the solution of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ and $\mathbf{(1{\cdot}2{\cdot}3)_n}$ + ESY ($c_1 = c_2 = c_3 = 1.0 \times 10^{-5}$ mol/L, $c_{ESY} = 1.0 \times 10^{-6}$ mol/L). Moreover, light-emitting diodes (LEDs) with different colours were prepared by coating the H_2O/acetone (v:v = 9:1) solution of $\mathbf{(1{\cdot}2{\cdot}3)_n}$ and $\mathbf{(1{\cdot}2{\cdot}3)_n}$ + ESY ($c_1 = c_2 = c_3 = 1.0 \times 10^{-5}$ mol/L, $c_{ESY} = 1.0 \times 10^{-6}$ mol/L) on commercially available UV-LED bulbs. Bright blue and green light could be generated when a 1.5 V bias was applied (Figs. 5b and d).

Fig. 5. Color and fluorescence images of characters written by the solution of (a) $\mathbf{(1{\cdot}2{\cdot}3)}_n$ and (c) $\mathbf{(1{\cdot}2{\cdot}3)}_n$ + ESY after irradiation with UV light at 365 nm. Images of the LEDs prepared by coating the solution of (b) $\mathbf{(1{\cdot}2{\cdot}3)}_n$ and (d) $\mathbf{(1{\cdot}2{\cdot}3)}_n$ + ESY.

In conclusion, we have constructed a supramolecular oligo[2]rotaxane driven by orthogonal platinum(II) metallacycle and pillar[5]arene-based host–guest interactions. The supramolecular oligo[2]rotaxane was used for fabricating a light harvesting system. Moreover, the oligo[2]rotaxane and the fabricated light harvesting system were further used as fluorescent ink and applied for preparation of light-emitting diodes. This work provided a new strategy for the preparation of mechanically interlocked molecules and this new type of supramolecular oligo[2]rotaxane may be of highly importance for developing novel functional fluorescent materials and molecular devices in the future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.109540.

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