

Multistimuli-Responsive and Photocontrolled Supramolecular Luminescent Gels Constructed by Anthracene-Bridged Bis(dibenzo-24-crown-8) with Secondary Ammonium Salt Polymer

Hong-Guang Fu,[†] Yong Chen,[†] and Yu Liu^{*,†,‡,§}

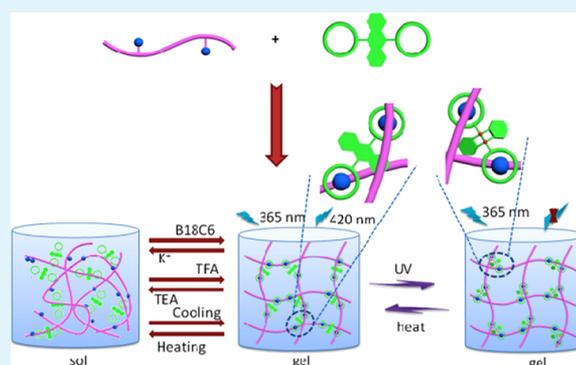
[†]College of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

[‡]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China

Supporting Information

ABSTRACT: A novel multistimuli-responsive and photcontrolled supramolecular luminescent gel is fabricated from anthracene-bridged bis(dibenzo-24-crown-8) (**1**) and secondary ammonium salt-functionalized graft polymer (**3**). X-ray crystallographic analysis reveals that the dibenzo-24-crown-8 (DB24C8) ring is located at the opposite site of **1**, which will greatly hinder the mutual intermolecular π - π stacking between anthracene groups. By taking advantage of the controllable binding of **1** with **3**, the unique gel-sol transition could occur under different temperatures, pH, and competitive guest bindings. Benefiting from the photo-oxygenation of anthracene, the luminescence behavior of the supramolecular gel could be switched off and on under UV light (365 nm) and heating treatment, which provides a new approach for constructing photocontrolled supramolecular luminescent gel.

KEYWORDS: supramolecular assembly, gel-sol transition, noncovalent interactions, crown ether, photoresponsiveness, single crystal



INTRODUCTION

Macrocyclic-mediated stimuli-responsive assemblies¹ have attracted more and more attention in the development of super-resolution imaging,² optoelectronics devices,^{3,4} drug nanocarriers,⁵ data storage,⁶ optical switches,^{7,8} ion transport,⁹ and functional vesicles.¹⁰ Crown ethers, especially dibenzo-24-crown-8 (DB24C8) composed of oxygen atoms linked by alkyl chains, are regarded as one of the most powerful macrocyclic receptors in supramolecular chemistry.¹¹ Their unique structure endows them a strong binding ability with organic ammonium and metal cations and further facilitates the synthesis of a variety of highly complicated and ordered mechanically interlocked molecules (pseudorotaxanes,^{12,13} rotaxanes,^{14,15} catenanes,¹⁶ cryptands,¹⁷ and molecular daisy chains¹⁸) with interesting topologies and stimuli responsiveness. As a kind of receptor, crown ethers have been used to model the interaction of ammonium ions with protein receptors.¹⁹ Huang et al. have reported a multiple fluorescent sensor constructed from a conjugated crown ether polymer and a bisammonium cross-linker. Thanks to the multistimuli responsiveness of the supramolecular network, the system can serve as a good multiple fluorescent sensor.^{20–22} Borisov et al. also presented a series of indicator dyes based on an aza-crown and borondipyromethenes dyes. The sensors showed excellent and fast responding ability toward K^+ in a variety of formats with a high K^+/Na^+ selectivity and no pH dependency within physiologically relevant range.²³ In addition, we successfully

prepared a crown ether triad containing acylhydrazone units. UV-light-induced *E/Z* isomerization of the novel host caused the channel to disassemble and assemble in the bilayer, which endowed the transmembrane channel with a photogated behavior.²⁴

Up to now, multiple noncovalent interactions such as hydrogen,^{25–27} π - π stacking,²⁸ hydrophobic bonding,²⁹ coordination interactions,^{30,31} and charge transfer³² have been employed to construct supramolecular cross-linked networks and gels. In general, there are two main strategies for forming stimuli-responsive supramolecular networks. One is using low-molecular-weight compounds containing association units of host and guest.^{33,34} For example, we have successfully constructed a three-dimensional network structure via a hierarchical assembling strategy. Benefitting from a photoinduced secondary assembly, the supramolecular polymer could form a larger three-dimensional network structure.³⁵ The other way is to modify the host and guest to polymers.^{36–38} Then, the functionalized supramolecular polymers are constructed by cross-linking.³⁹ Relatively easy synthesis and high stability cause supramolecular polymers to have better mechanical properties that can be easily controlled by the degree of functionalization. Although great progress has

