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Photo-induced conversion from supramolecular to covalently linked polymers based on anthracene-appended amphiphiles†

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A photosensitive amphiphile **2** was synthesized, in which the anthracene moiety in each arm was connected to a dipyrindinium center by an alkyl chain. Using host–guest interactions between γ -CD and the anthracene moiety in **2**, a supramolecular polymer was achieved, and such a supramolecular polymer can be further converted into its corresponding covalent polymer upon irradiation at 365 nm via [4 + 4] photocycloaddition of anthracenes within the cavity of γ -CD. This approach affords a strategy in the transformation from supramolecular to covalently linked polymers.

Introduction

Research on polymers has attracted considerable interest during the past few decades¹ due to their wide applications in catalyst supports,² drug carriers,^{3,4} biosensors,⁵ and photoresistors.⁶ Generally, polymers can be classified into covalent and supramolecular non-covalent subgroups based on the bonding types. Covalent polymers have long or hyperbranched chains, multifunctional groups, excellent solubility and viscosity,^{7–13} while supramolecular polymers combine polymeric structures and non-covalent interactions such as metal–ligand interactions,^{14–16} π -stacking,^{17–19} hydrogen bonding,²⁰ charge-transfer interactions,^{21–23} and host–guest interactions.^{24–26} Moreover, these non-covalent interactions can endow supramolecular polymers with self-healing and stimuli-responsive properties.^{27–31} By combining the advantageous properties of both covalent and supramolecular polymers, a system which can switch between these two types of polymers can be established.

To date, only a few studies regarding the conversion between supramolecular and covalent polymers have been reported.^{32–36} For example, Tian and co-workers have developed a supramolecular linear dual-modality polymer which could be switched to its corresponding covalent polymer in response to light stimuli because of the [2 + 2] photocyclo-

dimerization of coumarin groups in the cavity of γ -cyclodextrin (γ -CD).³² Zhang's group constructed a photosensitive supramolecular hyperbranched polymer by host–guest interactions between cucurbit[8]uril and an azastilbene derivative. This polymer can be further converted into the covalently attached polymer as the [2 + 2] cycloaddition of C=C bonds in azastilbene upon UV irradiation.³³ Previously we found that pyridinium-tailored 2-anthracene can form a supramolecular hydrogel driven by π -stacking and electrostatic interactions.³⁷ A gel–sol transition of this gel was observed under UV irradiation at 365 nm on account of the dimerization of anthracene groups. Inspired by these results, we hypothesize that these anthracene groups could be used in the conversion between supramolecular and covalently linked polymers induced by photocycloaddition. To achieve this, an amphiphilic monomer **2** was designed and synthesized, and its ability to generate supramolecular and covalent polymers was investigated (Fig. 1).

In monomer **2**, the anthracene moiety in each arm is connected to the dipyrindinium center by an alkyl chain, which is able to adjust the molecular arrangement during the assembly process. The dipyrindinium cation can not only be a center to connect hydrophobic ends, but can also increase the molecular hydrophilicity. It is well-known that γ -CD is one of the best candidates in host–guest interactions which can coordinate [4 + 4] photocycloaddition of anthracene moieties.^{38–43} Therefore, the inclusion of γ -CD onto anthracene moieties may allow for the fabrication of supramolecular polymers, where γ -CD can provide a hydrophobic cavity necessary for the dimerization event. Our results show that a supramolecular polymer was attained by host–guest interactions between γ -CD and anthracene moieties. In addition, such supramolecular polymers could be further converted into their corresponding covalent polymers by irradiation at 365 nm via

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† Electronic supplementary information (ESI) available: TEM image of amphiphilic monomer **2** (Fig. S1); NMR and MS spectra of **1** and **2** (Fig. S2–S7). See DOI: 10.1039/c5py00476d

