Self-Assembly Triggered Cis-to-Trans Conversion of Azobenzene Compounds

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1. Materials and Methods:

1) Synthesis of the bisligand Azo-C4-L2:



Chart S1: Synthesis protocol of AZo-C4-L2 (compound 9).

Synthesis of compound 2. 136g of sodium ethanol was dissolved in 500 mL of ethanol, the obtained solution was divided into two uniform parts for standby application. 58g of anhydrous acetone and 150g of diethyl oxalate (compound 1) were mixed in a 3L flask, slowly added into one of stocked sodium ethanol solution at room temperature, during the adding process, the temperature had a distinct increase, the solution gradually became thick and separated out plenty of yellow solid. Then, dropwise added other 160 g of diethyl oxalate and remaining part of sodium ethylate into the reaction liquid. The colour of the reaction liquid became dark. Continue stirring for 30 minutes, the reaction liquid had a large number of solid precipitation. Heat the reaction liquid to 120° C, after distilling 150 mL of ethanol, add 300 mL of concentrated hydrochloric acid and 800 mL of water, the mixture was reacted under 100° C for 20 hours. The reaction mixture was cooled to room temperature and filtered, after water washing and drying, 120 g of compound 2 was obtained. ¹HNMR (400 MHz, DMSO), δ (TMS, ppm): 6.96 (s, 2H).

Synthesis of compound 3. 50 g of compound 2 was dissolved in 250 mL of ammonia, reacted 4 hours under 100°C, in the process, adding 20 mL ammonia in the reaction liquid every 1 hour. The reaction mixture was filtered, and the solvent was evaporated under vacuum. The residue and 10g of activated carbon were refluxed in 500 mL of water for 30 minutes. HCl solution was then added to precipitate the product. The mixture was filtered, and washed with water several times. After drying, 45g compound 3 (white solid) was obtained. ¹H NMR (400 MHz, DMSO), δ (TMS, ppm): 7.56 (s, 2H).

Synthesis of compound 4. 45g of compound 3 and 5mL sulfuric acid were refluxed in 450 mL of ethanol for 4 hours. The solution was cooled to room temperature and NaHCO₃ solution was then added to tune the pH to 7. After evaporating most of the ethanol, extracting the product with ethyl acetate. The mixture was filtered, and washed with water several times. After drying and recrystallization, 35g compound 4 was obtained. ¹H NMR (400 MHz, CDCl3), δ (TMS, ppm):7.20 (s, 2H),4.37~4.42(m, 4H), 1.34~1.43(m, 6H).

Synthesis of compound 6. 50g of compound 5 was dissolved in 500Ml of 3

HCl(1M). The solution was cooled to $0-5^{\circ}$ C with ice-salt bath and 31.5g of NaNO₂ was added carefully. At 0°C, 1L of ice methanol was added into the reaction mixture slowly. Then, 165mL phenol-NaOH solution was added into above mixture, the reaction mixture was warmed to room temperature and reacted for 2h under continuous stirring. After filtration and solvent evaporation, the product was purified by recrystallization using ethanol/water (1:9) as solvent. Hereto, 32g compound 6 was obtained. ¹H NMR (400 MHz, CDCl3), δ (TMS, ppm): 10.10 (s, 2H), 7.7(d, 4H), 6.9(d, 4H).

Synthesis of compound 7. 5g of compound 6 was dissolved in 50mL of DMF, 16g of K_2CO_3 and 12g $C_4H_8Br_2$ were added into above solution, the mixture was stirring for 24h under room temperature and a N₂ atmosphere. After reaction, the reaction mixture was extracted with CH₂Cl₂, then the organic phase was washed with NaCl solution. After filtration and solvent evaporation, the product was purified by silica gel column. Hereto, 5.2g compound 7 was obtained. ¹H NMR (400 MHz, CDCl3), δ (TMS, ppm): 7.8(d, 4H), 7.1(d, 4H), 4.1(t, 4H), 3.5(t, 4H), 1.9(m, 8H).

