Engineering Rotaxane-Based Nanoarchitectures via Topochemical Photo-Cross-Linking

Mingjie Zhu, Liyuan Yin, Yunyun Zhou, Hongwei Wu, and Liangliang Zhu*

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China

Supporting Information

ABSTRACT: Polymerization of monomers included by macrocyclic hosts has been found as an efficient way to synthesize sophisticated rotaxane-based nanostructures, whereas such a process triggered by photon has received little coverage so far. Herein, a new diphenyldiacetylene (DPDA) derivative (compound 1) comprising viologen as a binding site toward cucurbit[7]uril (CB[7]) macroring, and isophthalate as a bulky stopper, was rationally designed and prepared. After verifying the photo-cross-linking efficiency of compound 1 upon its regular self-assembly, we also achieved a straightforward construction of rotaxane-based nanoarchitecture 2⊂CB[7] through an in situ photoirradiation on the corresponding pseudo[2]rotaxane 1⊂CB[7]. Although the threading of CB[7] changed the self-assembly behavior of the DPDA derivative, the topochemical reaction could be definitely observed to afford the corresponding photo-cross-linked species. Such a process could be facilely indicated by distinctive photoluminescence enhancement on the basis of π-conjugated skeleton change of DPDA toward potential usage of rotaxane-based systems as smart optoelectronic materials. We anticipate this unique strategy will allow new visions for the synthesis and application of novel luminescent host–guest nanoarchitectures.

INTRODUCTION

As typical examples of mechanically interlocked molecules (MIMs), rotaxanes are commonly dumbbell-shaped axles threaded by one or more macrocyclic components.1–6 The bulky groups at both ends of a rotaxane act as stoppers to prevent the dissociation, while the noncovalent interaction between the axle and macrocyclic components allows controlled slipping, shuttling, or other relative motion patterns between the axle and macrocyclic components.7–11 In this way, rotaxanes can normally play a significant role in these supramolecular systems and provide feasible prototypes for the fabrication of artificial molecular machines.12–20 While a polymerization process can generally enable grand technological advancements in fields of chemistry and material science, major improvements have also been achieved in constructing polymer-based host–guest nanoarchitectures or rotaxane analogues since the first discovery of inclusion macromolecular complexes prepared by simple mixture of α-cyclodextrins and poly(ethylene glycol) (PEG) by Harada and co-workers.21 Traditionally, an inclusion complex where many ring components are threaded onto a linear polymer chain is called a pseudopolyrotaxane (PPRx).22–24 Moreover, through capping both the chain ends with bulky stoppers, a polyrotaxane (PRx) is obtained.25,26 These new kinds of host–guest polymeric species exhibit broad application prospects in self-healing materials,27,28 targeting transportation,29 drug and gene delivery,30,31 and so forth. The past decades have also witnessed emerging construction of advanced rotaxane-type nanoarchitectures through alternative methods like transition-metal-ion coordination,32–37 in situ polymerization,38–41 organic–inorganic hybridization,42–44 etc. Among all these methodologies, monomers cross-linked in situ within ring components upon photolirradiation could be regarded as a promising strategy that is conducted remotely without employment of any additional reagents. However, such a photochemical strategy has received little coverage thus far, probably due to lack of end-capping design along with a photo-cross-linking process.

To realize this supposition, topochemical strategy of a pseudo[2]rotaxane 1⊂CB[7] based on amphiphilic diphenyldiacetylene (DPDA) axle threaded by cucurbit[7]uril (CB[7]) was presented (see Figure 1). Compared with aliphatic diacetylenes, DPDA bears an extended π-conjugation,62 allowing its corresponding polymers to exhibit more sensitive optical45,46 and electrical properties47,48 upon the topochemical 1,4-addition reaction. To perform the topochemical transformation, as illustrated in many reports, preorganization of DPDA monomers is widely regarded as a crucial factor for polymerization initiated by either heat or UV irradiation.49 Thus, such strategies as single crystals,50,51 cocrystals,52 liquid crystals,53 gelation,54–56 and self-assemblies57–61 are developed. All these strategies rely much on molecular design since the bulky phenyl rings directly attached to the diacetylene unit will...
On account of the large intermolecular stacking tendency of DPDA moiety, herein we report an intriguing self-assembly mode formed from a surfactant-like amphiphilic DPDA derivative compound 1 in aqueous media. Such a self-assembly is supposed to align the reaction moiety into serviceable positions to promote the topochemical photo-cross-linking. Furthermore, CB[7] is an outstanding macrocyclic host due to its water solubility and high binding constants toward cationic guests. The hydrophobic cavity enhances the threading behavior when guest molecules are mainly composed of hydrocarbon chains. In addition, positively charged viologen readily combines the CB[7] ring, and the ion-dipole interaction restricts the shuttling behavior within a limited space along the axle, inhibiting the dissociation of the two components.