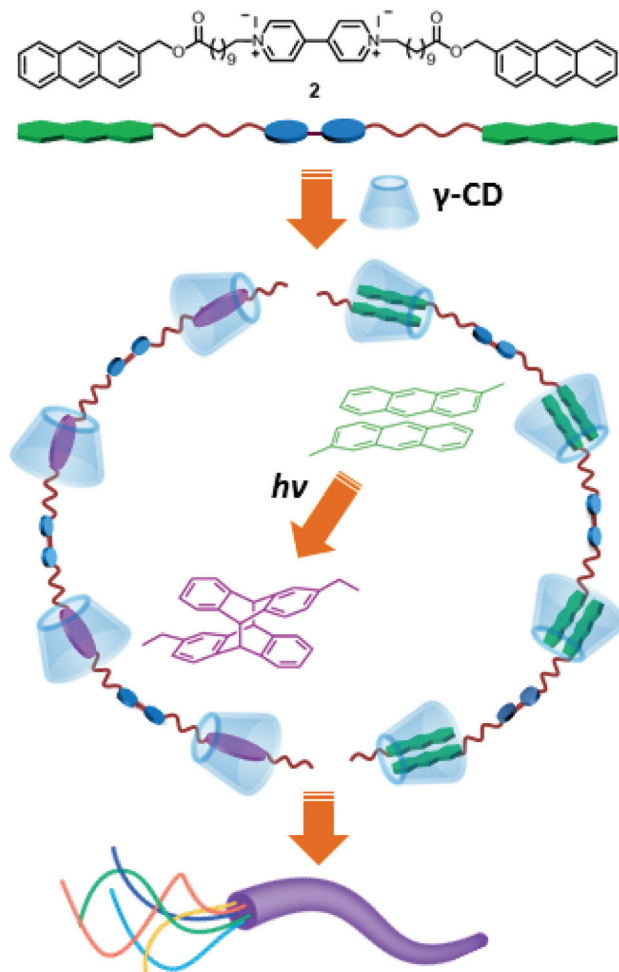


Fig. 1 Schematic representation for the formation of supramolecular polymers driven by host–guest interactions between 2 and γ -CD, and the conversion to their corresponding covalent polymers by UV light irradiation at 365 nm.

the [4 + 4] photocyclodimerization of anthracene within the cavity of γ -CD (Fig. 1).

Experimental section

Materials

Briefly, 11-iodoundecanoic acid was prepared according to protocols previously reported.^{44,45} 2-Anthracenemethanol and 4,4'-dipyridine were purchased from VWR. γ -CD was purchased from Aladdin. Other reagents were commercially available and used as received. All organic solvents were dried and distilled before use.

Instruments

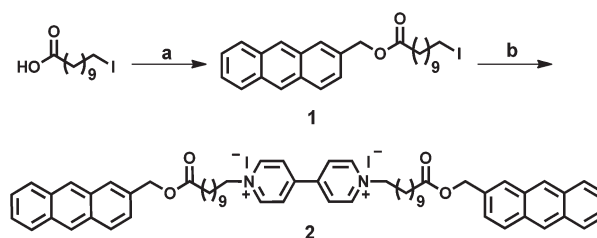
NMR spectra were characterized on a Bruker AVANCE III HD 300/400/600 MHz spectrometer. Mass Spectra were collected and analyzed by using a Bruker ESQUIRE-LC mass spectrometer. UV-Vis spectra were acquired on a TU-1901 spectro-

photometer. Fluorescence spectra were recorded by using a Hitachi F-2500 fluorescence spectrophotometer. Transmission electron microscopy (TEM) measurements were carried out on a JEOL JEM-1011 microscope operating at an accelerating voltage of 100 kV. Irradiation was provided by a WFH-204B portable ultraviolet lamp (8 W).

