

Electronic Supplementary Information (ESI)

A Photo- and Thermo- Responsive Topological Gel Prepared from Anthracene-Modified Polyrotaxanes

Zhao Li,^{‡^a} Shan Su,^{‡^b} Lin Yu,^a Zhen Zheng^a and Xinling Wang^{*^a}

^a School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

^b Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, 5 Yiheyuan Road, Beijing 100871, China

* Correspondence to: xlwang@sjtu.edu.cn

‡ These authors equally contributed to this work.

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1 Experimental Section

1.1 Materials

Polyethylene glycol (PEG) ($M_w = 20000$), α -cyclodextrin (α -CD), 1-adamantanamine, 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO), (benzotriazol-1-yloxy)tris(dimethylamino)phosphonium hexafluorophosphate (BOP), 4-(dimethylamino)-pyridine (DMAP) were purchased from Sigma-Aldrich Corp. and used as-received. Poly(vinyl alcohol) with 88% hydrolyzed degree (M_w is about 20000) was purchased from Acros Organics and used without further purification. 2-Aminoanthraquinone, triphosgene (BTC), sodium bromide (NaBr), sodium bicarbonate (NaHCO_3), sodium hydroxide (NaOH), stannous octanoate were purchased from Aladdin Industrial Co., Ltd. and used without further purifications. Aqueous NaClO with available chlorine > 5.2 %, anhydrous methanol, anhydrous ethanol and anhydrous ethyl ether were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. and used as-received. Zinc purum powder was purchased from Aladdin Industrial Co., Ltd. and activated by aqueous HCl before use. Methanol, Dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and trimethylamine (TEA) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. and distilled with CaH_2 before use. Dichloromethane (DCM) and chloroform (CHCl_3) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. and dried with 4A molecular sieve before use. *n*-Hexane and ethyl acetate were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. and used without further purification.

1.2 Characterizations

FTIR Measurement. Fourier transform infrared (FTIR) spectra were recorded on a Paragon 1000 instrument equipped with ATR accessory at room temperature. The scan range was 4000 to 500 cm^{-1} and seven scans were collected for each sample with a resolution of 2 cm^{-1} .

NMR Measurement. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopies in $\text{DMSO-}d_6$ was recorded on a Varian MERCURY plus-400 spectrometer at room

temperature with 64 and 1024 scans respectively for every sample.

GPC Measurement. Gel permeation chromatograph (GPC) measurements were performed on a HLC-8320 chromatograph (Tosoh Corporation, Japan) equipped with two HLC-8320 columns (TSKgel Super AWM-H, pore size: 9 μm , column size: 6.0 \times 150 mm) and a double-path, double-flow refractive index (RI) detector (Bryce) at 40 $^{\circ}\text{C}$. The elution phase was DMF (0.01 mol L⁻¹ LiBr, elution rate: 0.6 mL min⁻¹), and a series of poly(ethylene glycol) was used as the calibration standard.

UV-Vis Absorption Spectroscopy. UV-Vis spectra of samples were recorded at room temperature using a Peking-Elmer lamda20 spectrophotometer. The slit width was 2.0 nm. The scan rate was 200 nm min⁻¹ and the resolution was 0.5 nm.

Fluorescence Emission Spectroscopy. Fluorescent emission spectra were recorded at room temperature using a Perkin-Elmer LS 55 fluorospectrometer equipped with solid specimen holder. The excitation wavelength was 360 nm, the scan rate was 200 nm min⁻¹, and the resolution was 0.5 nm. For the measurement of gels, samples about 0.1 mm thickness and 15 mm diameter were sandwiched between two circular quartz plates in the solid specimen holder. For the measurement of pregel solutions, solutions was coated and sandwiched between two circular quartz plates and the distance between the two plates was about 0.1 mm which is the same as the thickness of the gel samples.

Swelling Measurement. The topological gel, **anth-PR** gel, was immersed in DMSO until its mass no longer increased. Then the swelled gel was dried in vacuum at 80 $^{\circ}\text{C}$ for 72 h. the swelling degree (Q)^{S1} of the gel was calculated by the following equation:

$$Q = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \quad (1)$$

Here m_{wet} and m_{dry} stand for mass of fully swelled gel in DMSO and dry gel respectively.

SEM Measurement. The internal morphology of the **anth-PR** gel was observed using

a Philips Sirion 100 instrument scanning electron microscope (SEM). Photographs were taken with a Canon IXUS 800IS digital camera. The gel sample was frozen in liquid nitrogen and broken. Then the sample was put into large amount of water with temperature of 4 °C and the system was frozen with liquid nitrogen again. After freeze drying, the sectioned surface of the sample was caught out SEM examination. The dried sample was mounted on metal holder and vacuum coated with a platinum layer prior to SEM examination.

