

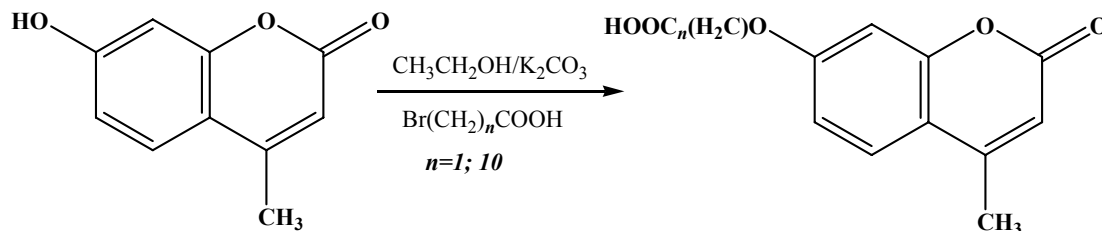
Photoinduced Bending of A Coumarin-Containing Supramolecular Polymer

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1. Materials

All chemicals were purchased from Aldrich and used as received. The coumarin-containing carboxylic acids were synthesized according to a modified literature method (Scheme 1).¹



Scheme S1. Synthesis of coumarin-containing carboxylic acids

Synthesis of 7-(carboxymethoxy)-4-methylcoumarin (n=1): 2-Bromoacetic acid (2.0 g, 14.5 mmol), 7-hydroxy-4-methylcoumarin (2.0 g, 11.3 mmol), potassium carbonate (4.8 g, 35 mmol), a trace of potassium iodide and 150 mL of ethanol were placed into a 250 mL round bottomed flask equipped with a magnetic stirrer and heated under reflux for 20 h. The mixture was then poured into 200 mL of water, and the pH value of the solution was adjusted to be ~ 5 by adding hydrochloric acid (5 wt%). After evaporation of the ethanol at room temperature, a white precipitate was filtered off, and washed with water twice. Yield: 64%. MS (m/e): 234 (M^+). ^1H NMR (d_6 -DMSO, ppm, δ): 13.1 (w, 1H, -COOH), 7.7 (d, 1H, aromatic hydrogen), 6.9 (t, 2H, aromatic hydrogen), 6.2 (m, 1H, =C-H), 4.8 (m, 2H, -CH₂-), 2.3 (m, 3H, -CH₃).

Synthesis of 7-(carboxydecyloxy)-4-methylcoumarin (n=10): It was prepared by using the same procedure as described above, only with 11-bromoundecanoic acid replacing 2-bromoacetic acid. Yield: 58%. MS (m/e): 360(M^+). ^1H NMR (d_6 -DMSO, ppm, δ): 12.1 (w, 1H, -COOH),

7.67 (d, 1H, aromatic hydrogen), 6.94 (d, 2H, aromatic hydrogen), 6.2 (m, 1H, =C-H), 4.1 (t, 2H, -CH₂-), 2.35 (m, 3H, -CH₃), 2.16 (t, 2H, -CH₂-), 1.69 (m, 2H, -CH₂-), 1.5~1.0 (m, 14H, -CH₂-).

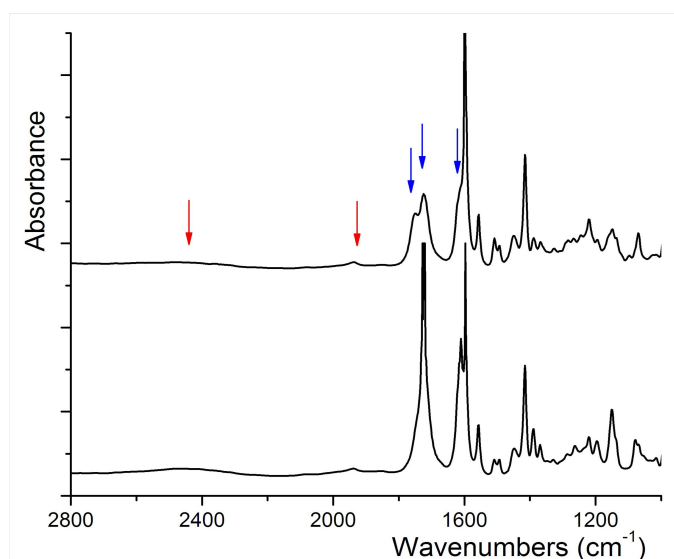
Complexation of poly(4-vinyl pyridine) (P4VP) with 7-(carboxymethoxy)-4-methylcoumarin (CMC) and preparation of free-standing films