In our study, the photo-cross-linking efficiency of the above-mentioned compound 1 upon self-assembly was verified first upon UV-irradiation. As illustrated in Figure 1, after CB[7] rings were threaded onto the axes, isophthalates attached to the viologen units prevented the rings dethreading from one side, resulting in the formation of a pseudo[2]rotaxane 1 ⊂ CB[7]. Once irradiated by UV light, the DPDA units were expected to undergo topochemical photo-cross-linking to afford polymeric/oligomeric species, and therefore CB[7] rings were trapped along the axle to afford a [2]rotaxane-analogue nanostructure 2 ⊂ CB[7]. This strategy takes advantage of the fact that (1) the surfactant-like molecule can readily generate regular self-assemblies in aqueous media to improve the photo-cross-linking behavior; (2) DPDA is linked to viologens via long alkyl chains on one side and also terminated by alkyl chains on the other side, which is believed to regulate the self-assembly modes with and without CB[7] rings; (3) a rational design of employing a distinctive photoluminescence enhancement on the basis of π-conjugated skeleton change of DPDA; and (4) to the best of our knowledge, photochemical reaction of host-guest complexes to prepare rotaxane-based nanostructures remains seldom reported, especially when it comes to the case of topochemical photo-cross-linking process performed remotely without additional reagents. The synthesis of all corresponding compounds is detailed in the Experimental Section.

**RESULTS AND DISCUSSION**

**Self-Assembly of 1 and 1 ⊂ CB[7] in Aqueous Solution.** In consideration of the surfactant-like chemical structure of 1, investigations on the self-assembly properties were started with the UV–vis absorption spectrum first. Compound 1 was supposed to exist as monomeric state in anhydrous dimethyl sulfoxide (DMSO), and the multiple peaks from 270 to 346 nm (curve 1, Figure S1) originated from the isophthalate, bipyridinium, and diphenyldiacetylene. However, the absorption bands of compound 1 dispersed in DI water turned broad, and all the main peaks exhibited a blue-shift for ca. 4 nm (curve 2, Figure S1). These changes could be attributed to a slightly distorted conformation adopted to bury the hydrophobic hydrocarbon core from water, resulting in the disturbance of the conjugated p orbitals. The blue-shift can also indicate a H-type aggregation-like packing of the DPDA skeletons, allowing a relatively large degree of face-to-face alignment of the light-active moiety for facilitating the photo-cross-linking process. The variation of absorbance upon the concentration change clearly showed that the critical aggregation concentration (CAC) in DI water was determined to be 0.122 mM (Figure S2).

Transmission electron microscopy (TEM) visualized the self-aggregated architectures. Rodlike nanostructures were observed in the self-assembly patterns of compound 1 prepared from an aqueous solution of 0.15 mM (Figure 2b). Most of these nanostructures aligned in short-range and presented a twisted pattern overall as shown in Figure 2a. Besides, larger particles with the shape of parallelogram or quasi-triangle were also observed. These were assumed to be crystals arising from the preparation of samples by drop-casting and evaporating. Such a hypothesis was confirmed by polarized optical microscopy (POM) using the same sample preparation process (Figure S3). Upon increasing solution concentration, a globally ordered arrangement emerged and the above-mentioned crystallization behavior can be greatly suppressed (Figure S4). Dynamic light
scattering measurement (DLS) was employed as well to further prove the formation of self-assembly in solution (a Z-average diameter of ∼110 nm) rather than on a substrate (Figure S5).