Synthesis of compound 8. 5.2g of compound 7, 5.5g of compound 4 and 7g of K_2CO_3 were refluxed in 50mLof 2-butanone for 3 days. After filtration and solvent evaporation, the product was purified by silica gel column. Hereto, 5g of compound 8 was obtained. ¹H NMR (400 MHz, CDCl3), δ (TMS, ppm):7.86~7.88 (d, 4H),7.82(d, 4H), 6.98(d, 4H),4.13~4.25(m,8H),4.0(m,8H),2.0(m,8H),1.3(m,12H).

Synthesis of compound 9. 5g of compound 8 was dissolved in mixed solvent which composed of THF: acetonitrile, methanol= 5:1:1, then conducting a hydrolysis reaction by adding KOH solution. Hereto, 5g of compound 9 was obtained. ¹H NMR (400MHz, DMSO), δ (TMS, ppm): 7.81~7.83(d, 4H),7.7(d, 4H), 7.1(d, 4H),4.3(m,4H),4.1(m,4H),1.9(m,8H). Elemental analysis: C (56.86%),H (4.71%), N (7.67%), C₃₄H₃₂N₄O₁₂·2H₂O; calcd: C (56.35%),H (5.01%), N (7.73%).

2) Other materials:

Zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), and other chemicals were purchased from Beijing Chemical Reagents

Co. and used without further purification. Distilled water was purified through Milli-Q Advantage A10 Ultrapure Water System.

3) Sample preparation:

The desired amount solutions of Azo-C4-L2 (KOH solution), $Zn(NO_3)_2$ were mixed in a glass vial. The final concentration of Azo-C4-L2 and Zn^{2+} were both 0.5 mM, to allow the ligand and metal ion at stoichiometric mixing ratio ([Azo-C4-L2]/[Zn²⁺] =1/1). D₂O (J&K) and EDTA (Beijing Chemicals Company, AR) were used without further purification. All experiments were performed at room temperature (~25 °C) unless otherwise specified.

4) Methods:

Transmission electron microscopy (TEM): A FEI Tecnai G2 T20 TEM was employed to observe the morphology of aggregations. Drops of samples were put onto 230 mesh copper grids coated with Formvar film. Excess water was removed by filter paper, and samples were then allowed to dry in ambient air at room temperature before TEM observation.

Cryo-TEM image: For cryo-TEM studies, a sample droplet of 2μ L was put on a lacey carbon film covered copper grid (Science Services, Munich, Germany), which was hydrophilized by glow discharge (Solarus, Gatan, Munich, Germany) for 30s. Most of the liquid was then removed with blotting paper, leaving a thin film stretched over the lace holes. The specimen was instantly shock frozen by rapid immersion into liquid ethane and cooled to approximately 90 K by liquid nitrogen in a temperature-and humidity controlled freezing unit (Leica EMGP, Wetzlar, Germany). The temperature and humidity were monitored and kept constant in the chamber during all sample preparation steps. The specimen was inserted into a cryo transfer holder (CT3500, Gatan, Munich, Germany) and transferred to a Zeiss EM922 Omega energy-filtered TEM (EFTEM) instrument (Carl Zeiss Microscopy, Jena, Germany). Examinations were carried out at temperatures around 90 K. The TEM instrument was operated at an acceleration voltage of 200 kV. Zero-loss-filtered images (DE = 0 eV)

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were taken under reduced dose conditions (100-1000 e/nm2). The images were recorded digitally by a bottom-mounted charge-coupled device (CCD) camera system (Ultra Scan 1000, Gatan, Munich, Germany) and combined and processed with a digital imaging processing system (Digital Micrograph GMS 1.9, Gatan, Munich, Germany). The images were taken very close to focus or slightly under the focus (some nanometers) due to the contrast enhancing capabilities of the in-column filter of the employed Zeiss EM922 Omega. In EFTEMs, deep underfocused images can be totally avoided.

NMR: ¹H spectra were measured on a Bruker-500 MHz NMR spectrometer.

Ultraviolet-visible (UV-vis) spectroscopy: UV-vis absorption spectra were measured on a UV-1800 spectrophotometer (Shimadzu, Japan) which in the visible range of 200-1100 nm by the scan rate of fast. 1 mm quartz cuvets were used.