For example, to prepare the sample of P4VP-CMC (10 mol% of CMC), 0.2 g of P4VP and 0.05 g of CMC were dissolved in 1.8 g DMF, the solution was stirred at room temperature for 24 h. Afterwards, the solution was cast onto a mold made with Teflon. After the removal of most solvent at room temperature, the film was further dried at 120°C for 12 h in a vacuum oven. The dried film of P4VP-CMC could easily be peeled off from the Teflon surface.

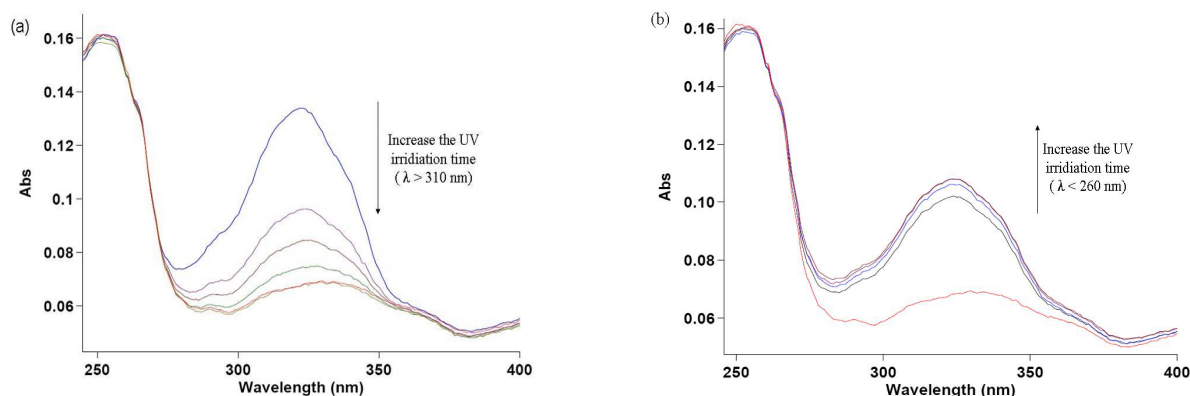
2. Characterizations

¹H NMR spectra were obtained using a Bruker Spectrometer (300 MHz, AC 300). Mass spectra were recorded on a Micromass ZAB-1F high-resolution mass spectrometer. Transmission FT-IR spectra were recorded on a Nicolet Avatar 370 spectrometer. Reflectance FT-IR spectra were recorded on a Nicolet Nexus 470 spectrometer equipped with accessories for reflectance spectra. UV-vis spectra were taken using a Varian 50 Bio spectrophotometer. A Perkin-Elmer DSC-7 differential scanning calorimeter was utilized to measure the glass transition temperature T_g of the samples (calibration with indium and heating rate of 10 °C min⁻¹). T_g was taken as the midpoint of the step change in the heat flow. The photocrosslinking was performed by applying the UV light to one surface of the film placed in a home-made thermostat stage. Using a flexible light guide from a UV-Vis spot curing system (Novacure), UV light with adjustable spot size could easily be directed to the film. For the photodimerization of coumarin, a 320-500 nm filter was used to generate UV light at $\lambda > 310$ nm (~750 mW cm⁻²), while for the photodimerization of anthracene, a 365 nm filter was used to obtain UV light centered at 365 nm (~90 mW cm⁻²). Finally, a UV-C Air sterilizer lamp (1.25 W) peaked at $\lambda = 254$ nm was used for photocleavage of cyclobutane (photodecrosslinking).