Synthesis of the amphiphilic monomer 2

As shown in Scheme 1, 11-iodoundecanoic acid (335 mg, 1.07 mmol) was added to thionyl chloride (5 mL), and then the solution was refluxed for 6 h. After evaporating the solvent under reduced pressure, the resulting crude was re-dissolved in dry THF (2 mL), which was added dropwise to a solution of 2-anthracenemethanol (199 mg, 0.93 mmol) and triethylamine (500 μ L) in dry THF (5 mL). The mixture was stirred at room temperature for 12 h, and then the solvent was removed. The resulting crude was re-dissolved in dichloromethane, washed using water, brine, dried by anhydrous sodium sulfate, and evaporated to dryness. The residue was purified by flash chromatography (dichloromethane/hexane = 2/1, v/v) to give anthracen-2-ylmethyl 11-iodoundecanoate 1 as a yellow powder (394 mg, yield 73%). EI-MS (+): m/z = 502; HRMS (ESI): m/z calcd for $C_{26}H_{31}IO_2$: 502.1369, found: 502.1382; 1H NMR (300 MHz, $CDCl_3$, ppm): δ 8.42 (s, 2H, anthracene-H), 8.00 (m, 4H, anthracene-H), 7.48 (m, 3H, anthracene-H), 5.32 (s, 2H, CH_2O), 3.16 (t, 2H, J = 8.0 Hz, CH_2I), 2.42 (t, 2H, J = 8.0 Hz, O_2CCH_2), 1.79 (m, 2H, CH_2), 1.69 (m, 2H, CH_2), 1.25 (m, 12H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 173.92 (C=O), 133.14, 132.11, 132.09, 131.41, 131.34, 128.92, 128.36, 128.34, 127.46, 126.62, 125.74, 125.60 (14C, anthracene-C), 66.50 (CH_2O), 34.56 (CH_2I), 33.72 (O_2CCH_2), 30.64, 29.50, 29.38, 29.29, 28.67, 25.17, 7.52 (8C, CH_2).

4,4'-Dipyridine (40 mg, 0.26 mmol) and 1 (270 mg, 0.53 mmol) were dissolved in anhydrous DMF (5 mL), and then the mixture was stirred at 60 $^{\circ}C$ for 72 h. After evaporating the solvent under reduced pressure, the crude was washed using dichloromethane, and filtered to afford monomer 2 as a red powder (93 mg, yield 33%). ESI-MS (+): 453.5 [(M – 2I)/2]⁺; HRMS (ESI): m/z calcd for [($C_{62}H_{70}N_2O_4$)/2]⁺: 453.2663, found: 453.2663; 1H NMR (400 MHz, d_6 -DMSO, ppm): δ 9.35 (d, 4H, J = 8.0 Hz, pyridinium-H), 8.75 (d, 4H, J = 8.0 Hz, pyridinium-



Scheme 1 Synthetic route of the photosensitive amphiphilic monomer 2. Reagents and conditions: (a) (i) $SOCl_2$, reflux, 6 h; (ii) 2-anthracenemethanol, triethylamine, dry THF, r.t., 12 h; (b) 4,4'-dipyridine, DMF, 60 $^{\circ}C$, 72 h.

H), 8.57 (m, 4H, anthracene-H), 8.08 (m, 8H, anthracene-H), 7.52 (m, 6H, anthracene-H), 5.29 (s, 4H, CH₂O), 4.70 (t, 4H, *J* = 8.0 Hz, CH₂N), 2.40 (t, 4H, *J* = 8.0 Hz, O₂CCH₂), 1.93 (m, 4H, CH₂CH₂N), 1.57 (m, 4H, CH₂), 1.25 (m, 24H, CH₂). ¹³C NMR (100 MHz, *d*₆-DMSO, ppm): δ 172.93 (2C, C=O), 148.56, 145.78 (4C, pyridinium-C), 133.43, 131.51, 131.43, 130.80, 130.68, 128.53, 128.12, 128.07, 126.66, 126.19, 126.04, 125.82, 125.62 (28C, anthracene-C), 65.57, (2C, CH₂O), 60.96 (2C, CH₂N), 33.57 (2C, CH₂I), 30.77 (2C, O₂CCH₂), 28.78, 28.74, 28.66, 28.46, 28.39, 25.45, 24.54 (16C, CH₂).

