ACS Macro Letters
Letter
Cite This: *ACS Macro Lett.* 2018, 7, 1034−1038
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Cylindrical NIR-Responsive Metallopolymer Containing Möbius Metalla-aromatics

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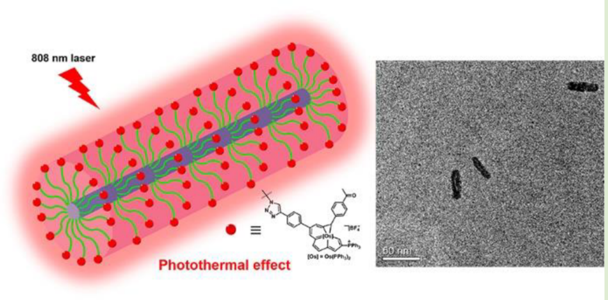
Supporting Information

ABSTRACT: Metalla-aromatic complexes are very stable and excellent light-absorbing compounds, owing to their highly conjugated frameworks. The metallopolymers containing metalla-aromatic substructures consist of a new type of functional polymer, because they exhibit characteristics of both metalla-aromatic and polymeric units. Herein, we reported a corn-like cylindrical metallopolymer, prepared from the controlled polymerization of *N*-isopropylacrylamide (NIPAM) by a polyrotaxane-based macroinitiator, followed by postpolymerization modification with a photothermal metalla-aromatic complex. The corn-like shape of this metallopolymer was confirmed by transmission electron microscopy (TEM). Combining the photothermal effect of the metalla-aromatic unit and the thermosensitive property of PNIPAM, the corn-like metallopolymer exhibits a NIR-responsive behavior and represents a new smart material.



Metalla-aromatics constructed with at least one metal and conjugated carbon-framework(s) are very interesting and valuable materials due to their aromatic system.[1,2] Most of these materials have excellent thermodynamic stability and display the properties of both aromatic compounds and organometallics. For example, the reactivity of metallabenzene (a well-known metalla-aromatics) is similar to those of benzene (e.g., electrophilic aromatic substitution) and dialkyl organometallics (e.g., reductive elimination).[3,4] We have recently developed a type of brand-new highly conjugated Craig-type Möbius[5] metalla-aromatics,[6−12] in which the transition metals were chelated with "carbolongs".[12,13] Depending on their specific structures, these "carbolong complexes"[14,15] could show different properties, including light absorption[16] or emission[17] ability, *J*-aggregates behavior,[18] single-molecular conductivity,[19] photothermal conversion,[8,12,14,18,20,21] and photoacoustic imaging capability.[8,21]

Among these properties, photothermal conversion is the most important for carbolong complexes. As an example, the photothermal efficiency of complex **1** (Figure 1a) is about equal to that of Au nanoparticle,[21] which can only be used by the surface or physical modification.[22] In contrast, complex **1** is very easy to be chemically modified to yield the designed product by the retrosynthetic approach. Thus, based on the highly effective photothermal complex **2**, we have synthesized the first photothermal metal-containing macromolecules **3**,[20] whose shape can be viewed as "head−tail" (Figure 1b). Recently, we also synthesized a photothermal copolymer **4**, which can be viewed as a side-chain type metallopolymer[18] (Figure 1c).

Metallopolymers that contain at least one metal in their skeleton could display unexpected or fantastic properties resulting from the combination of organometallic and polymeric units.[23−28] Among those reported well-characterized metallopolymers, purely cylindrical metallopolymers are rare, despite the fact that cylindrical metallo-supramolecular polymers[29,30] can be grown by self-assembly[31,32] or living crystallization-driven polymerizations.[33−35] Cylindrical polymers are very interesting macromolecules in terms of structural topology.[36−38] A well-characterized cylindrical polymer brush **8** has been prepared from methyl methacrylate (MMA) and a polyrotaxane-based macroinitiator **7** (Figure 2), which was produced from the esterification reaction of 2-bromoisobutyryl bromide and the inclusion complex (**6**) between α-cyclodextrins (α-CDs) and linear polyethylene glycol (PEG) capped by 9-methylanthracenyl groups.[39] Its well-characterized copolymer has been successfully developed as polymeric templates to prepare a variety of 1D inorganic nanonecklaces

