Supporting Information

Visible light mediated BODIPY/Azo/Cyclodextrin based supramolecular polymer assemblies in different water content solution

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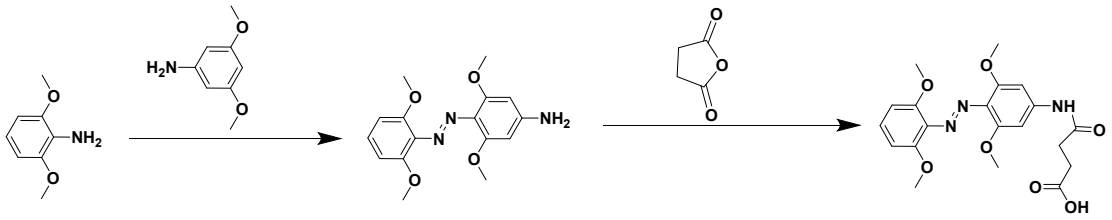
1. Synthesis of Azo

BDP and *β*-CD-C were synthesized according to our previous work[s1, s2].Azo was prepared by two steps and afforded the yield about 12%. The molecular structures are confirmed by NMR and mass spectra, which are shown in Supporting Information (Figure S13-S16).



Scheme S1. Synthetic routes of tetramethoxy azoaniline monomer and Azo.

Synthesis of Tetramethoxyazobenzene[s3]: 2,6-Dimethoxy-aniline (0.46 g, 3.00 mmol) was dissolved in a mixture of H_2O (0.56 mL) and HCl (0.73 mL, 37 wt.%). The mixture was cooled to 0-5 ^{o}C and an aqueous solution (2 mL) of $NaNO_2$ (0.21 g, 3.00 mmol) was slowly added. The solution was stirred for another 20 min at 0-5 ^{o}C. Then, diazonium salt was then slowly introduced to a suspension of 3,5-dimethoxy-aniline (0.46 g, 3.00 mmol) in H_2O (20 mL) at 0-5 ^{o}C. Saturated $NaHCO_3$ solution was added to adjust the pH value to ~ 8-9. After stirring overnight, the red precipitate was filtered and purified by chromatography using 1/1 methanol/ethyl acetate as eluent to give the product as a red solid (598 mg, yield: 31%).^{1}H NMR (400 MHz, DMSO-d_6): δ =3.66 (d, J = 2.4 Hz 12H, CH_3), 5.93 (s, 2H, CH), 5.96 (s, 2H, CH),

6.71 (d, J = 3.4 Hz 2H, NH_2), 7.13 (t, J = 8.3 Hz, 1H, CH).

Synthesis of Azo: Weigh tetramethoxyazobenzene (0.10 g, 3.15 mmol) and succinic anhydride (0.05 g, 4.73 mmol) were dissolved in toluene solvent, heated to reflux for 24 h. The solvent was evaporated under reduced pressure to afford the crude product. The crude product was purified with a silica gel column to obtain brick red viscous Azo (52 mg, yield: 39%). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.62 (s, 4H, CH_2), 3.75 (d, J = 3.6 Hz 12H, CH_3), 6.75 (d, J = 8.4 Hz, 2H, CH), 7.09 (s, 2H, CH), 7.26 (t, J = 8.4 Hz, 1H, CH), 8.62 (s, 1H, COOH). ^{13}C NMR (100 MHz, D_2O): δ = 29.4, 49.0, 56.3, 96.7, 105.6, 119.1, 152.3, 177.1. ESI-MS: Calculated for $C_{20}H_{23}N_3O_7$ $[M+H]^+$: 418.1609, Found: 418.1693.

2. Reference

(s1) J.-F. Yin, Y. Hu, D. G. Wang, Z. Jin, Y. Zhang, G.-C. Kuang, *ACS Macro Letters* 2017, **6**, 139-143.

(s2) L.-L. Zhou, J.-Y. Chen, X.-Y. Li, H. Li, H. Wang, D.-G. Wang, G.-C. Kuang, *Macromol. Rapid. Comm.* 2019, **40**, 1900182.

(s3) D. Wang, M. Wagner, H.-J. Butt, S. Wu, *Soft Matter*, 2015, **11**, 7656-7662.