Dynamical Mechanical Measurement. The viscoelastic properties of the topological gel, **anth-PR** gel, were measured with an Anton Paer Physica MCR 501 rheometer. The rheometer can detect torques within the range of 0.1 μNm – 230 mNm and was equipped with a motor having a frequency range of 10^{-5} – 100 Hz. The gel sample was cut into a disk about 0.5 mm thickness and 8 mm diameter after it reached equilibrium at room temperature. The sample was immersed in DMSO during all the experiments to avoid it drying and deswelling during the time of the experiments. To ensure that the sample was always under compression, 5% pre-strain was applied it during the experiments. The linear viscoelastic region of the sample was firstly determined with the frequency-controlled dynamic strain sweep test with a frequency of 10 Hz and a strain range of 0.01 – 5%. Then the strain-controlled dynamic frequency sweep test was used as a test setup, and a 0.05% strain was selected which was in the linear viscoelastic region of the sample. The data of storage (E') and loss (E'') moduli were analyzed in the frequency range of 0.05 – 250 rad s^{-1} . The temperature during the tests was 25 °C.

1.3 Synthesis

The anthracene-modified polyrotaxane, 2-anthrylcarbamate polyrotaxane (An-PR), was synthesized from PEG/ α -CD-based PR and 2-anthryl isocyanate (An-NCO). The PEG/ α -CD-based PR was synthesized according to the method in the literature^{S2} with the oxidation step of terminal hydroxyl groups in PEG carefully modified, PEG ($M_w = 20000$) was oxidized in pH 8.5 sodium bicarbonate buffer solution with TEMPO, NaBr and aqueous NaClO. An-NCO was synthesized through the reduction of 2-

aminoanthraquinone and isocyanation of the resulted 2-aminoanthracene (An-NH₂) by the bis(trichloromethyl) carbonate (BTC) method. Besides, the anthracene modified poly(vinyl alcohol) (An-PVA) with anthracene units fixed on the chain of PVA was synthesized from PVA and 2-An-NCO and used to compare with the An-PR.

In addition, a model compound to the 2-anthrylcarbamate group, methyl 2-anthrylcarbamate (An-Car) was synthesized which was used to determine the modification degree of the anthracene unit in the An-PR and the An-PVA.

Synthesis of PEG-Carboxylic Acid (PEG-COOH). PEG (10 g, 0.50 mmol), TEMPO (0.044 g, 0.28 mmol) and NaBr (0.21 g, 2.08 mmol) were dissolved in 100 mL of NaHCO₃ buffer solution with pH 8.5 followed by addition of 1.2 mL of aqueous NaClO. The reaction solution was stirred at room temperature for 15 min and then quenched by 10 mL of anhydrous ethanol. The solution was acidified with aqueous HCl to pH < 3 and extracted with DCM for three times. The combined DCM layers were dried under reduced pressure and dissolved in 250 mL of ethanol of 40 °C, followed by precipitation in a freezer overnight. The separated crystal was precipitated in 400 mL anhydrous ethyl ether and dried *in vacuo* overnight. The product PEG-COOH was in 92 % yield with M_w of 19314 and M_w/M_n of 1.4. The carboxyl content was determined to be 0.0586 mmol g⁻¹ by titration with 0.01 M aqueous NaOH. ¹H NMR (DMSO-*d*₆): δ 4.00 (s, 2H, -CH₂-COOH), 3.52 (m, ca. 1810H, [CH₂CH₂O]_n). FTIR (cm⁻¹): 3466 (ν_{OH of COOH}), 2888 (ν_{CH}), 1099 (ν_{C-O-C}).

Synthesis of PEG/α-CD-Based Polyrotaxane (PEG/α-CD-based PR).^{S2} PEG-COOH (5.0 g 0.26 mmol) and α-CD (15.0 g 15.42 mmol) were dissolved in 150 mL of DI water. The solution was stirred at 70 °C for 2 h and then cooled to 35 °C which was kept for 24 h to give a white paste-like raw *pseudo*-polyrotaxane. The freeze-dried raw *pseudo*-polyrotaxane (20 g) was mixed with 1-adamantanamine (1.87 g, 12.38 mmol), BOP (1.11 g, 2.50 mmol) and DMAP (0.72 g, 5.86 mmol) in 130 mL of DMF. The mixture was stirred under argon at room temperature for 24 h followed by centrifugation. The solid was washed by centrifugation two times respectively with DMF/methanol (1 : 1) and methanol. The DMSO solution of the obtained solid was

precipitated into plenty of water and the precipitate was repeatedly washed with DI water by centrifugation. Freeze-drying gave the polyrotaxane as a white solid in 86 % yield. The number of α -CD molecules per chain was 51 according to the calculation method in literature,⁵² which is corresponded to an inclusion ratio of ca. 19 %. ¹H NMR (DMSO-*d*₆): δ 6.79 (s, 2H, -NH-CO-), 5.62 [s, ca. 306H, O(2)H of α -CD], 5.47 [s, ca. 306H, O(3)H of α -CD], 4.79 [s, ca. 306H, C(1)H of α -CD], 4.41 [t, ca. 306H, O(6)H of α -CD], 3.49 (m, ca. 1810H, [CH₂CH₂O]_n), 3.20 - 3.80 [ca. 1500H, C(2)H, C(3)H, C(5)H and C(6)H of α -CD], 2.31 (s, 2H, adamantane), 1.92 (s, 2H, adamantane), 1.61 (s, 2H, adamantane). FTIR (cm⁻¹): 3426 (ν_{OH}), 2903 (ν_{CH}), 1646 ($\nu_{C=O}$), 1154 (ν_{C-O-C} of PEO), 1028 (ν_{C-O-C} of α -CD).