Preparation of supramolecular polymers

Supramolecular polymers 2/γ-CD were fabricated by mixing 50 μL storage solution of 2 (0.01 mmol, DMSO) and 5 μL γ-CD storage solution (0.1 mmol, H₂O) in 1 mL mixed solvents of DMSO–H₂O (7/3, v/v).

Preparation of covalently linked polymers

Covalently linked polymers were prepared by UV irradiation of the above 2/γ-CD solution at 365 nm for 10 h using an ultraviolet lamp.

Results and discussion

UV-Vis spectroscopy of the formation of supramolecular polymers and their transformations into covalently linked polymers

Monomer 2 displays absorption peaks at 326, 343, 360, and 379 nm, respectively, due to the presence of anthracene moieties (Fig. 2a). The addition of γ-CD to the solution of 2 causes a decrease in the absorbance of anthracene units, which indicates that the anthracene groups are encapsulated in the cavity of γ-CD,³³ resulting in the formation of supramolecular polymer 2/γ-CD. A Job's plot was used to confirm the binding stoichiometry between 2 and γ-CD. According to the dependence of the absorption intensity at 360 nm on the molar ratio, the change in absorption reaches a maximum at 0.5 for [2]/([2] + [γ-CD]), revealing a 1 : 1 complex between 2 and γ-CD (Fig. 2b). Conversely, a significant decrease in the absorbance is observed, and the peaks disappear completely after irradiating 2/γ-CD at 365 nm for 10 h (Fig. 2c and d). This strongly indicates that a [4 + 4] photocyclodimerization of anthracene groups occurs within the cavity of γ-CD, which leads to the transformation of supramolecular polymer 2/γ-CD into its covalently linked polymers.

Fluorescence spectroscopy of the formation of supramolecular polymers and their transformations into covalently linked polymers

As shown in Fig. 3a, four emission peaks of 2 were detected at 390, 411, 436, and 465 nm, respectively, and an increase in intensity was observed when γ-CD was added to the solution of 2. This phenomenon is ascribed to the limited cavity of γ-CD which can serve as a trap to prevent the occurrence of non-radiative pathways such as vibration, rotation, and collision

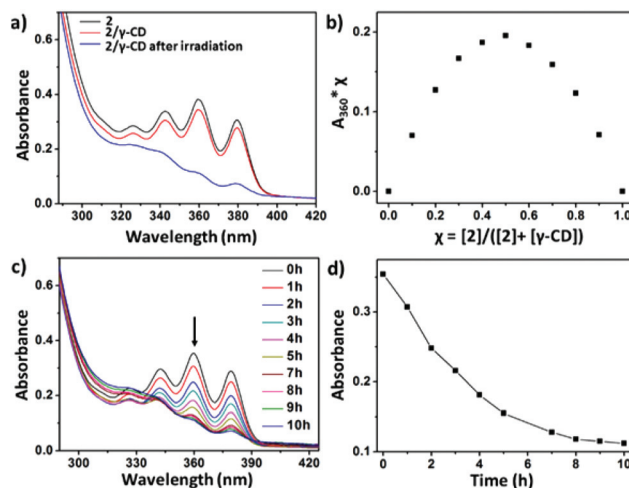


Fig. 2 (a) UV-Vis spectra of 2 (0.05 mM), and 2/γ-CD (0.05 mM, molar ratio = 1 : 1) before and after UV irradiation at 365 nm; (b) Job's plot for complexation between 2 and γ-CD (total concentration, 0.1 mM) based on UV-Vis absorption changes at 360 nm; (c) the absorption changes in UV-Vis spectra of 2/γ-CD (0.05 mM, molar ratio = 1 : 1) with the UV irradiation time; (d) absorbance intensity of 2/γ-CD (0.05 mM, molar ratio = 1 : 1) at 360 nm as a function of the irradiation time.