X-ray diffraction (XRD): Reflection XRD studies were carried out on the film with a model Rigaku Dmax-2000 diffractometer. The X-ray beam was generated with a Cu anode and the wavelength of the K_{a1} beam was 0.15406 nm . The X-ray beam was directed toward the film edge, and scanning was performed in the range of 0.6–50 deg. For XRD measurements, several drops of the dispersion were loaded on a clean glass slide and dried in air.

2. Figures



Figure S1. TEM images of the aggregates formed in Azo-C4-L2 system before (a) and after (b) UV irradiation. [Azo-C4-L2]=0.5mM. λ_{ir} =360 nm.



Figure S2. a) ¹H NMR spectrum of Azo-C4-L2 before UV irradiation; b) ¹H NMR spectrum of Azo-C4-L2 after UV irradiation, [Azo-C4-L2]=0.5mM, D₂O solution.



Figure S3. UV-vis spectrum of *cis*-Azo-C4-L2 solution in the dark overtime.



Figure S4. AFM measurements on the thickness of the nanoribbons of Azo-C4-L2/Z n^{2+} at the

molar ratio of 1:1.



Figure S5. Change in UV-vis spectra occurred within 5 min after addition of Zn^{2+} at the molar ratio of 1:1 to the solution of *cis*-Azo-C4-L2. [Azo-C4-L2]=0.5mM, pH=11.0.



Figure S6. UV-Vis spectrum of Azo-C4-L2/Zn²⁺ at different molar ratios (1:1.0~1:2.5) [Azo-C4-L2]=0.5Mm



Figure S7. Molecular structure of L_2EO_4 (inset) and the UV-vis spectra of Zn- L_2EO_4 . The coordinating head of L_2EO_4 is the same as that in Azo-C4-L2, so that the UV-Vis absorbance triggered by Zn²⁺ coordination is the same for the two systems. It is clear that the coordination dose not arouse UV absorbance at wavelength above 300 nm.



Figure S8. UV-Vis spectrum of Azo-C4-L2/Zn²⁺/EDTA=1:1:2.



Figure S9. ¹H NMR (a) and UV-Vis spectrum(b) of Azo-C4-L2/DEAB at different molar ratios.



Figure S10. ¹H NMR (a) and UV-Vis spectrum (b) of AzoNa/CTAB at different molar ratios.



Figure S11. UV-Vis spectrum of Azo-C4-L2/Ni coordinating system. The left panel shows the comparison of spectrum with that formed in Azo-C4-L2/Zn system and the single system of Azo-C4-L2. The right panel demonstrates the change of the spectrum formed in the Azo-C4-L2/Ni²⁺ system under 1 hour irradiation with 360 nm. It is clear that Ni²⁺(from Ni(NO₃)₂) cannot trigger the same extent of absorbance shift as Zn^{2+} , and the Ni²⁺ triggered photo state cannot be locked.



Figure S12. UV-Vis spectrum of Azo-C4-L2/Cu coordinating system. The left panel shows the comparison of spectrum with that formed in Azo-C4-L2/Zn system and the single system of Azo-C4-L2. The right panel demonstrates the change of the spectrum formed in the Azo-C4-L2/Cu²⁺ system under 1 hour irradiation with 360 nm. It is clear that Cu^{2+} (from Ni(NO₃)₂) cannot trigger the same extent of absorbance shift as Zn²⁺, and the Cu²⁺ triggered photo state cannot be locked.



Figure S13. UV-Vis spectrum of the Azo-C4-L2/Cd coordinating system. The left panel shows the comparison of spectrum with that formed in Azo-C4-L2/Zn system and the single system of Azo-C4-L2. The right panel demonstrates the change of the spectrum formed in the Azo-C4-L2/Cd²⁺ system under 1 hour irradiation with 360 nm. It is clear that Cd^{2+} (from Ni(NO₃)₂) cannot trigger the same extent of absorbance shift as Zn^{2+} , and the Cd^{2+} triggered photo state cannot be locked.