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Scheme 1. Cartoon Representation of Anthracene-Bridged Divalent Crown Ether **1, **1**_{EPO}, Secondary Ammonium Salt Functionalized Graft Polymer **3** and Cross-Linked Conjugated Polymer Network Gel**

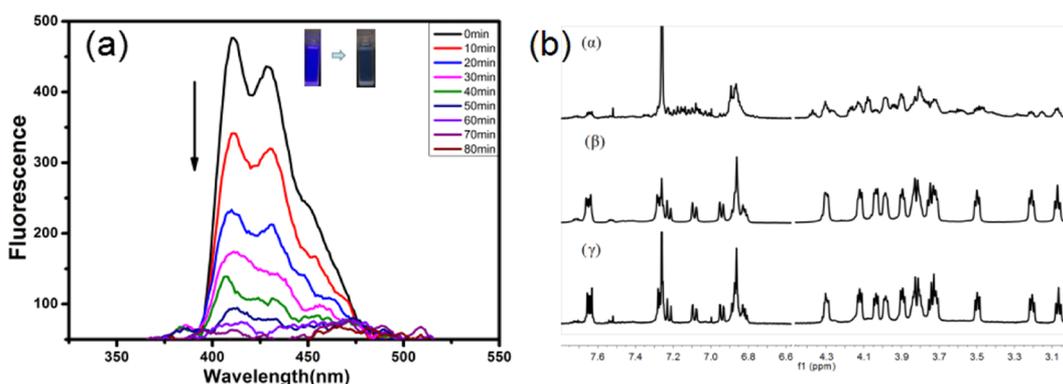
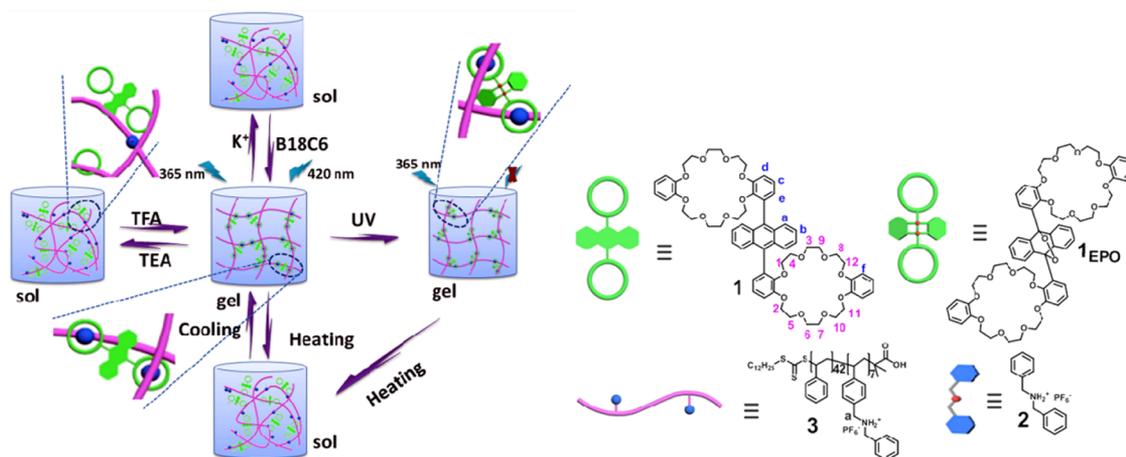


Figure 1. (a) Fluorescence emission spectra of **1** (5×10^{-5} M) in CHCl_3 irradiated at 365 nm under O_2 ($\lambda_{\text{ex}} = 365$ nm). (b) ^1H NMR spectra of **1** (1×10^{-3} M) in CDCl_3 irradiated under O_2 (α), no irradiation (β), under N_2 (γ) for 2 h under 365 nm. Inset: Photographs of **1** (5×10^{-5} M) in CHCl_3 under O_2 atmosphere before (left) and after irradiation (right) under 365 nm.

been made in the study of cross-linked supramolecular gels based on crown ether, it is still a challenge to construct an illuminant gel that can respond to multiple stimuli.^{40,41} This kind of gel has different luminescent states, but there is no significant change in other properties. Therefore, it is our special interest to develop a feasible strategy for constructing a multistimuli-responsive luminescent supramolecular gel.