Synthesis of 2-Aminoanthracene (An-NH₂).⁵³ 2-Aminoanthraquinone (20.0 g, 89.59 mmol) and activated zinc powder (20.0 g, 307.7 mmol) were added to 100 mL of 10 % aqueous NaOH. This suspension was stirred for 1 h at 40 °C and then refluxed for 1 h at 80 °C. After another 20.0 g of activated zinc powder was added, the suspension was continuously stirred for 24 h at 80 °C. The whole reaction process was under argon. The reaction solution was acidified with aqueous HCl to pH 7 to give precipitate which was washed by plenty of DI water. This precipitate was then extracted with DCM. Dried the above DCM solution under reduced pressure gave product of 2-aminoanthracene as yellowish green solid in 78% yield. ¹H NMR (DMSO-*d*₆): δ 8.27 [s, 1H, C(9)H], 8.03 [s, 1H, C(10)H], 7.90 [d, 1H, C(5)H], 7.86 [d, 1H, C(8)H], 7.81 [d, 1H, C(4)H], 7.36 [t, 1H, C(7)H], 7.28 [t, 1H, C(6)H], 7.04 [d, 1H, C(3)H], 6.89 [s, 1H, C(1)H], 5.55 (s, 2H, -NH₂). FTIR (cm⁻¹): 3333 (ν_{NH}), 3043 (ν_{arC-H}), 1638 (β_{NH}), 1482, 1459 (ν_{arC-C}), 889, 740 (ν_{arC-H}).

Synthesis of 2-Anthrylcarbamate Polyrotaxane (An-PR). Firstly, the An-NH₂ was isocyanated with bis(trichloromethyl) carbonate method. BTC (1.25 g, 2.12 mmol) was dissolved in 30 mL of DCM and the solution was cooled to -10 °C under argon via an additional funnel. An-NH₂ (1.22 g, 6.34 mmol) and TEA (1.25 g, 12.37 mmol) dissolved in 125 mL of DCM was added dropwise to this solution in 20 min. The reaction was stirred at -10 °C for another 1 h and then stirred at 30 °C for 1 h. The

solution was washed with 1.0 M HCl aqueous solution twice and the organic layer was dried with magnesium sulfate and filtered. Evaporation of all the DCM gave dark green solid of raw product of 2-anthryl isocyanate (An-NCO) which was used directly in the following reaction.

Then the An-PR was synthesized through the reaction between the An-NCO and the PEG/ α -CD based PR. The raw product of the An-NCO obtained in the above step and the PR (0.36 g, 5.18 μ mol) were dissolved in 80 mL of DMSO. After addition of catalyst of stannous octanoate (0.016 g, 39 μ mol), the solution was stirred under argon for 48 h at 60 °C. The reacted solution was filtered and the filtrate was distilled under reduced pressure to remove of all the DMSO. The resulted solid was washed with methanol thrice followed by dissolved in 15 mL of DMF and precipitated in plenty of ethyl ether. The precipitate was washed with ethyl ether until the supernatant was colorless followed by DI water washing to give black solid as product of 2-An-PR (0.28 g). ^1H NMR (DMSO- d_6): δ 9.88 (s, -NH-COO-), 8.80 – 7.00 (anthryl), 6.25 – 5.38 O(2,2',3,3')H of CD, 5.20 – 4.73 C(1,1')H of CD, 4.68 – 4.29 O(6,6')H of CD, 3.51 (m, ca. 1810H, [CH₂CH₂O]_n), 3.20 – 4.00 [ca. 1500H, C(2,2')H, C(3,3')H, C(5,5')H and C(6,6')H of CD], 2.31, 1.92, 1.61 (adamantane). FTIR (cm⁻¹): 3381 (ν_{OH}), 3320 (ν_{NH}), 3053 ($\nu_{\text{arC-H}}$), 2874 (ν_{CH}), 1718 ($\nu_{\text{C=O}}$), 1641, 1552, 1462 ($\nu_{\text{arC-C}}$), 1081 ($\nu_{\text{C-O-C}}$ of PEO), 1041 ($\nu_{\text{C-O-C}}$ of α -CD).

Synthesis of Methyl 2-Anthrylcarbamate (An-Car). First of all, the An-NH₂ (1.22 g, 6.34 mmol) was isocyanated with the same method in the preparation of the 2-An-PR. Then the raw product of the An-NCO was dissolved in 100 mL chloroform, followed by the addition of 18 mL methanol. After adding the catalyst of stannous octanoate (0.0792 g, 0.193 mL), the solution was stirred under argon for 24 h at 60 °C. Evaporation of the solvent and unreacted methanol gave the raw product of An-Car which was purified by column chromatography with *n*-hexane/ethyl acetate (4 : 1) to get brown solid of 2-An-Car in 76% yield. ^1H NMR (DMSO- d_6): δ 9.97 [s, 1H, -NH-], 8.47 [s, 1H, C(9)H], 8.42 [s, 1H, C(10)H], 8.27 [s, C(4)H], 8.07 – 7.99 [m, 3H, C(5,8,1)H], 7.57 [d, 1H, C(3)H], 7.52 – 7.40 [m, 2H, (7,6)H]. ^{13}C NMR (DMSO- d_6): δ

