

Aggregation induced emission of azobenzene towards a sensitive indication on the self-assembly of cellulose material

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1. General remarks

2. Synthesis of ammonium surfactant AZO

3. Synthesis of CMC-AZO

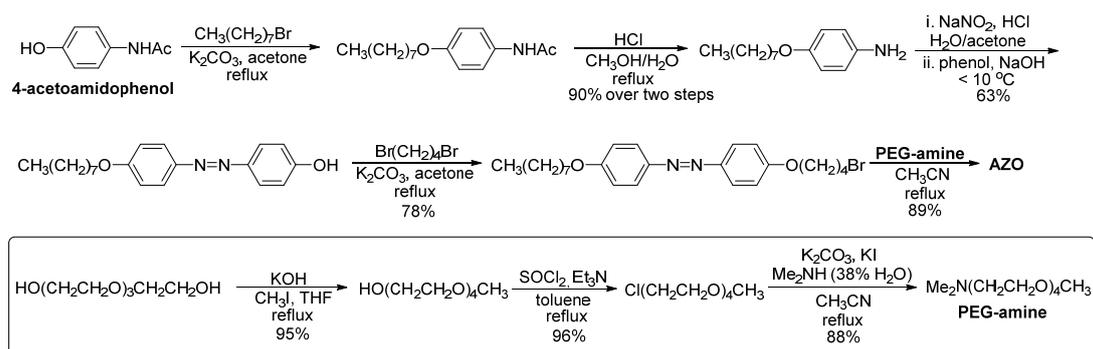
4. Characterizations of AZO and CMC-AZO

1. General remarks

Materials: carboxymethyl cellulose sodium (CMC-Na) used for the preparation of cellulose complexes was purchased from TCI (Shanghai) Development Co., Ltd., with the following characteristics: 1) chemical formula: $[C_6H_7O_2(OH)_x(OCH_2COONa)_y]_n$, $n \approx 500$; 2) appearance: white to light yellow powder to crystal; 3) content (Na, drying substance): 6.0 to 8.5 %; 4) etherification value (as drying substance): 0.5 to 0.8; 5) drying loss: max. 10.0 %; 6) viscosity: 500.0 to 900.0 mPa.s (2 %, H₂O, 25 °C). All the chemicals used for the synthesis of AZO were purchased and used directly. All the aqueous solutions were prepared using ultrapure water through a Millipore Milli-Q 185 water purification system (Millipore, USA).

Characterizations of AZO and CMC-AZO: ¹H NMR and ¹³C NMR spectra were recorded on Bruker Avance 500 (500 and 125 MHz, respectively) or Bruker Avance 400 (400 and 100 MHz, respectively) with CDCl₃ as solvent. Chemical shifts were determined relative to the residual solvent peaks (CHCl₃, $\delta = 7.26$ ppm for ¹H NMR, $\delta = 77.0$ ppm for ¹³C-NMR). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. TGA was carried out using a Netzsch STA 449C thermal analyzer in a nitrogen atmosphere and with a heating/cooling rate of 10 °C min⁻¹. POM was conducted on a Nikon ECLIPSE LV100NPOL machine with a computational controlled heating plate. TEM was performed by a JEOL JEM-2100PLUS electron microscope machine. SAXS was performed by employing a conventional X-ray source with radiation wavelength of $\lambda = 1.54$ Å. The sample holder is a metal plate with a small hole (diameter ≈ 0.5 cm, thickness ≈ 0.5 cm), where the X-ray beam passes through and the sample-to-detector distance was 18 cm. The scattering vector q is defined as $q = 4\pi \sin\theta/\lambda$ with 2θ being the scattering angle. Fluorescence spectra were recorded by using a F-4600 fluorescence spectrophotometer from Hitachi, Japan. PL quantum yields and lifetimes were measured by using FLS1000 from Edinburgh Instruments, UK. The excitation source is 365 nm UV light. The UV-Vis absorption spectra in solution were recorded on a Shimadzu UV-2600 UV-Vis spectrophotometer, and all the related studies were carried out on fast scan mode with slit widths of 1.0 nm, using matched quartz cells. Test solutions were 200 μ L. The wavelengths of UV and Vis photoirradiations are 365 nm (32 mW cm⁻²) and 520 nm (95 mW cm⁻²), respectively. All spectral scans were saved as ACS II files and further processed in OriginLab software to produce all graphs shown.