RESULTS AND DISCUSSION

Herein, an anthracene-bridged divalent crown ether **1** was designed and synthesized via Suzuki–Miyaura coupling reaction. Detailed synthesis process and corresponding characterization of **1** are shown in the Supporting Information (Scheme S1 and Figures S1–S11). All hydrogen atoms of **1** were further investigated with the help of NMR spectroscopy (Figures S3 and S4, Supporting Information) and ^1H – ^1H COSY (Figure S11, Supporting Information). The intermediate product to **1** was also characterized by NMR spectroscopy (Figures S1 and S2, Supporting Information). The resulting anthracene-bridged divalent crown ether as a typical AA monomer was applied in constructing a supramolecular gel with a well-defined secondary ammonium salt functionalized polymer (Scheme 1) with several inherent advantages such as (1) the **1** linker enabled the strong luminescent properties of the gel and (2) the reversible transformation between **1** and **1**_{EPO} makes the gel possess controllable fluorescent turn on/off

feature (“EPO” refers to endoperoxide), (3) collapse would occur in the gel after treatment with triethanolamine (TEA), KPF_6 , or heating, and the corresponding recovery would be achieved with the help of trifluoroacetic acid (TFA), B18C6, or cooling. Hence, this gel can be utilized as a type of sensor. It is well documented that under UV light irradiation, anthracenes are photoresponsive and can transform to dimeric type.⁴² If there are bulky groups in the 9,10 positions of anthracene, it could trap singlet oxygen ($^1\text{O}_2$) to form stable EPOs. Thus, these large macrocyclic groups in **1** could facilitate the photo-oxygenation with $^1\text{O}_2$ by [4 + 2]-cycloaddition.⁴³

To prove our hypothesis, **1** was dissolved in CHCl_3 and irradiated under 365 nm light under O_2 atmosphere. The fluorescence emission intensity of **1** at 410 nm showed a great decrease accompanied by a color change of the solution from blue to gray (Figure 1a). However, when irradiated under N_2 atmosphere, **1** showed only a slight quenching phenomenon probably due to the residual O_2 in CHCl_3 (Figure S19, Supporting Information). The more favorable evidence was an intense peak at m/z 1125.44 assigned to $[\text{I}_{\text{EPO}} + \text{Na}]^+$ in UV-irradiated solution under O_2 (Figure S12, Supporting Information) by matrix assisted laser desorption ionization-time of flight (MALDI-TOF). The UV-light-induced photo-reaction of **1** was further investigated by ^1H NMR spectroscopy in CDCl_3 . Upon irradiation under N_2 , the characteristic

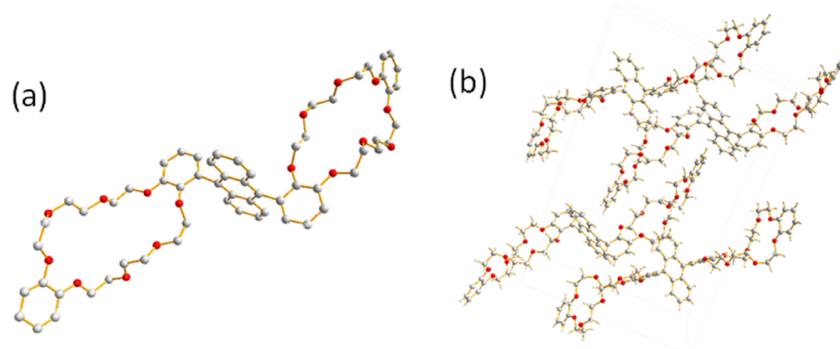


Figure 2. (a) Crystal structure of **1** and (b) its dimer.

spectrum of **1** showed no obvious transformation. In contrast, the ^1H NMR spectrum of **1** irradiated under O_2 became very complicated (Figure 1b). Interestingly, when 1_{EPO} was heated at $60\text{ }^\circ\text{C}$ for 100 h, a reconversion to **1** occurred, but the transformation process was time-consuming and incomplete. According to the above-mentioned results, we could draw the conclusion that the π -aromatic core of the crown ether could undergo a reversible oxidation–reduction process. It should be noted that all photochemical experiments were carried out in degassed organic solvents.