3. ^{1}H NMR titration data of BDP/Azo

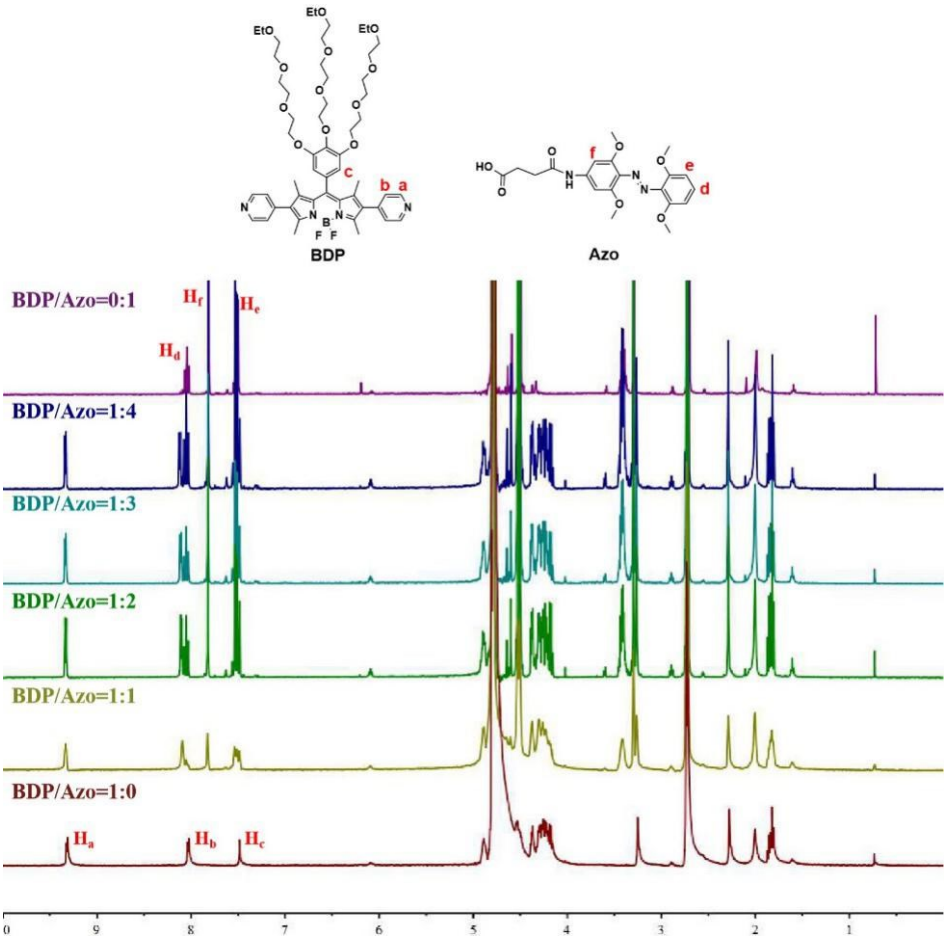


Figure S1. ^{1}H NMR spectra of BDP (4 mM) with different ratios of Azo in D_2O/CD_3CN (1:2, v/v).

4. Nuclear Overhauser effect spectroscopy (NOESY) experiments of BDP/Azo complex

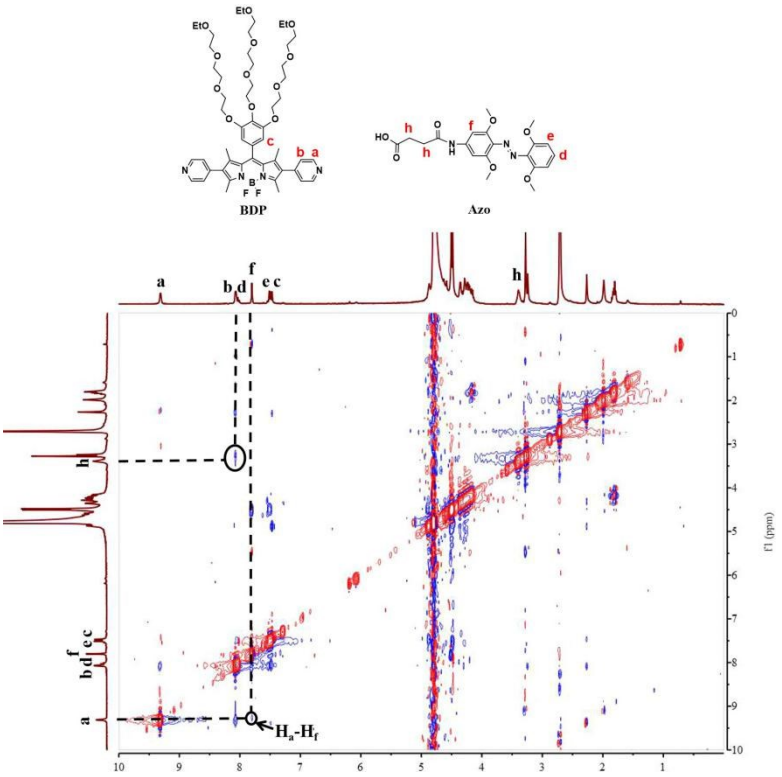


Figure S2. 2D ^{1}H NMR NOESY spectrum of a mixture of BDP/Azo (molecular ratio 1:2, C_{BDP} = 4 mM) in D_2O/CD_3CN (1:2, v/v).