The preparation of pseudo[2]rotaxane \( 1 \subset \text{CB}[7] \) was carried out readily through mixing compound \( 1 \) and \( \text{CB}[7] \) (mole ratio = 1:1) at 40 °C and then cooling down to room temperature. \(^1\)H NMR is a powerful tool to distinguish the existence of host–guest complexes since the noncovalent interactions will enable the proton resonances of guest molecules to exhibit different shifts. Generally, when a guest molecule is threaded by a CB ring, the shielding effect will cause the resonances of protons located in the CB cavity to go upfield while those of protons outside the cavity or near the portal of the ring will go downfield due to the deshielding effect.\(^{10,12,73,74}\) Herein, the resonances of the protons \( \text{H}_{\text{i}-\text{j}} \) in \( 1 \subset \text{CB}[7] \) underwent upfield shift as compared with the corresponding protons in the axle molecule compound \( 1 \), whereas those of the protons \( \text{H}_{\text{h}-\text{l}} \) and \( \text{H}_{\text{j}-\text{k}} \) shifted downfield. These results clearly showed that the protons \( \text{H}_{\text{i}-\text{j}} \) were inside the \( \text{CB}[7] \) cavity, and the \( \text{CB}[7] \) ring shuttled around the viologen unit within the range between the edge of DPDA moiety and isophthalate moiety on the NMR time scale at room temperature. Other protons in the axle component were far away from the \( \text{CB}[7] \) ring and remained unaffected.

Aggregation behaviors of \( 1 \subset \text{CB}[7] \) were also investigated before the photoirradiation performed, since the preorganization of monomers is required for the topochemical reaction as mentioned above. Considering the possibility that altering the concentration of \( 1 \subset \text{CB}[7] \) solution can affect the threading behavior of \( \text{CB}[7] \) ring, the measurement on CAC was not carried out. However, the DLS measurement clearly showed

Figure 2. TEM images of the self-assembly patterns of compound \( 1 \) prepared from an aqueous solution of 0.15 mM. (a) Large particles were attributed to crystals and the self-assemblies aligned into a twisted pattern. (b) Monomers self-assembled into rodlike nanostructures. The schematic diagram of the stacking mode is inserted.

Figure 3. \(^1\)H NMR spectra (400 MHz, DMSO-\( d_6 \), 298 K) of (a) compound \( 1 \) and (b) \( 1 \subset \text{CB}[7] \) along with a conformational representation of the \( \text{CB}[7] \) shuttling distribution. (c) Schematic illustration of the aggregation behavior in water solution. The hydrophobic DPDA moiety was buried inside and the viologen included by \( \text{CB}[7] \) ring stretched toward aqueous phase. (d) TEM images of \( 1 \subset \text{CB}[7] \) aggregates formed in aqueous media (0.25 mM). The original regular pattern was disturbed after the \( \text{CB}[7] \) ring was threaded onto compound \( 1 \).
the Z-average size of 1⊂CB[7] aggregates increased slightly after CB[7] ring was threaded onto the axle at the concentration of 0.25 mM (up to ∼120 nm, Figure S6). Meanwhile, TEM image presented a disparate morphology that the original rodlike nanostructures vanished, and irregular aggregates were observed instead (Figure 3d). It means that the bulky size of CB[7] significantly interfered with the self-assembly behavior of the surfactant-like axle molecule, and the steric hindrance between two CB[7] rings greatly hampered the parallel stacking interaction. Furthermore, the hydrophilic CB[7] ring included the hydrophobic hexamethylene block via shuttling along the axle and facilitated the water solubility of compound 1, which made the viologen unit more prone to stretch toward aqueous phase. Such a shuttling behavior also influenced the ability of the long alkyl chain to regulate the molecular conformation since the alkyl chain became more rigid.

**Topochemical Photo-Cross-Linking upon Self-Assemblies.** To verify the photo-cross-linking efficiency on the basis of the self-assemblies, emission spectra were utilized to trace the reaction progress since the enlargement of the π-conjugated skeleton of diaryldiacetylenes usually shows a clear transition from weak fluorescence to strong fluorescence.55,75,76 No apparent emission band of compound 1 in aqueous solution was recorded before photoirradiation (black curve, Figure 4a). The peak at 417 nm was attributed to the Raman band of water when exciting light at 365 nm was used.77 Upon 2 h of continual UV irradiation, intensity of the emission band at 525 nm corresponding to contributions from polymeric species kept increasing dramatically, and no slowdown was observed, indicating the polymerization equilibrium remained far from reached as confirmed later by prolonging the irradiation time to 8 h (Figure S7). A change in photoluminescence could also be observed with naked eye by giving out green luminescence with λex = 365 nm accordingly (Figure 4c). The photoirradiation was under a relatively mild condition of irradiation at a 254 nm beam (∼1 mW light power upon the sample with a 1–2 cm distance in between), and the efficiency can be further improved once an optimized light source could be applied.