154.14, 136.22, 131.74, 130.23, 128.88, 128.26, 128.06, 127.63, 125.85, 125.58, 124.77, 124.60, 120.56, 112.18, 51.78. FTIR (cm^{-1}): 3265 (ν_{NH}), 3054 ($\nu_{\text{arC-H}}$), 2945 ($\nu_{\text{C-H}}$), 1698 ($\nu_{\text{C=O}}$), 1557 ($\nu_{\text{arC-C}}$), 895, 738 ($\nu_{\text{arC-H}}$).

1.4 Preparation of Gels

Preparation of Topological Gels Based on An-PR by UV Irradiation. An-PR was dissolved in deoxygenated DMSO to give the solution which was irradiated under inert gas atmosphere (N_2) at room temperature with a PLS-SXE300UV Xe lamp (PerfectLight Sci. & Tech. Co. Ltd.) equipped with a filter of which transmission wavelengths are longer than 360 nm. In the experiments, the distance between the lamp and the solution was 20 cm, and the light intensity at the sample surface was 45 mW cm^{-2} .

In the experiment to investigate the mechanism of the sol-gel reversible transition of the 2-An-PR solution, a 15 wt% An-PR DMSO solution was prepared in a 2-mL vial and irradiated by a Xe lamp. After 3 h, a gel formed. Then the gel was heated at $70 \text{ }^\circ\text{C}$ for 24 h and it turned to the sol. This sol-gel-sol transition process was repeated for four UV irradiation/heating cycles.

For the preparation of the **an-PR** gel, a 10 wt% An-PR DMSO solution was prepared which was sealed between two quartz plates with distance of 0.5 mm and irradiated by the Xe lamp for 10 h. The formed gel was washed thoroughly with DMSO for 3 d to remove any uncross-linked An-PR or reaction residue and incubated in DMSO to fully swell before further characterizations.

1.5 Structure Investigation of An-PR before and after Dimerization through UV Irradiation and after Thermal Dissociation of the Anthracene Dimer

Investigation with ^1H NMR Spectroscopy. An-PR was dissolved in deoxygenated DMSO- d_6 in NMR sample tube and the ^1H NMR spectrum of the sample was recorded. Then the tube was irradiated under inert gas atmosphere (N_2) at room temperature for 6 h with the PLS-SXE300UV Xe lamp equipped with the filter of which

transmission wavelengths are larger than 360 nm. The distance between the lamp and the NMR sample tube is 20 cm, and the light intensity at the sample surface was 45 mW cm⁻². After the UV irradiation, the NMR sample was performed ¹H NMR spectroscopy measurement again.

Investigation with UV-Vis Spectroscopy. An-PR was dissolved in deoxygenated DMSO to give a solution of which concentration was about 4 × 10⁻⁵ mol L⁻¹ and the UV-Vis spectrum of the sample was recorded. Then the solution was added in a 10-mL vial which was irradiated under inert gas atmosphere (N₂) at room temperature for 6 h with the PLS-SXE300UV Xe lamp equipped with the filter whose transmission wavelengths are longer than 360 nm. The distance between the lamp and the vial is 20 cm, and the light intensity at the sample surface was 45 mW cm⁻². After the UV irradiation, the sample's UV-Vis spectrum was recorded again. The irradiated sample was then heated to 70 °C and kept this temperature for 24 h, after which the sample's UV-Vis spectrum was recorded.

2 Further Results

2.1 Characterization of the PEG/ α -CD-based PR

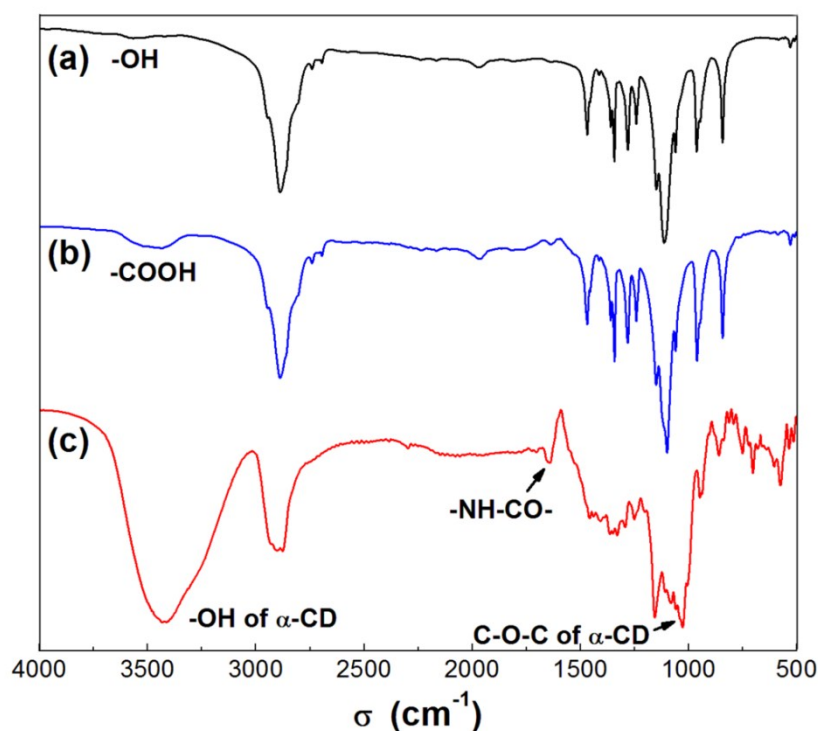


Fig. S1 FTIR spectra of (a) PEG, (b) PEG-COOH and (c) PEG/ α -CD-based PR.