5. UV-vis and fluorescence spectra of BDP with different ratio of Azo in water

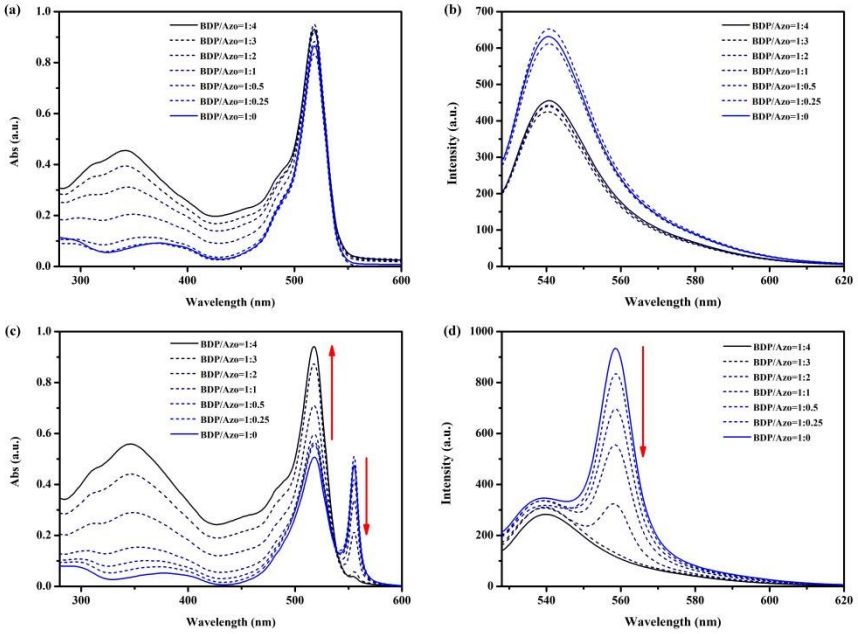


Figure S3. (a, c) UV-vis and (b, d) fluorescent emission spectra of BDP/Azo (C_{BDP} = 10 μM) complex with increasing molar ratio of Azo at (a, b) f_w = 80%; (c, d) f_w = 95% in the H_2O/ACN. λ_{ex} = 518 nm.

6. DLS result of BDP/Azo at different water contents

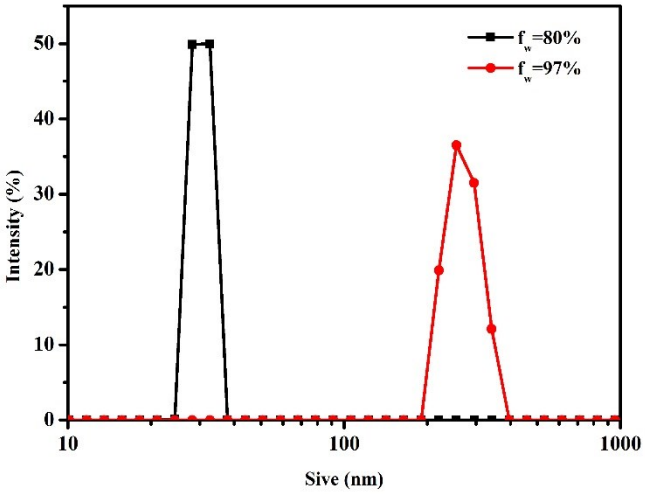


Figure S4. DLS diagrams of BDP/Azo (molecular ratio 1:2, C_{BDP} = 10 μM) in a mixed solvent of water and acetonitrile (f_w = 80% and 97%).