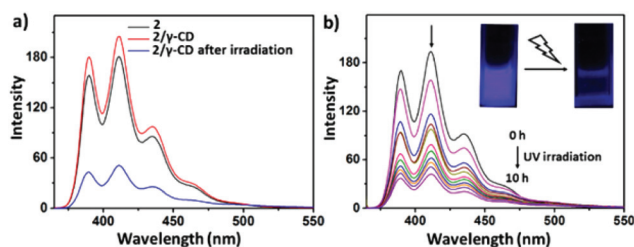


Fig. 3 (a) Fluorescence spectra of 2 (0.05 mM), and 2/γ-CD (0.05 mM, molar ratio = 1 : 1; excitation = 360 nm) before and after UV irradiation at 365 nm; (b) fluorescence intensity changes of 2/γ-CD (0.05 mM, molar ratio = 1 : 1) with the UV irradiation time. Inset: photograph of 2/γ-CD before and after UV irradiation at 365 nm.

with the solvent,³³ which results in an increase in the intensity. After UV irradiation at 365 nm for 10 h, a significant decrease in the fluorescence intensity occurs (Fig. 3b), because γ-CD facilitates the [4 + 4] photocyclodimerization of C=C bonds in anthracene groups of supramolecular polymers, thus leading to the formation of the covalently linked polymer 2/γ-CD. Therefore, the combination of supramolecular polymerization and photochemistry may allow for the construction of traditional covalently attached polymers with tuneable optical properties.

Mass spectrum of the formation of supramolecular polymers and their transformations into covalently linked polymers

Before irradiation, a peak at *m/z* 1102 belonging to [(M + γ-CD – 2I[–])/2]⁺ is found in Fig. 4a, which provides convincing

evidence for the construction of supramolecular polymers. It can be further confirmed by other peaks at m/z 531 [$C_{36}H_{39}N_2O$] $^{+}$ and 1750 [$(M + 2\gamma\text{-CD} - 2I^-)/2$] $^{+}$ which is a fragment broken between N and its adjacent methylene. Conversely, all the peaks of supramolecular polymers disappear after irradiation with only the presence of [$\gamma\text{-CD} + Na$] $^{+}$ and [$\gamma\text{-CD} + 2H_2O + K$] $^{+}$ at m/z 1319 and 1371, respectively (Fig. 4b), further verifying the dimerization of anthracene moieties.

NMR spectroscopy of the transformation from supramolecular polymers to covalently linked polymers

Upon irradiating 2/ γ -CD, proton signals at 7.41 (H₃, H₆, H₇) and 7.97 ppm (H₁, H₄, H₅, H₈) shift to one set of broad peaks around 8.01 ppm (H_{1'}, H_{3'}, H_{4'}, H_{5'}, H_{6'}, H_{7'}, H_{8'}) with the disappearance of H₉ and H₁₀ (Fig. 5a), suggesting the [4 + 4] photocyclo-dimerization of anthracene groups. To further substantiate the conversion between supramolecular and covalently linked polymers, 2D diffusion-ordered NMR spectroscopy (DOSY) was performed. As shown in Fig. 5b, the diffusion coefficient of 2/ γ -CD decreases from 0.150×10^{-9} to $0.110 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ after irradiation, which reveals the formation of large polymeric species according to the Stokes-Einstein equation.^{33,46}

Morphology study of supramolecular and covalent polymers

TEM images show that both supramolecular and covalently linked polymers of 2/ γ -CD display nanofibers with a few micrometers in length (Fig. 6a and b), whereas nanosheets were observed for amphiphilic monomer 2 (Fig. S1†). These nanofibers consist of many single molecular chains with the diameter around 1.50–1.75 nm (Fig. 6c and d), which is consistent with the size of torus-like γ -CD (the outer diameter of the large rim is 1.69 nm).⁴⁷ It should be noted that the combination between the molecular chains driven by the side-side associations is a common phenomenon in cyclodextrin-based polymer systems.⁴⁸ Although the covalent polymers have been fabricated by UV irradiation, the diameter of a single molecular chain still depends on the size of the large rim in γ -CD which is the widest motif in the chain. Therefore, both supra-