Received: June 11, 2018
Accepted: August 8, 2018
Published: August 10, 2018

ACS Publications
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DOI: 10.1021/acsmacrolett.8b00442
ACS Macro Lett. 2018, 7, 1034−1038

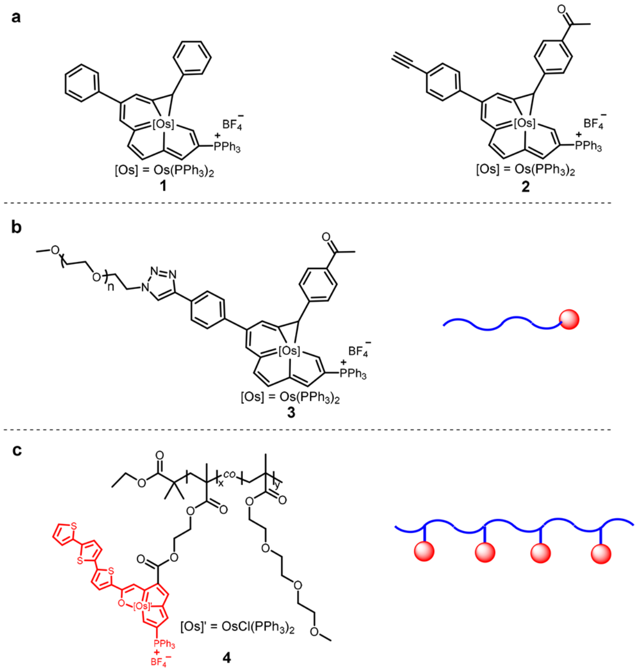

Figure 1. (a) Carbolong complexes **1** and **2**; (b) metallopolymer **3** with a "head−tail" shape; (c) metallopolymer **4** with a side-chain shape.

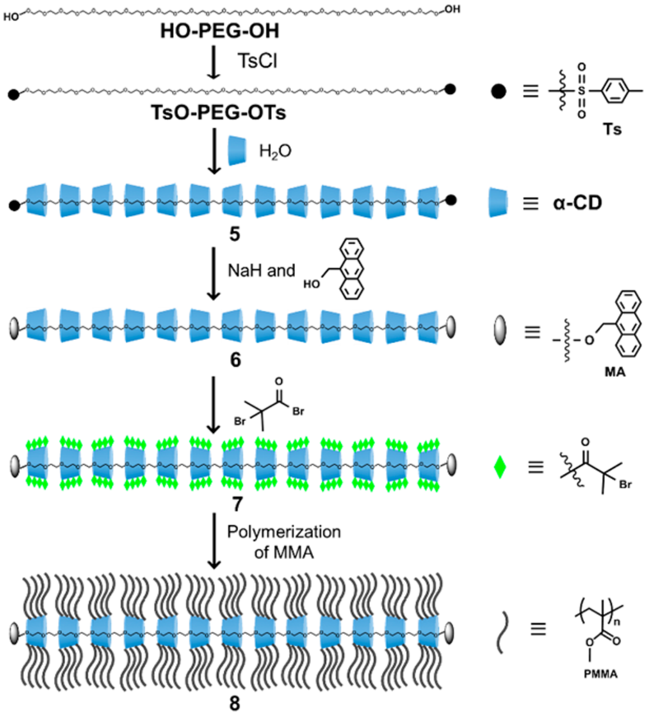

Figure 2. Synthesis of macroinitiator **7** and cylindrical polymer **8**.

(uniform nanocrystal "kebabs") with precisely controlled size and composition.[40]

Inspired by this work, we envisioned that the cylindrical polymer can be further improved to produce a cylindrical metallopolymer with multifunctional properties by grafting its polymeric derivative with our photothermal metalla-aromatics. Herein, we report the first cylindrical NIR-responsive metallopolymer (**11**) with the combination of thermally responsive and photothermal properties in 3D corn-like shape. Metallopolymer **11** can be considered as a polyrotaxane-based macromolecule.