2. Synthesis of ammonium surfactant AZO



Scheme S1. Synthesis of ammonium surfactant AZO.

Ammonium surfactant AZO was synthesized by following our reported work, which affords the light orange solid in 39% yield over 5 steps.¹ ¹H NMR (500 MHz, CDCl₃): δ 7.84-7.82 (m, 4 H), 6.98-6.95 (m, 4 H), 4.09 (t, *J* = 6.0 Hz, 2 H), 4.01-3.95 (m, 4 H), 3.88-3.87 (m, 2 H), 3.76-3.72 (m, 2 H), 3.64-3.62 (m, 2 H), 3.57-3.56 (m, 8 H), 3.50-3.49 (m, 2 H), 3.38 (s, 6 H), 3.33 (s, 3 H), 2.03-1.97 (m, 2 H), 1.92-1.89 (m, 2 H), 1.81-1.76 (m, 2 H), 1.48-1.42 (m, 2 H), 1.35-1.23 (m, 8 H), 0.87 (t, *J* = 6.5 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 161.2, 160.4, 147.1, 146.7, 124.3, 114.62, 114.60, 71.8, 70.4, 70.33, 70.30, 70.28, 70.1, 68.3, 67.0, 65.4, 64.9, 63.2, 58.9, 51.9, 31.7, 29.3, 29.14, 29.12, 25.93, 25.86, 22.6, 19.8, 14.0.

3. Synthesis of CMC-AZO

The aqueous solution of AZO (26.4 mM, 500 μL) was added into the aqueous CMC solution (103.2 μM, 256 μL) using a pipette, which led to the precipitate of CMC-AZO complex. The precipitate was purified with water-washing and then by centrifugation over three times to provide the wet sample. After a lyophilization, the needed ionic CMC-AZO material could be afforded. Note: the preparation of CMC-AZO is based on the assumption that one sugar unit contains one negative charge.

4. Characterizations of AZO and CMC-AZO

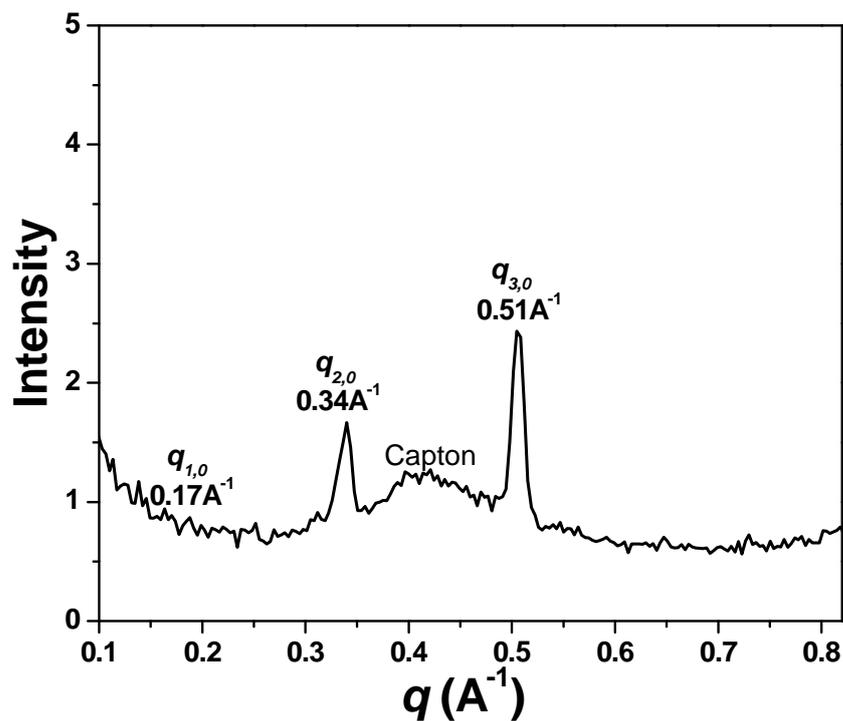


Figure S1. The SAXS profile of AZO, giving one weak peak at 0.17 \AA^{-1} and two following harmonic peaks at 0.34 and 0.51 \AA^{-1} , which indicate an ordered structure of AZO.