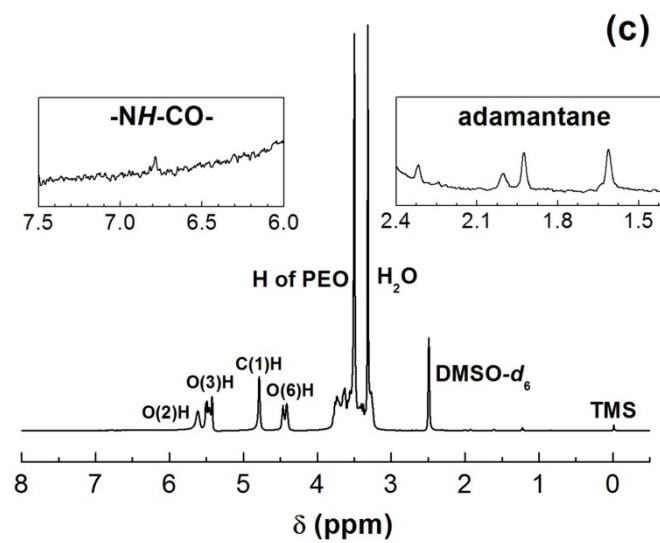
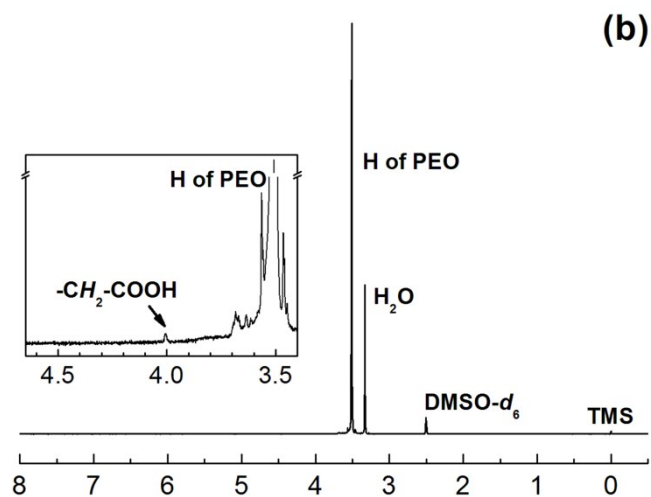
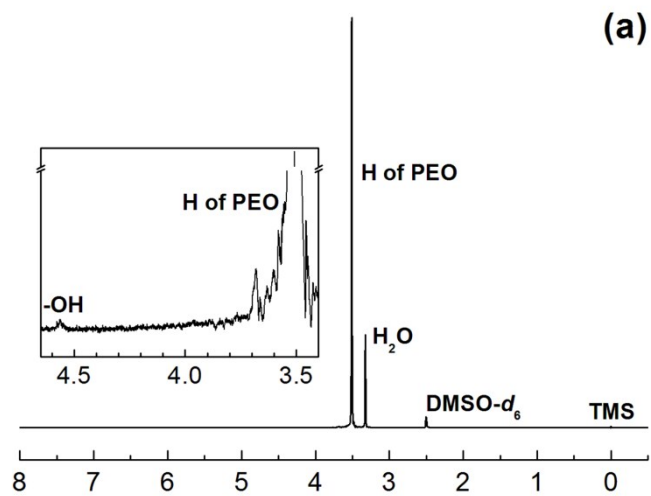


Fig. S2 ^1H NMR spectra of (a) PEG, (b) PEG-COOH and (c) PEG/ α -CD-based PR.