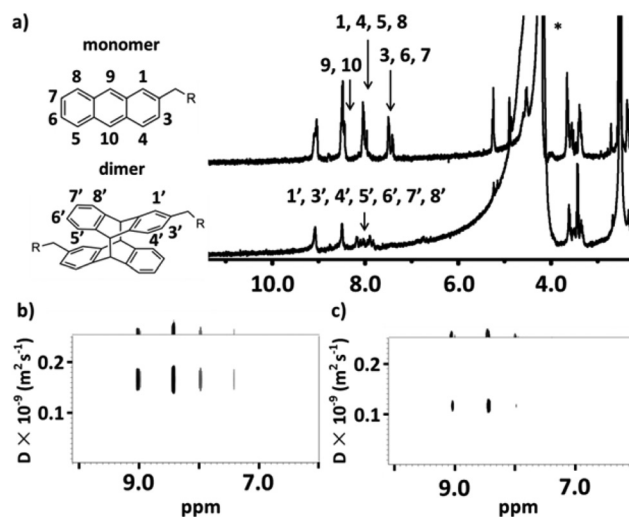


Fig. 5 (a) ^1H NMR spectra (400 MHz, d_6 -DMSO/ D_2O = 7/3, v/v) of 2/ γ -CD (0.85 mM, molar ratio = 1 : 1) before (top) and after (bottom) UV irradiation at 365 nm (# represents DMSO, * represents H_2O); DOSY spectra (600 MHz, d_6 -DMSO/ D_2O = 7/3, v/v) of 2/ γ -CD (0.85 mM, molar ratio = 1 : 1) before (b) and after (c) irradiation, respectively.

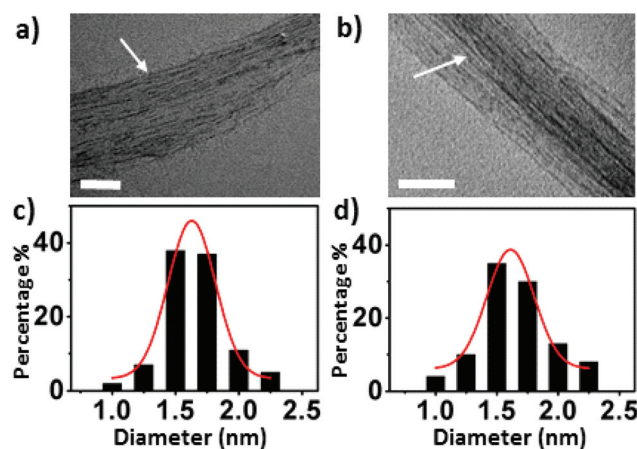


Fig. 6 TEM images of (a) supramolecular and (b) covalent polymer of 2/ γ -CD (0.05 mM, molar ratio = 1 : 1), scale bar = 100 nm. The diameter distribution histogram of the fibers before (c) and after (d) irradiation.

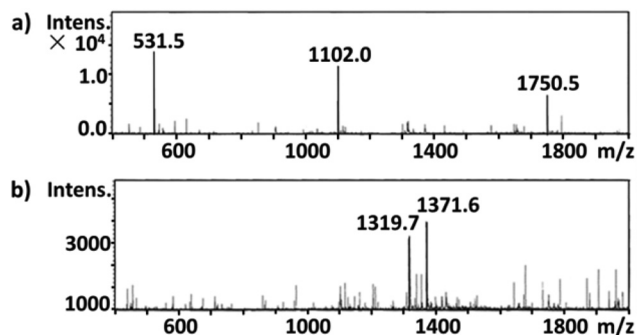


Fig. 4 ESI-MS (+) spectra of 2/ γ -CD before (a) and after (b) irradiation at 365 nm.

molecular and covalent polymers have similar morphologies and dimensions.

Conclusions

By taking advantage of host-guest interactions between γ -CD and anthracene moieties, a supramolecular polymer was achieved based on the photosensitive amphiphilic molecule 2. Such supramolecular polymers could be further converted into their corresponding covalent polymers driven by the [4 + 4] photocyclodimerization of anthracene within the cavity of γ -CD. This approach affords a strategy in the transformation from supramolecular to covalently linked polymers.

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