7. Host-guest interaction between *β*-CD-C and Azo

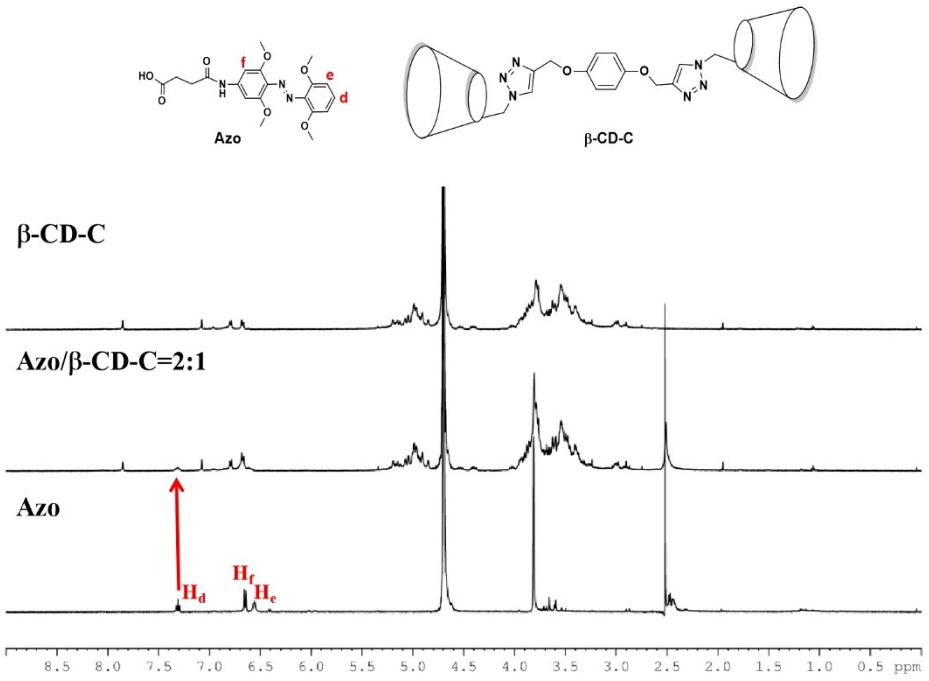


Figure S5. ^{1}H NMR spectra of Azo, *β*-CD-C and Azo/*β*-CD-C (molecular ratio 2:1, C_{Azo} = 4 mM) mixture in D_2O/CD_3CN (1:2, v/v).

8. ^{1}H NMR spectra of supramolecular complexes

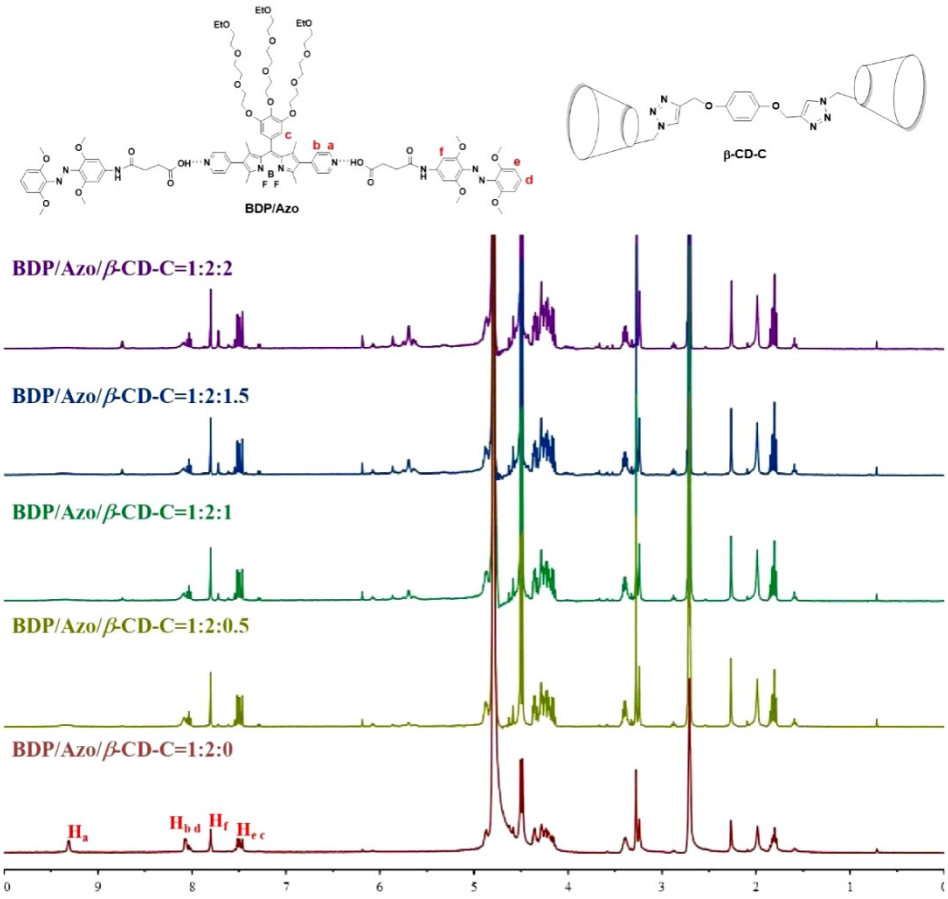


Figure S6. ^{1}H NMR spectra of BDP/Azo (molecular ratio 1:2, C_{BDP} = 4 mM) with different molar ratio of β-CD-C in D_2O/CD_3CN (1:2, v/v).