2.2 Characterization of the An-NH₂

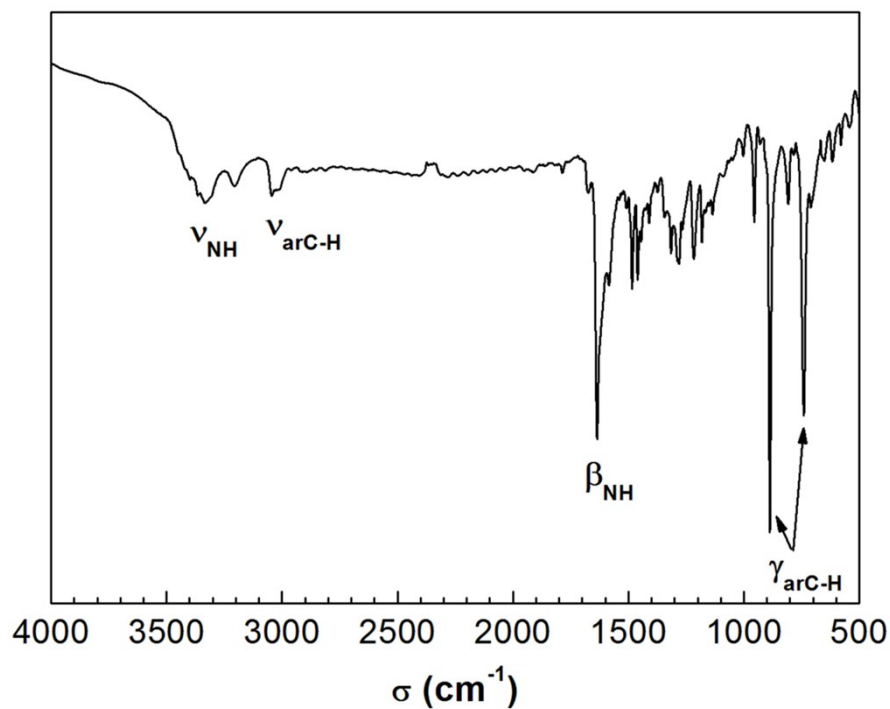


Fig. S3 FTIR spectrum of the An-NH₂.

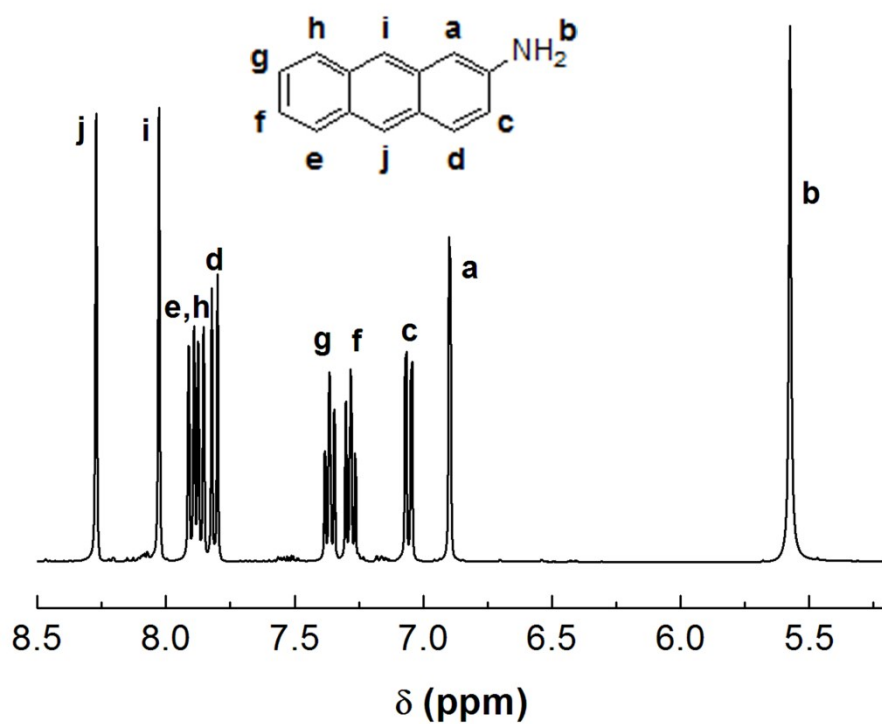


Fig. S4 ^1H NMR spectrum of the An-NH₂.

2.3 Characterization of the An-Car

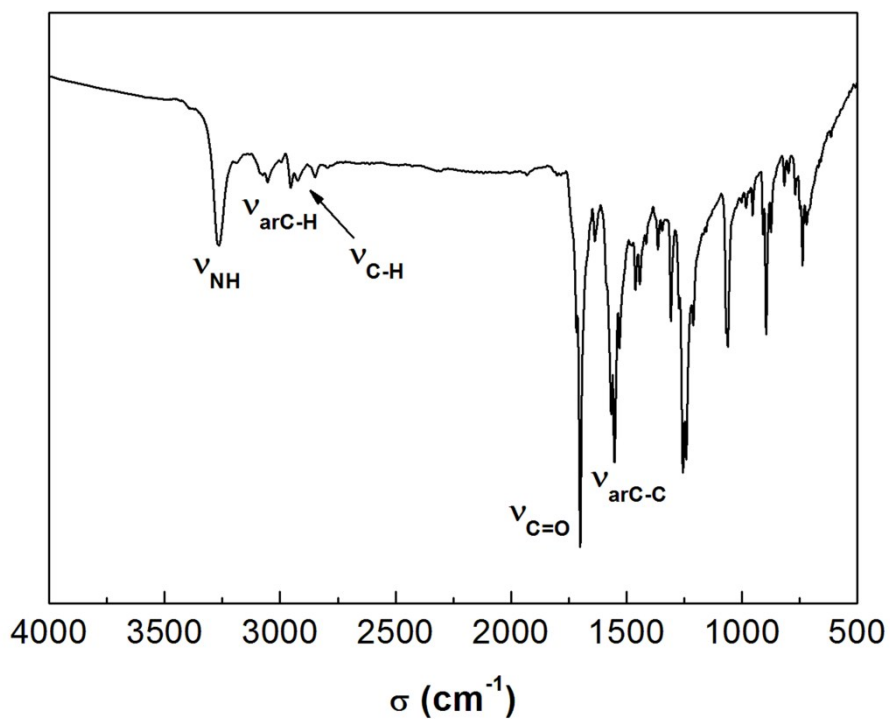


Fig. S5 FTIR spectrum of the An-Car.