Significantly, we obtained a single crystal of **1** by slow evaporation from a CHCl_3 /hexane solution. The molecular structure of **1** and packing mode are illustrated in Figure 2. In accordance with our assumption, the sterically demanding DB24C8 was located at the opposite site of anthracene, revealing a thermodynamically favorable *cis*-conformation in the solid state. This conformation could greatly hinder the intermolecular π – π stacking between anthracene groups. One *cis*-**1** packs with DB24C8 and is parallel to DB24C8 of two adjacent molecules. Nevertheless, the rotating single bonds allow the crown ethers to capture guest molecules in a sandwich-like mode and adopt a *cis* conformation. The distinctive conformational structure of the crown ether and our interest in investigating its special ability in supramolecular chemistry motivate us to carry out further research.

First, we selected a simple monotopic secondary ammonium ion **2** as a model molecule to study the interactions between host and guest by two-dimensional (2D) ROESY (Figure S13, Supporting Information) and ^1H NMR spectroscopy. As can be seen in Figures 3, a 1:2 mixture of **1** and **2** showed two sets

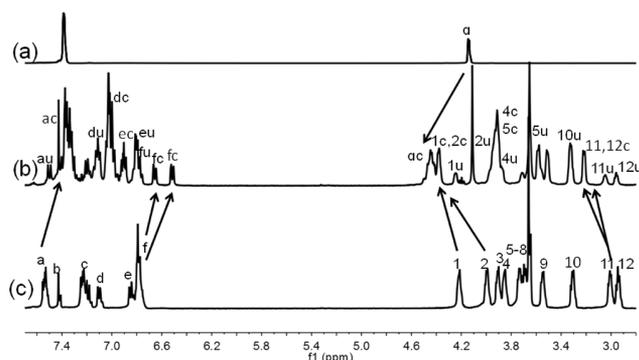


Figure 3. Partial ^1H NMR spectra ($\text{CDCl}_3/\text{CD}_3\text{CN} = 2:1$, 400 MHz, 298 K) of (a) free **2**, (b) a 1:2 mixture of **1** and **2**; $[\mathbf{2}] = 2[\mathbf{1}] = 2.0 \times 10^{-3}$ mol/L, (c) free **1**; for the full proton labeling, see Scheme 1. (“c” and “u” denote complexed and uncomplexed moieties, respectively).

of peaks assigned to the uncomplexed and complexed molecules, indicating that the formation of [3]pseudorotaxane was a slow exchange process. The benzylic protons (H_a) shifted downfield ($\Delta\delta \approx 0.33$ ppm) upon complexation, whereas the aromatic protons H_f ($\Delta\delta \approx 0.14$ ppm) and H_a ($\Delta\delta \approx 0.07$ ppm) of **1** showed upfield shifts. These large chemical shifts were contributed to the deshielding effect of H_a via the C–H \cdots O hydrogen bonding with oxygen atoms of **1**. Besides, the anthracene’s ring current also made some positive contribution to their chemical shifts. The association constants between the host and dibenzylammonium salt motif were calculated to be $(9.1 \pm 0.5) \times 10^5 \text{ M}^{-2}$ based on the ^1H NMR.⁴⁴ Electrospray ionization (ESI) mass spectrometry (MS) was also an important evidence of the formation of the complex $2_2@1$ (Figure S14, Supporting Information). All evidence shows the NH_2^+ of secondary ammonium salt was located in the center of the **1**.