The strategy to prepare the titled metallopolymer was depicted in Figure 3. Initiated by the polyrotaxane-based macroinitiator **7**, copper wire, and tris[2-(dimethylamino)-ethyl]amine (Me$_6$TREN) in acetone, the controlled polymerization of *N*-isopropylacrylamide (NIPAM) worked smoothly at room temperature to give the designed thermosensitive polymer **9**.

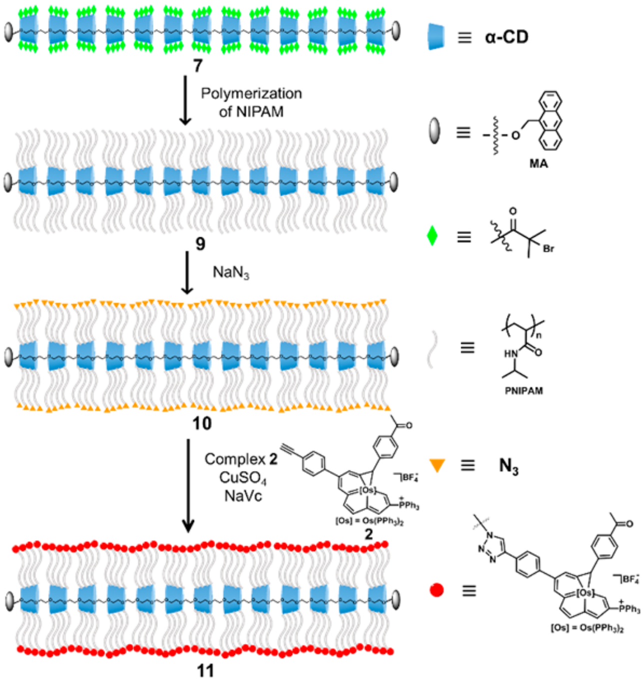

Figure 3. Synthesis of cylindrical metallopolymer **11**.

The molecular weight (M_w) of cylindrical polymer **9** was 7.59 × 10^5 g/mol, determined by gel permeation chromatography (GPC) and (2.08 ± 0.32) × 10^6 g/mol determined by static light scattering (SLS) in *N,N*-dimethylformamide (DMF). The presence of the terminal bromide in macromolecule **9** can be identified by the stretching wavenumber of 735 cm^{-1} (Figure 4b), which was assigned to the stretching of C−Br bond, in the FT-IR spectroscopy. The results show that the polyrotaxane-based macromolecule **9** was successfully prepared.

Macromolecule **10** was subsequently obtained by the treatment of macromolecule **9** with NaN$_3$ in DMF. The presence of terminal azide groups in macromolecule **10** can be confirmed by the stretching wavenumber of 2026 cm^{-1}, which was assigned to the stretching of azide group, in FT-IR spectroscopy (Figure 4c). Thus, the successfully manufactured macromolecule **10** with functional azide groups represents a new thermoresponsive polymer, which can be used in postpolymerization modification.[41]

Click reaction has been demonstrated to be a powerful method for preparing functional polymers.[42−45] Utilizing the click reaction, the postpolymerization modification of macromolecule **10** with complex **2**, which contained a terminal alkynyl group, occurred easily to give the functional metallopolymer **11**. Compared with macromolecule **10**, no appreciable stretching signal of azide group was observed for