3. Infrared and UV-Vis Spectra of P4VP-CMC

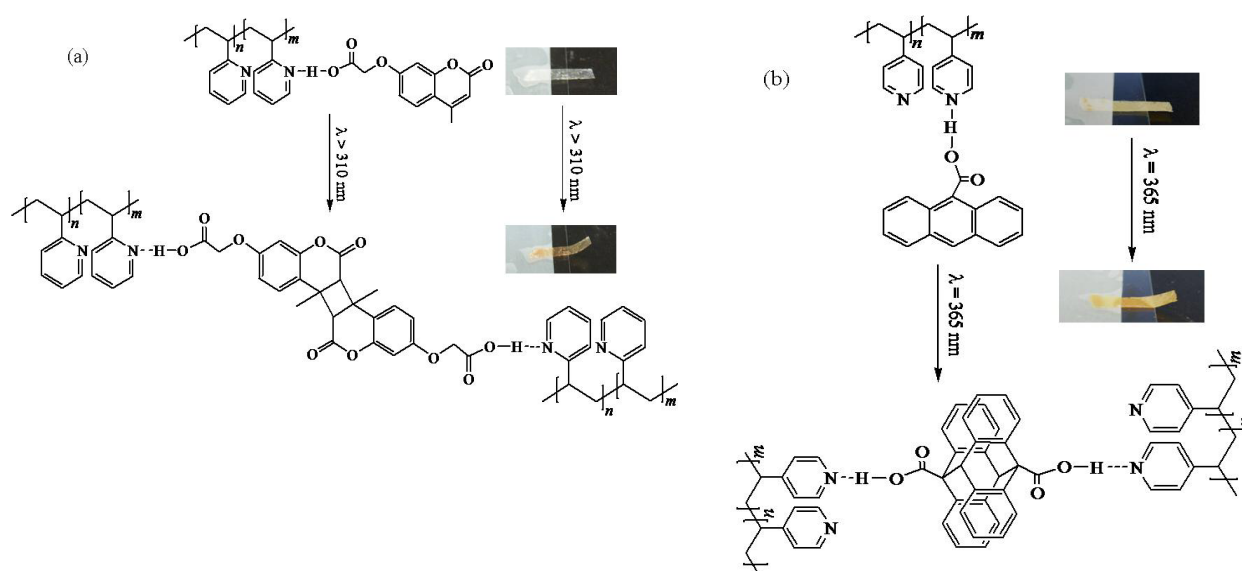


Supporting Figure 1. Transmittance IR spectra of a film of P4VP-CMC (10 mol% of CMC) before (down) and after (top) UV irradiation for photocrosslinking ($\lambda > 310$ nm). Compared the spectrum before UV irradiation, the spectrum after UV irradiation displays a new absorption band for C=O at 1750 cm^{-1} and a decrease in the intensity for the C=O band at 1720 cm^{-1} and the C=C band at $\sim 1610\text{ cm}^{-1}$ (marked by blue arrows), which confirms the photodimerization of coumarin groups.² On the other hand, the characteristic H-bonds between pyridine and carboxylic acid units, appearing around 1940 and 2500 cm^{-1} (marked by red arrows),³ can be noticed before and after the UV irradiation.



Supporting Figure 2. UV-vis spectra for a film of P4VP-CMC (10 mol% of CMC) recorded at 115°C: (a) upon UV irradiation at $\lambda > 310$ nm, the decrease in absorbance at ~ 320 nm indicates the photodimerization of coumarin groups, and (b) upon subsequent UV irradiation and $\lambda < 260$ nm, the partial recovery of the absorbance indicates a partial photocleavage of cyclobutane groups. The spectra were taken with a time interval of 1 min. The film used in this experiment, solution cast and dried on a quartz plate, was much thinner than those used for the photoinduced bending experiments.

3. Photoinduced Bending of Other Systems



Supporting Figure 3. Photographs showing the photoinduced bending for (a) a film of poly(2-vinyl pyridine) (P2VP) complexed with 10 mol% of CMC, upon UV irradiation at $\lambda > 310$ nm (750 mW cm^{-2}) and 90°C ; and (b) a film of P4VP complexed with 10 mol% of an anthracene carboxylic acid, upon UV irradiation at $\lambda = 365$ nm (90 mW cm^{-2}) at 115°C . Irradiation time in both cases is 15 min.

References

- (1) J. Jiang, B. Qi, M. Lepage and Y. Zhao, *Macromolecules* 2007, 40, 790-792.
- (2) J. Motoyanagi, T. Fukushima, N. Ishii and T. Aida, *J. Am. Chem. Soc.*, 2006, 128, 4220-4221.

Supplementary Material (ESI) for Soft Matter

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(3) T. Kato, N. Hirota, A. Fujishima and J. M. J. Frechet, *J. Polym. Sci., Part A, Polym. Chem.*, 1996, 34, 57-62.