Given the promising binding ability between the novel host and the secondary ammonium ion, we further fabricated a secondary ammonium salt functionalized graft polymer by reversible addition fragmentation chain transfer polymerization (Scheme S2, Supporting Information). As a polymer, the ^1H NMR spectroscopy of the guest was very complicated (Figure S9, Supporting Information). The gel permeation chromatography (GPC) showed that the number average molecular weight (M_n) of the resulting positive co-polymer **3** was around 7278, whereas the polydispersity index value was 1.10 (Figure S10, Supporting Information). The intermediate product to **3** was also characterized by NMR spectroscopy (Figures S5–S8, Supporting Information). When 4.2 mmol **1** and 1.2 mmol **3** (1:1 molar ratio, DB24C8/DBA) were mixed in $\text{CHCl}_3/\text{CH}_3\text{CN}$ ($v/v = 2:1$), the linked network displayed a fairly complicated picture. First, we confirmed that no gel was formed under this condition. ^1H NMR spectra gave us direct evidence for the binding of **1** and **3** in a solution. As shown in Figure S15, the aromatic protons H_a ($\Delta\delta \approx 0.06$ ppm) and H_e ($\Delta\delta \approx 0.33$ ppm) of **1** showed upfield shifts. H_a of the benzylic protons shifted downfield ($\Delta\delta \approx 0.45$ ppm) upon complexation. These almost disappeared resonances suggested that a supramolecular polymer network was formed through multivalent host–guest interactions between **1** and **3**. After confirming their binding abilities, we used KPF_6 , heating, and TEA to control the networks. These external stimuli could result in the transition from polypseudorotaxane to polymer. For instance, ^1H NMR of the polypseudorotaxane between **2** and **5** ppm showed complicated wide peaks. When 3.3 equiv Et_3N was added to the mixture, its ^1H NMR became clearer. Figure 4 shows that the peaks assigned to **1** become very

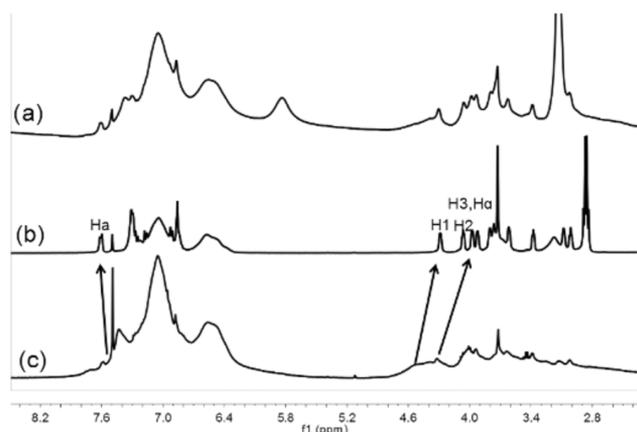


Figure 4. Et₃N-induced disassembly of 3@1, partial ¹H NMR spectra (400 MHz, CDCl₃/CD₃CN = 2:1, 298 K): (a) a mixture of 4.2 mmol **1**, 1.2 mmol **3**, 28 mmol TEA, and 56 mmol TFA; (b) a mixture of 4.2 mmol **1**, 1.2 mmol **3**, and 28 mmol TEA; (c) a mixture of 4.2 mmol **1** and 1.2 mmol **3**. More detailed information about **1**, **3**, and 3@1 is given in Figure S15.

obvious. H_a, H₁₋₃, and H₄ were assigned to the individual host and guest. Then, 6.6 equiv trifluoroacetic acid (TFA) was added to the supramolecular assembly, and the ¹H NMR became quite similar to that of the polypseudorotaxane, indicating the recovery of the system. In addition, we also confirmed its stimuli responsiveness upon heating and KPF₆ treatments (Figures S16 and S17, Supporting Information).

Notably, the supramolecular gel was obtained simply by dissolving **1** (90 mg/mL) and **3** (174.7 mg/mL) in CHCl₃/CH₃CN (v/v = 2:1). All the resulting gels were transparent and pale yellow. In sharp contrast, no gels were obtained of net **1** or **3** in organic solvents. Such phenomena could be reflected from the viewpoint that the multivalent interactions between **1** and **3** played an important role in the gel formation. Benefiting from the light-responsive property of **1**, the gel exhibited a strong blue fluorescence emission. When irradiated under 365 nm UV light under O₂ atmosphere, the gel emission intensity was weakened and could be observed by the naked eyes. Amazingly, when the nonluminescent gel was put in a 60 °C oil bath, the fluorescence emission of the gel was recovered gradually. During this procedure, the gel suffered a transformation from gel to sol–gel. This unique feature makes it a great potential application in biotechnology, diagnostic, and drug delivery systems (Figure 5b).