In spite of the prominent enhancement in the emission spectra, absorption spectra changed tardily in answer to UV irradiation (Figure S8). The absorption band from 360 to 500 nm lifted up while the peaks at 342, 320, and 266 nm underwent a significant attenuation after 2 h (red curve, Figure 4b). An analogous spectral change has been observed in our previous work.79 Both absorption and emission spectral variations became saturated after 8 h. Upon 8 h of irradiation, the emission band intensity centered at 525 nm decreased and showed a blue-shift along with the isoabsorptive point vanishing, indicating the occurrence of photodegradation or photobleaching. An apparent color change from pale yellow to yellow was also observed (inserted in Figure S8). Given the low degree of polymerization (or oligomerization) learned from these spectra, the yellow color was supposed to originate from a solvated polydiacetylene in addition to unreacted monomers and oligomers.79

In addition to such a spectrometry method, the existence of the corresponding polymer/oligomer can also be figured out by gel permeation chromatography (Figure S9).

Although assemblies of 1⊂CB[7] were short of regularity in aggregation state, both absorption and emission spectra also indicated a successful photo-cross-linking upon UV irradiation and signified that the preorganization of monomers at the molecular level still worked. As 1H NMR showed, the shuttling behavior of CB[7] did not affect the DPDA moiety, making the photopolymerization of 1⊂CB[7] feasible. The absorption band from 360 to 500 nm lifted up, indicating the formation of the “ene” bond alternation and the enlarged π-conjugation range (Figure 4e). This conjugated alkene—alkyne bond linked...
two diacetylene units so as to function as a stopper to prevent the dethreading of CB[7], as illustrated in Figure 1. The emission band at 525 nm originated from the polydiacetylene moiety became prominent after 1 h (Figure 4d). Although a legible shoulder peak centered at 450 nm was observed, the solution still gave out a green luminescence consistent with the main emission band (Figure 4f). It is worth noting that the shorter-wavelength absorption band made up a relatively significant share of the whole absorption band from 360 to 500 nm, which is likely to be attributed to oligomers resulting from a lower degree of polymerization compared with the case of 1. This assumption was also supported by the considerable contribution of emission band centered at 450 nm corresponding to oligodiacylene species. Since the ordered self-assemblies were disturbed after CB[7] was introduced, the topochemical polymerization suffered a certain degree of inhibition and caused the broadening of the emission band at 525 nm.

Finally, this unique rotaxane-based nanoarchitecture was visualized via transmission electron microscopy (TEM). In the case of 2, although the oriented nanostructures faded away due to the change of crystallinity after photo-cross-linking, rodlike patterns still existed compared with the morphology of 1 self-assemblies (Figures 2 and 5a). The persistence of the original nanostructures and the absence of new patterns indicated that the packing mode of monomers was preserved and further fixed through the formation of the “enye” bond. Such a bonding effect lays the foundation for the construction of the rotational nanoarchitectures. To differentiate 1 ⊂ CB[7] aggregates were difficult because no clear boundaries were displayed (Figure 3d); however, channel-like gaps in TEM image appeared after photoirradiation. Figure 5b presents an intriguing nanostructural morphology where 2 ⊂ CB[7] showing a molecular length of ∼55 Å. A possible hypothesis is that there remain unreacted 1 ⊂ CB[7] complexes gathered via photo-cross-linking of diacetylene unit to afford aggregates where the violagen included by hydrophilic CB[7] rings stretch out toward the aqueous media, and the hydrophobic polydiacetylene core is still buried inside, forming nanostructures with a diameter of ∼10 nm as illustrated in Figure 5c. An energy-minimized molecule model shows a dimeric structure in 2 ⊂ CB[7] occupying a spatial size of ∼55 Å. Larger aggregates observed are believed to arise from the accumulation of polymeric species and monomers, basically in agreement with the nanostructural size observed from TEM. DLS measurement also confirmed the existence of the rotaxane-based nanoarchitecture in solution despite the polydisperse size distribution arising from photo-cross-linking and aggregation (Figure S10). These contrasting results, together with the spectral analysis, show the construction of a rotaxane-based nanoarchitecture is successfully achieved via photo-cross-linking.