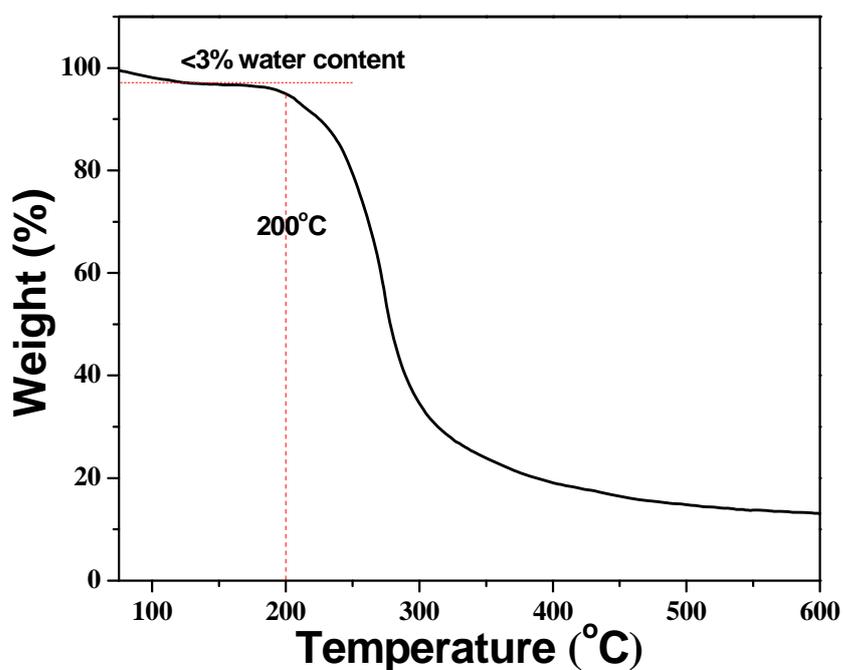


Figure S2. TGA profile of CMC-AZO, indicating the water content less than 3% and thermal integrity higher than $200 \text{ }^\circ\text{C}$.