Then, we study the gel's multiresponsiveness to external stimuli in the sol–gel transition process (Figure 5a). A formation of soliquid was obtained by heating the supramolecular gel at 60 °C. When the temperature dropped to room temperature, a new gel was formed again. This phenomenon suggested the thermally responsive sol–gel transition. In addition, the interactions between DB24C8 and DBA also responded to potassium ion and pH. When 1.2 equiv of KPF₆ was added to the cross-linked networks, the gel collapsed immediately. As reported, the binding ability of K⁺ ion is stronger than that of DBA with DB24C8, the added K⁺ would squeeze out the secondary ammonium salt, accompanied by the collapse of the supramolecular gel. Compared with DB24C8, benzo-18-crown-6 (B18C6) exhibits higher affinity toward K⁺. Therefore, when 1.5 equiv of B18C6 was added, a new gel was formed again. In addition, the secondary ammonium salt was base-sensitive. The elevated pH would

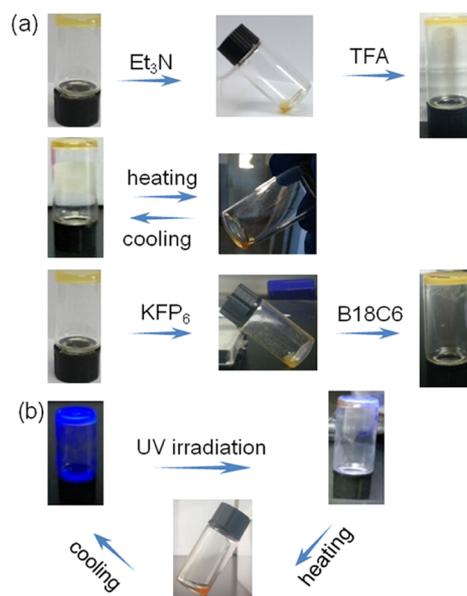


Figure 5. (a) Reversible sol–gel transitions of supramolecular gel under a variety of external stimuli. (b) Light-controlled fluorescence emission behavior of the supramolecular gel.

result in the deprotonation of the secondary ammonium salt, further leading to gel disruption. After the addition of TFA, the neutral secondary ammonium was protonated, thus leading to the cationic state. According to the aforementioned sol–gel transition experiments, we could draw a conclusion that our supramolecular gel was responsive to external stimuli (pH, K⁺, temperature). Additionally, the formation and disturbance of gels were directly judged by naked eyes.

Scanning electron microscopy (SEM) studies were also carried out to test the different morphologies of **1**, **3**, and the supramolecular cross-linked polymer network. As shown in Figure S18 (Supporting Information), images of **1** presented a number of nanoparticles with an average length of hundreds of nanometers, and **3** showed a morphology of nanosphere. But the pseudorotaxane showed an interconnected 2D sheet structure with some holes, indicating the formation of a network owing to the interaction between host and guest. After irradiation with 365 nm light, its morphology was also a nanosheet with larger holes. It could be illustrated by the photo-oxidation of anthracene.

CONCLUSIONS

In summary, an anthracene-bridged crown ether **1** was synthesized, and the crystal structure of the crown ether illustrated that the two DB24C8 rings were located at the opposite directions of anthracene. As there are bulky groups in the 9,10 positions of anthracene, **1** tends to trap singlet oxygen to form stable ¹EPO. Benefiting from DB24C8/secondary ammonium salt recognition, **1** could form a supramolecular illuminant gel with secondary ammonium salt functionalized styrene copolymer **3**. As the linker was a crown ether furnished by anthracene, the gel could emit strong fluorescence under the irradiation of 365 nm light. The gel suffered from fluorescence quenching after 11 h, but its fluorescence emission was recovered upon heating up to 60 °C. Significantly, the gel possessed multistimuli responsiveness features. This obtained supramolecular system could undergo sol–gel transition with various external stimulation (thermo,

pH, and chemo), which may provide many potential applications in miscellaneous fields.

EXPERIMENTAL SECTION

Materials and Methods. All reagents and solvents were commercially available and used as received unless otherwise specified purification. Column chromatography was performed on a 200–300 mesh silica gel. The switch experiments were carried out using a Xe lamp (CEL-HXF300 14V 50W) with an optical filter that provides UV light around 365 nm. The light intensity was around 50 mW/cm² and the distance was kept at 10 cm. High-resolution mass spectra were made on a LC–MS, Q-TOF with an ESI mode, and a Varian 7.0T FT-MS with MALDI ion source. The NMR spectra were recorded on a Bruker AV400 instrument. Single-crystal X-ray diffraction data were collected on an Agilent Technologies Super Nova X-RAY diffractometer system. The SEM images were recorded on a JEOL JSM-7500F scanning electronic microscope operating at an accelerating voltage of 30 keV. The GPC characterizations of **3** were carried out on a Waters system equipped with a set of three Ultrastaygel columns (HT2, HT3, and HT4; 30 cm × 7.8 mm; 10 μm particles; exclusion limits: 100–10 000, 500–30 000, and 5000–600 000 g/mol, respectively), Waters 515 HPLC pump, Waters 717 plus Auto sampler, and an online Waters 2414 refractive index detector maintained at 35 °C. Tetrahydrofuran (THF) was used as the mobile phase with a flow rate of 1 mL/min. Polystyrene samples were used as standards in the calibration of the molar masses.