## CONCLUSION

A novel strategy to construct rotaxane-based nanoarchitecture was demonstrated here by photo-cross-linking of a pseudo[2]-rotaxane 1 ⊂ CB[7] composed of a diphenylidiacetylene (DPDA) monomer included by CB[7]. In situ topochemical reaction was smoothly conducted for capping the host–guest structure by the formation of polymeric/oligomeric species from DPDA monomer, whereby the self-assemblies in aqueous solution played a key role for the preorganization of the light-active moiety to facilitate the photo-cross-linking process. This strategy can also be tracked by luminescent spectra and luminescent signal change relying on the DPDA π-structural design that is sensitive to optoelectronic properties. Such an in situ cross-linking of monomers included by ring component initiated by photoirradiation could be beneficial to fabricate
novel luminescent host–guest nanodevices and allow new visions for sophisticated artificial molecular machines.

**EXPERIMENTAL SECTION**

**General.** 1H NMR and 13C NMR spectra were measured on a Bruker 400 MHz spectrometer. MS was measured by a matrix assisted laser desorption ionization—time of flight mass spectrometer (5800). Absorption spectra were recorded on a Shimadzu 1800 spectrophotometer. Fluorescence emission spectra were taken with a Shimadzu RF-5301 spectrofluorometer. All the UV irradiation and emission spectra were carried out in a cuvette with a path length of 10 mm, and the UV−vis absorption spectra were recorded in a cuvette with a path length of 1 mm at room temperature. The particle size distribution was measured on a Malvern Zetasizer Nano ZS90. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 20 TWIN.

**Synthesis of Compound 1:** A solution of butyl bromide (0.25 mL, 2.3 mmol) in anhydrous acetone (15 mL) was added dropwise into a mixture of compound 3 (0.6031 g, 2.5 mmol) and potassium carbonate (0.5237 g, 3.8 mmol) in anhydrous acetone (15 mL) at 60 °C. The mixture was stirred for 12 h at 60 °C under N2. The solvent was removed by rotary evaporator, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1) to afford pale yellow compound 2 (0.5635 g, 75.4%). 1H NMR (400 MHz, CDCl3, 298 K): δ 7.49–7.45 (m, 2H), 7.45–7.42 (m, 2H), 6.88–6.84 (m, 2H), 6.83–6.79 (m, 2H), 3.99 (t, J = 6.5 Hz, 2H), 1.79 (ddd, J = 14.4, 10.9, 6.5 Hz, 2H), 1.57–1.46 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H). 13C NMR (100 MHz, CDCl3, 298 K): δ 159.85, 156.29, 134.26, 134.04, 115.63, 114.63, 114.28, 113.57, 113.81, 80.97, 72.97, 72.78, 67.82, 31.18, 19.21, 13.85. MS (Maldi-ToF): calcd for [M]+ m/z = 290.1; found m/z: 290.3.

**Synthesis of Compound 5:** A solution of compound 4 (0.1463 g, 0.5 mmol) in anhydrous acetone (15 mL) and potassium carbonate (0.1552 g, 1.1 mmol) was added, and the mixture was refluxed for 12 h under N2. The solution was filtered, and the filtrate was precipitated in a 4-fold volume of hexane. The solid was filtered, washed with hexane (10 mL) and deionized water (10 mL), and dried under vacuum to afford pale yellow compound 5 (0.1561 g, 68.3%). 1H NMR (400 MHz, CDCl3, 298 K): δ 7.49–7.47 (m, 2H), 7.45 (dd, J = 2.7, 0.7 Hz, 2H), 6.88–6.86 (m, 2H), 6.86–6.83 (m, 2H), 3.99 (t, J = 6.5 Hz, 4H), 3.45 (t, J = 6.8 Hz, 2H), 1.97–1.88 (m, 2H), 1.87–1.74 (m, 4H), 1.52–1.45 (m, 6H), 1.00 (t, J = 7.4 Hz, 3H). 13C NMR (100 MHz, CDCl3, 298 K): δ 159.84, 159.70, 134.02, 134.01, 114.62, 114.60, 113.79, 113.63, 81.35, 81.24, 72.93, 72.85, 67.82, 67.80, 33.78, 32.65, 31.18, 28.98, 27.90, 25.27, 19.21, 13.83. MS (Maldi-ToF): calcd for [M]+ m/z = 452.1; found m/z: 452.4.