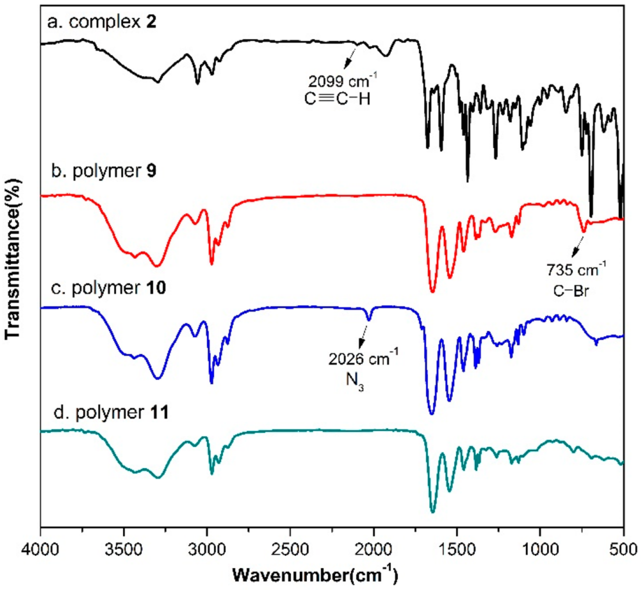

Figure 4. FT-IR spectra of organometallics **2** (a) and macromolecules **9** (b), **10** (c), and **11** (d).

metallopolymer **11**, confirming the accomplishment of the click reaction.

The molecular weight (M_w) of metallopolymer **11** was determined by GPC to be 8.06 × 10^5 g/mol and determined by SLS to be (2.44 ± 0.74) × 10^6 g/mol in DMF. These values of metallopolymer **11** are slightly higher than those of macromolecule **9**, which support the successful preparation of metallopolymer **11** and exclude the existence of free complex **2**.

To further confirm the presence of the metalla-aromatic substructure of complex **2** in metallopolymer **11**, we studied its UV−vis−NIR absorbing behavior. As shown in Figure S3, the absorbing behavior of metallopolymer **11** at 808 nm is similar to that of complex **2**, indicating the presence of metalla-aromatic substructure of complex **2** in metallopolymer **11**. In contrast, no appreciable absorption of wavelength longer than 300 nm was observed for macromolecule **9** (Figure S3). Based on the absorption value of metallopolymer **11** (0.36 mg/mL^{-1}) at 808 nm (Figure S3), the weight ratio of metalla-aromatic substructure of complex **2** in metallopolymer **11** can be calculated to be 5.4% using the standard UV−vis−NIR absorption curve (Figure S2) of complex **2**. For comparison, the weight ratio of metalla-aromatic substructure of complex **2** in metallopolymer **11** was determined to be 4.4%, using inductively coupled plasma mass spectrometry (ICP-MS) to analyze its percentage of osmium metal (Figure S4). Both results confirmed that complex **2** was successfully grafted to cylindrical macromolecule **10**.

As expected, metallopolymer **11** shows good photothermal characteristics. As shown in Figure 5, when a solution of metallopolymer **11** in water was irradiated with a NIR laser (808 nm, 1.0 W cm^{-2}), its temperature rose quickly from 24 to 36 °C in 5 min (Figure 5a). In contrast, the solvent (water) showed a negligible temperature change during the irradiation.

To further test the NIR photostability of metallopolymer **11**, we have performed five laser on−off cycles (Figure 5b). The temperature curves show that no significant increase was observed after five cycles, suggesting that metallopolymer **11** has a good photothermal stability under the laser irradiation conditions. It is noteworthy that NIR-absorbing organic molecules,[46−48] which are also easily to be chemically modified, often encounter a photobleaching problem.