Synthesis of 1. A two-neck flask was charged with **5** (1.87 mmol, 984.4 mg, see the Supporting Information (SI) for the detailed structure), anthracene-9,10-diboronic acid bis(pinacol) ester (0.91 mmol, 391.6 mg), K₂CO₃ (5.03 mmol, 695.5 mg), THF (40 mL), and H₂O (20 mL), and the mixture was degassed by three freeze–pump–thaw cycles. Pd(PPh₃)₄ (0.114 mmol, 49 mg) was then added under an argon atmosphere. The mixture was refluxed for 24 h. After removing the organic solvents under vacuum, CHCl₃ (60 mL) was added to the mixture and washed with H₂O. The organic layer was collected and dried with anhydrous Na₂SO₄ and filtered. After the removal of CHCl₃, the residue was purified by column chromatography (SiO₂, *n*-hexane/ethyl acetate = 1:2) to yield the desired compound **1** as a white solid (243 mg, 25%). ¹H NMR (400 MHz, CDCl₃, δ) 7.65 (dd, *J* = 6.8, 3.2 Hz, 4H), 7.28 (d, *J* = 3.3 Hz, 4H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.89–6.80 (m, 8H), 4.30 (t, 4H), 4.16–4.08 (t, 4H), 4.06–4.01 (t, 4H), 3.99 (t, 4H), 3.93–3.87 (t, 4H), 3.83 (t, *J* = 2.3 Hz, 4H), 3.82–3.79 (m, 4H), 3.77–3.69 (t, 8H), 3.53–3.47 (t, 4H), 3.25–3.18 (t, 4H), 3.07 (t, 4H). ¹³C NMR (101 MHz, CDCl₃, δ) 152.64, 149.23, 149.17, 133.71, 133.58, 130.17, 127.25, 125.26, 125.20, 124.13, 121.77, 121.69, 114.57, 114.32, 113.26, 72.37, 71.53, 71.45, 71.01, 70.41, 70.30, 70.26, 70.17, 69.93, 69.81, 69.33, 68.93. *m/z* calcd for C₆₂H₇₀O₁₆Na⁺: 1093.4562 (*M* + Na⁺), found: 1093.4558.

Synthesis of 3. Styrene (67.3 mmol, 7.00 g), secondary ammonium salt functionalized styrene monomer **7** (9.00 mmol, 3.31 g, see the SI for the detailed structure), azobisisobutyronitrile (AIBN) (0.034 mmol, 5.70 mg), and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (0.25 mmol, 90.0 mg) were dissolved in THF (20 mL). The solution was added into a polymerization Schlenk tube, and the resulting solution was degassed via three freeze–pump–thaw cycles. After the tube was sealed under N₂, the reaction proceeded under stirring at 80 °C for 48 h. Then, the reaction mixture was poured into hexane. The polymer was dialyzed in acetonitrile using a dialysis bag with a cutoff range of 1000 to get pure **3** (30%) after drying under vacuum at 25 °C for 24 h.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b04323.

¹H NMR, ¹³C NMR spectra, and ESI-MS of intermediates; GPC spectrum of the copolymer **3**;

¹H–¹H COSY spectrum of **1**; MALDI-TOF mass spectrum of compound **1**_{EPO}; ROESY 2D NMR spectrum of **2**_{2@1}; ESI-MS spectrum of **2**_{2@1}; heating- and KPF₆-induced disassembly of **3**_{@1}; fluorescence emission spectra of **1** in CHCl₃ irradiated at 365 nm under N₂; crystal data and structure refinement summary for complex **1**; SEM images (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: yuliu@nankai.edu.cn.

ORCID

Yu Liu: 0000-0001-8723-1896

Notes

The authors declare no competing financial interest.

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