**Synthesis of Compound 6:** A solution of compound 3 (0.4695 g, 1 mmol) and 4,4′-bipyridine (1.1324 g, 7 mmol) in anhydrous acetonitrile (40 mL) was stirred at 80 °C overnight under N2, and then cooled in ice baths. After filtration, the filtrate was washed with acetonitrile (20 mL) and dichloromethane (20 mL) and dried under vacuum to afford gray compound 6 (0.4711 g, 74.6%). 1H NMR (400 MHz, DMSO-d6, 298 K): δ 9.26 (d, J = 6.9 Hz, 2H), 8.88 (dd, J = 4.5, 1.6 Hz, 2H), 8.65 (d, J = 6.9 Hz, 2H), 8.05 (dd, J = 4.5, 1.7 Hz, 2H), 7.54–7.48 (m, 4H), 7.00–6.94 (m, 4H), 4.66 (t, J = 7.4 Hz, 2H), 4.02 (t, J = 6.5 Hz, 4H), 2.04–1.95 (m, 2H), 1.77–1.66 (m, 4H), 1.52–1.35 (m, 6H), 0.93 (t, J = 7.4 Hz, 3H). 13C NMR (100 MHz, DMSO-d6, 298 K): δ 160.25, 159.85, 156.29, 156.28, 154.78, 154.75, 151.45, 145.78, 141.29, 134.51, 122.37, 116.10, 115.50, 115.48, 115.27, 115.24, 82.12, 82.02, 73.19, 73.11, 68.00, 67.90, 60.76, 31.06, 31.03, 28.67, 25.38, 19.14, 14.14. MS (Maldi-ToF): calcd for [M]+ m/z = 529.3; found m/z: 529.6.
Synthesis of Compound 7: 5-Methylisophthalic acid (1.2526 g, 6.9 mmol) was dissolved in methanol (20 mL), and concentrated sulfuric acid (1 mL) was added dropwise into the mixture. The reaction solution was allowed to reflux overnight and then cooled down to room temperature. Saturated sodium bicarbonate solution (40 mL) was added, and the crude product was extracted by CHCl₃ (20 mL). The solvent was removed by rotary evaporator while the residue was washed with DI water to afford light yellow solid (1.201 g, 82.9%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.95 (s, 1H), 7.72 (d, J = 7.0 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 4.01 (t, J = 6.8 Hz, 4H), 3.39 (s, 6H), 2.05–1.95 (m, 2H), 1.77–1.65 (m, 4H), 1.49–1.33 (m, 6H), 0.92 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ 159.31, 156.28, 153.84, 134.91, 131.16, 129.93, 127.67, 127.15, 115.52, 115.49, 112.78, 112.62, 82.15, 82.01, 73.21, 73.09, 68.00, 67.91, 62.70, 61.32, 53.22, 51.09, 31.03, 28.70, 5.62, 25.37, 19.14, 14.13. MS (MALDI-ToF): calcd for [M + H⁺]⁺ m/z = 209.1; found m/z: 209.2.

**ASSOCIATED CONTENT**

1. Supporting Information
   - Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b02736.
   
2. Experimental data (including UV–vis, PL, TEM, Zetasizer, etc.) and synthetic scheme (PDF)

**AUTHOR INFORMATION**

Corresponding Author
* (L.Z.) E-mail: zhuliangliang@fudan.edu.cn.

ORCID®

Liangliang Zhu: 0000-0001-6268-3351

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the NSFC/China (21644005), National Program for Thousand Young Talents of China, and State Key Project of Research and Development (2016YFC1100300).

**REFERENCES**


DOI: 10.1021/acs.macromol.7b02736

Macromolecules 2018, 51, 746–754


(77) Parker, C. A. Raman spectra in spectrofluorometry. Analyst 1959, 84, 446–453.