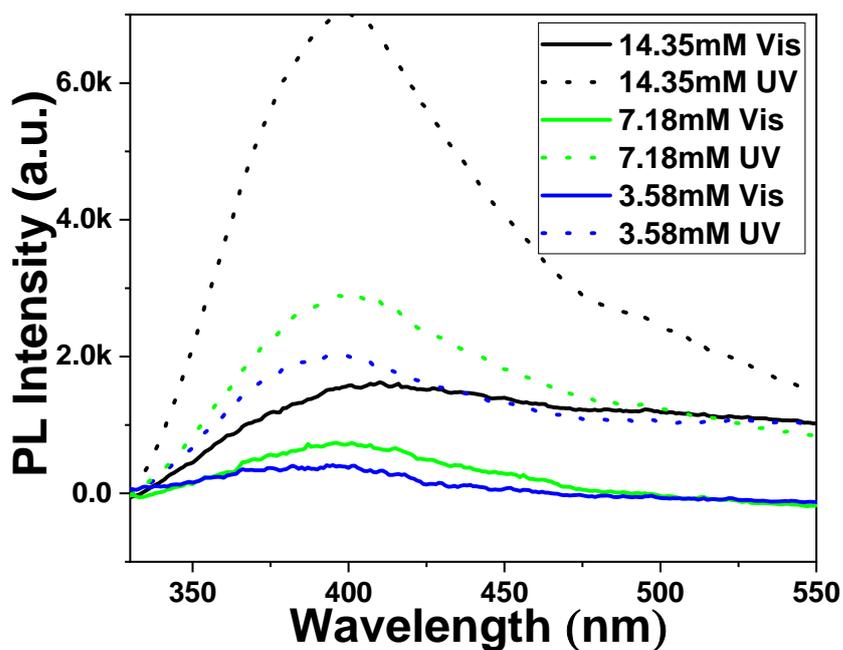


Figure S3. PL investigation of AZO with concentrations from 14.35 to 3.58 mM after UV and Vis irradiation in aqueous condition. With high concentrations of 14.35~3.58 mM, *trans*-AZO exhibited decreased PL intensity along with the concentration decrease. *Cis*-AZO showed higher PL intensity than that of *trans*-AZO for each specific concentration, which should be caused by the UV-promoted dissolving of *cis*-AZO into water.

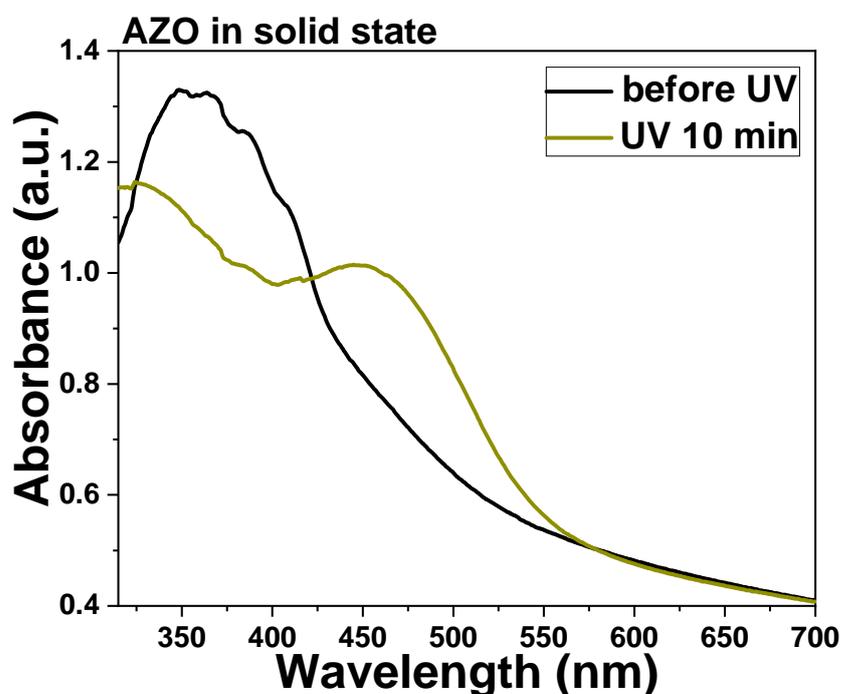


Figure S4. The UV-Vis absorption change of solid-state AZO after UV irradiation, indicating a UV light-induced *trans-cis* isomerization.