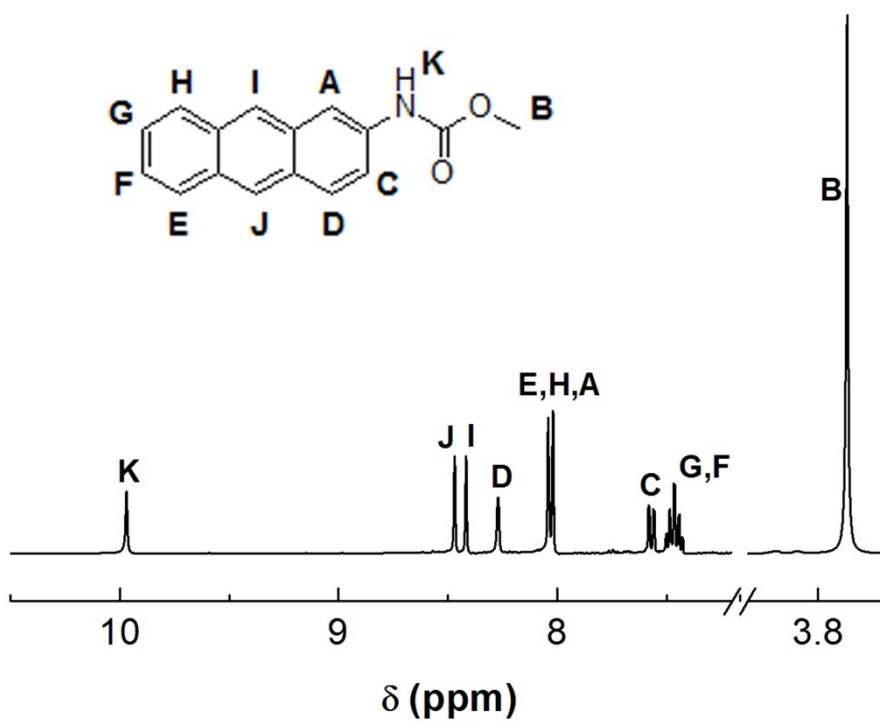


Fig. S6 ^1H NMR spectrum of the An-Car.

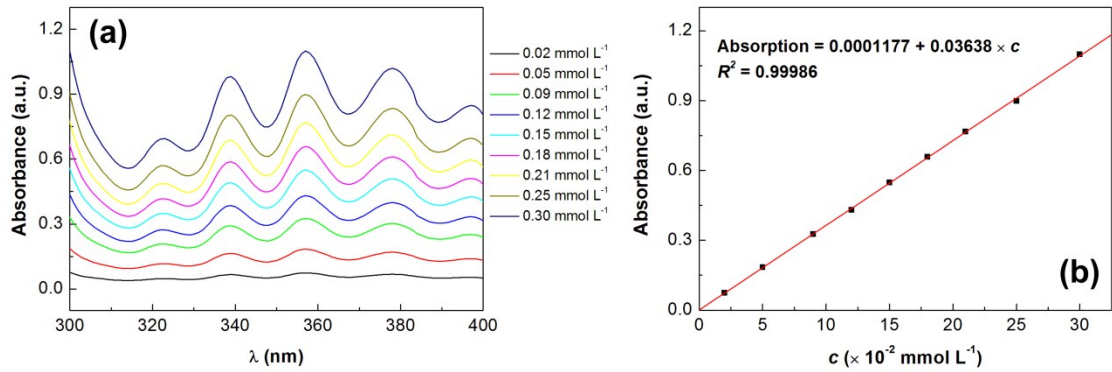


Fig. S7 (a) Absorption spectra of An-Car in DMSO with different concentrations. (b) Standard curve of absorption of An-Car in DMSO with wavelength of 357 nm (The red Line is the linear fitted curve).