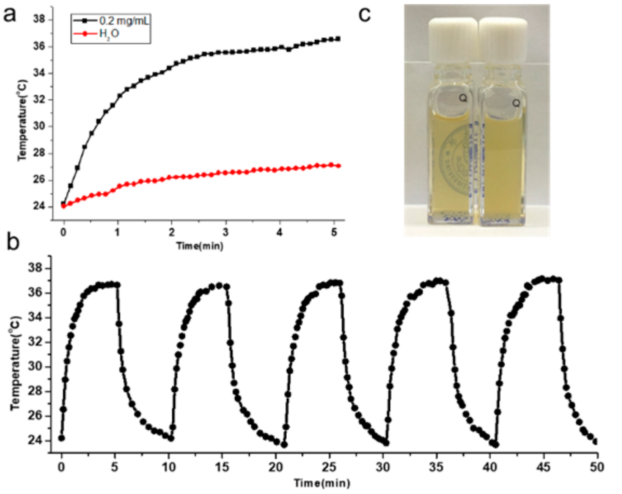

Figure 5. (a) Temperature curves of water (solvent) and a solution of metallopolymer **11** (0.2 mg mL^{-1} in water) irradiated with an 808 nm laser at a power density of 1.0 W cm^{-2}. (b) Temperature curves of a solution of metallopolymer **11** (0.2 mg mL^{-1} in water) irradiated with an 808 nm laser at a power density of 1.0 W cm^{-2} with five laser on−off cycles. (c) Solutions of metallopolymer **11** in water before (left) and after (right) NIR irradiation.

Poly(*N*-isopropylacrylamide) (PNIPAM) is a well-known and widely studied thermosensitive polymer, which displays a low critical solution temperature (LCST) of about 32 °C in water.[49,50] Thus, when it was irradiated with a NIR laser, the clear solution of metallopolymer **11** became turbid (Figure 5c), indicating the occurrence of a phase transition. When the temperature decreased to room temperature, the solution of metallopolymer **11** became clear again, indicating that its LCST behavior is reversible. Thus, the metallopolymer **11** represents a new NIR-responsive metallopolymer, which can be used as a molecular carrier with controlled release triggered by a NIR laser. It must be noted that, although many NIR-responsive materials[51] have been reported, pure NIR-responsive metallopolymers are rare.[18,52−54]

The characteristic corn-like structural topology of metallopolymer **11** was unambiguously evidenced by transmission electron microscopy (TEM), as shown in Figure 6. The length (*L*) and width (*W*) of the single metallopolymer **11** were in the range of 30−50 nm and 10−15 nm, respectively. The theoretical length (L_{peg}) of a fully stretched PEG (M_w = 2000) chain was about 17 nm. Therefore, the theoretical

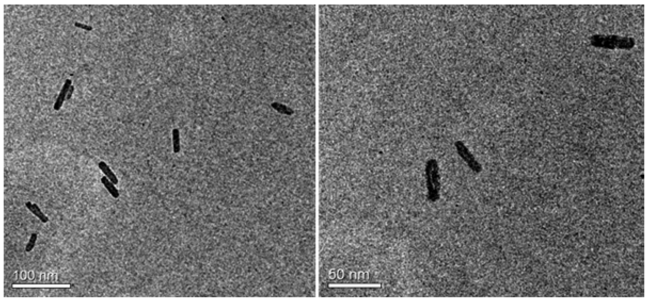

Figure 6. TEM images of cylindrical metallopolymer **11**.

DOI: 10.1021/acsmacrolett.8b00442
ACS Macro Lett. 2018, 7, 1034−1038

length ($L_{theor} = L_{peg} + W - 1$ nm) of cylindrical metallopolymer **11** was about 26−31 nm, which is consistent with the observed length and width of metallopolymer **11** in TEM images. This is, therefore, the demonstration of the first cylindrical NIR-responsive metallopolymer, which showed unimolecular structure in nanoscale.

In summary, the first cylindrical NIR-responsive metallopolymer (corn-like shape) was synthesized by controlled polymerization of NIPAM from a polyrotaxane-based macroinitiator and followed by the postpolymerization modification with a photothermal metalla-aromatic complex. The corn-like metallopolymer was fully characterized by GPC, LLS, UV−vis−NIR, ICP-MS, and TEM. Owing to the photothermal effect of the grafted metalla-aromatic unit and the thermosensitive property of PNIPAM unit, the metallopolymer showed an NIR-responsive behavior in water. It might be utilized in nanocapsules for the controlled delivery and release, triggered by a NIR-laser, or in the constructions for new NIR-responsive self-healing or shape memory materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.8b00442.

Supporting figures and experimental procedures (PDF).

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 21472155, 21490573, and 21472156).

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