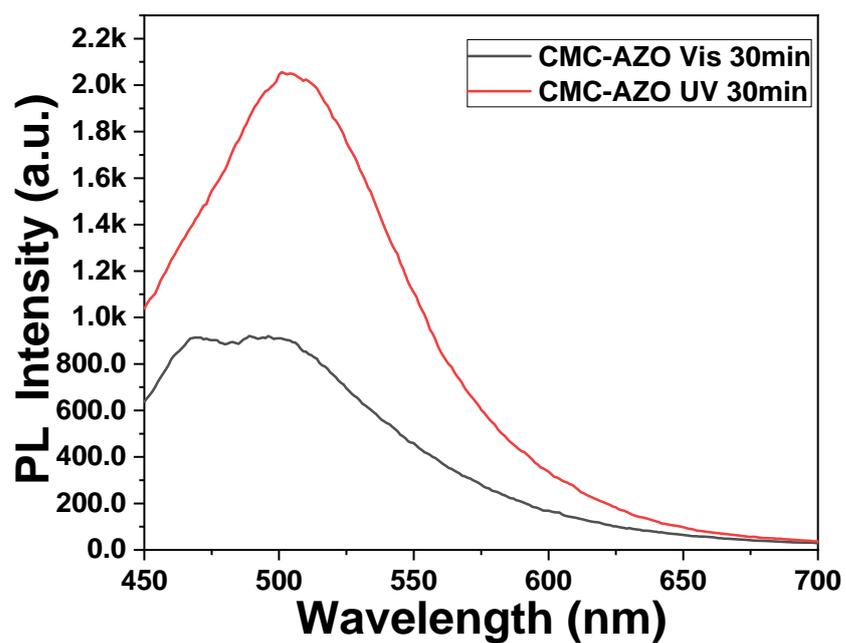


Figure S5. PL spectra of CMC-AZO dissolving into water under UV light and Vis light, respectively, indicating that UV illumination promotes the dissolving process.

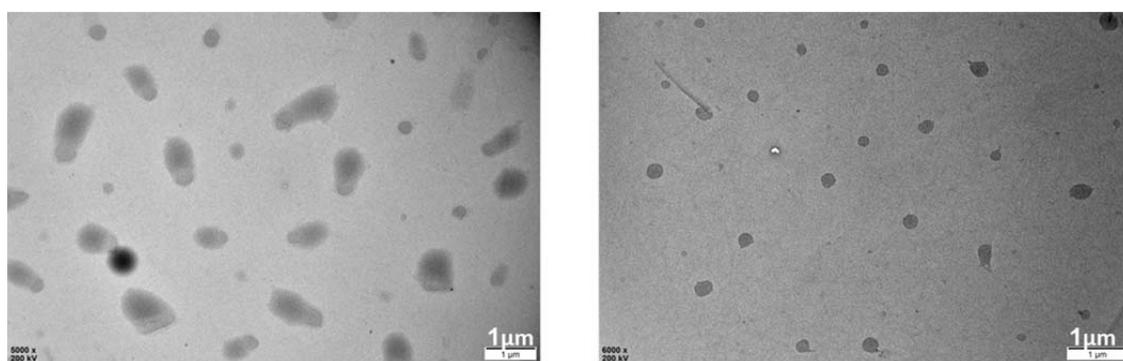


Figure S6. TEM images of saturated aqueous solution of CMC-AZO aggregates after UV irradiation. UV irradiation can promote the formation of small assemblies in aqueous condition, resulting in a well dispersion of CMC-AZO aggregates in water.

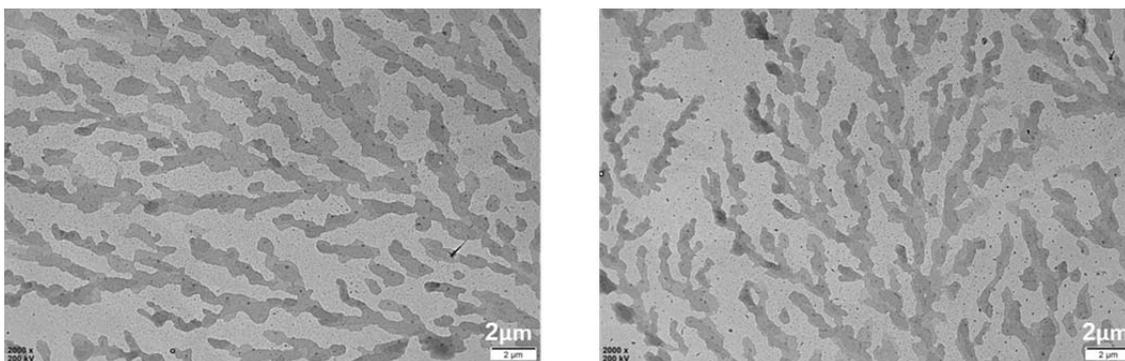


Figure S7. TEM images of saturated aqueous solution of CMC-AZO aggregates after Vis irradiation.

After Vis irradiation, much larger assemblies formed, which led to the formation of precipitate.

References

1. L. Zhang, Z. Tang, L. Hou, Y. Qu, Y. Deng, C. Zhang, C. Xie and Z. Wu, Selective mercury(II) detection in aqueous solutions upon the absorption changes corresponding to the transition moments polarized along the short axis of an azobenzene chemosensor, *Analyst*, 2020, **145**, 1641-1645.