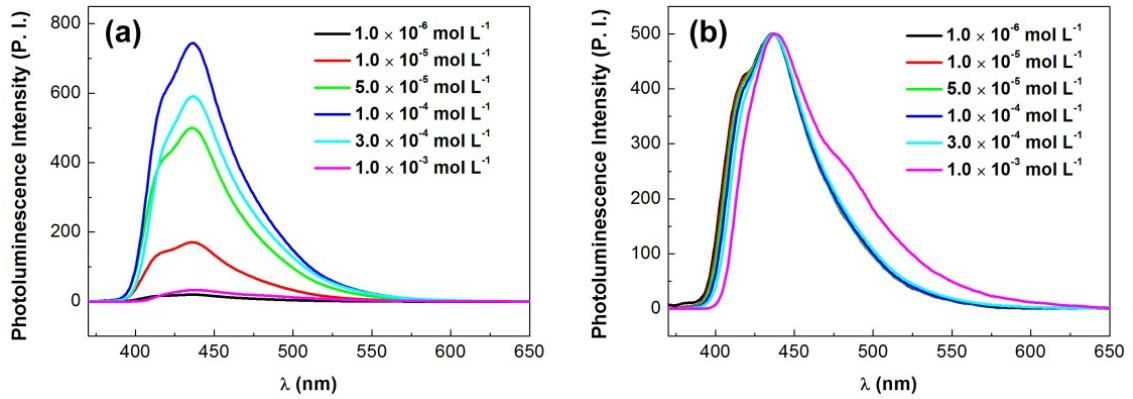


Fig. S8 (a) Pristine and (b) normalized fluorescence emission spectra of An-Car in DMSO with different concentrations ($\lambda_{\text{ex}} = 360 \text{ nm}$).

2.4 Repeated Sol-Gel-Sol Transitions of An-PR Solution

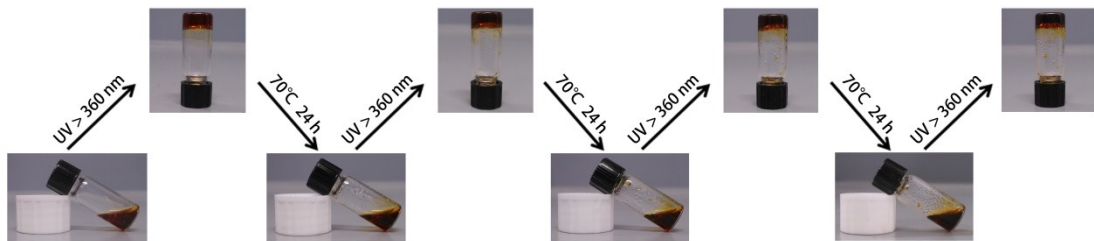


Fig. S9 Photographs of repeated sol-gel-sol transitions of DMSO solution of An-PR

under repeated UV irradiation/heating cycles.

2.5 Internal Morphology of the anth-PR Gel

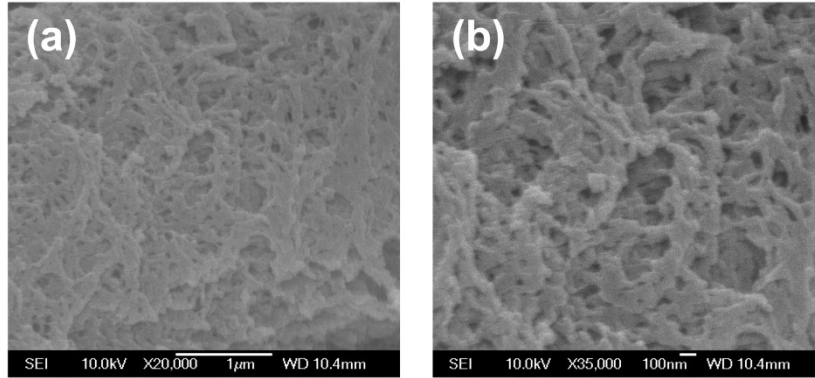


Fig. S10 SEM images of the sectioned surface of freeze-dried **anth-PR** gel with magnifications being (a) 20000 and (b) 35000 times the original size.

2.6 Fluorescent Property of the anth-PR Gel and Its Pregel Solution

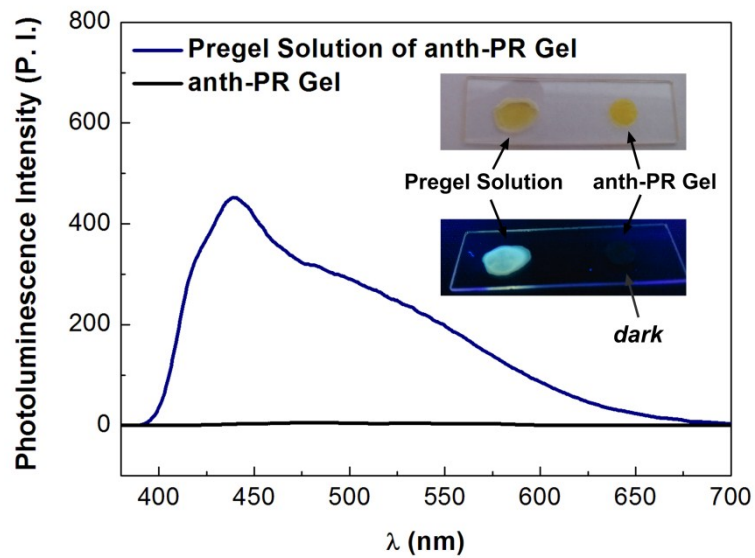


Fig. S11 Fluorescence emission spectra of pregel solutions and gel formed by > 360 nm UV-irradiating the pregel solutions at room temperature for 10 h of **anth-PR** gel. The excitation wavelength used to take the emission spectra is 360 nm. Insets are photographs of the pregel solutions and the gel under daylight and 365 nm UV light.

3 References

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