9. DLS result for different supramolecular complexes

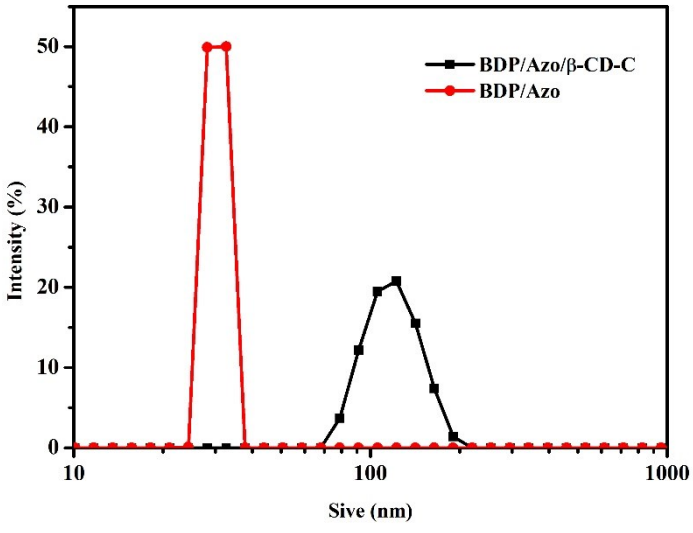


Figure S7. DLS diagram of BDP/Azo (1:2, C_{BDP} = 10 μM) and BDP/Azo/β-CD-C (molecular ratio 1:2:1) in H_2O/ACN with f_w= 80%.

10. UV-vis and fluorescence emission spectra of BDP/Azo with different ratio of β-CD-C in water

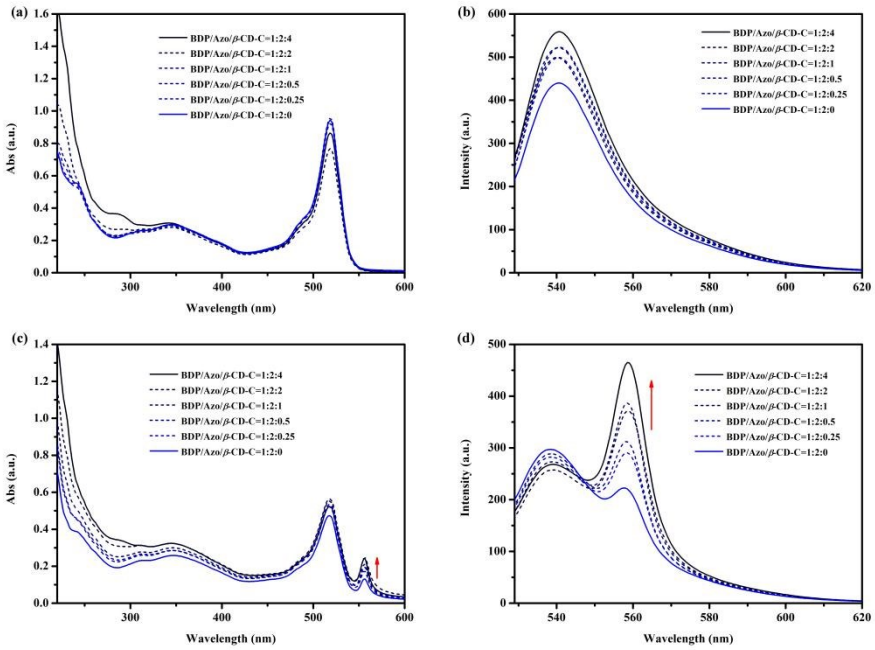


Figure S8. (a, c) UV-vis and (b, d) fluorescent emission spectra of BDP/Azo complex (molecular ratio 1:2, C_{BDP} = 10 μM) with increasing molar ratio of β-CD-C in the H_2O/ACN at (a, b) f_w = 80%; (c, d) f_w = 95%. λ_{ex} = 518 nm.

11. ^{1}H NMR spectra after irradiation with different visible light

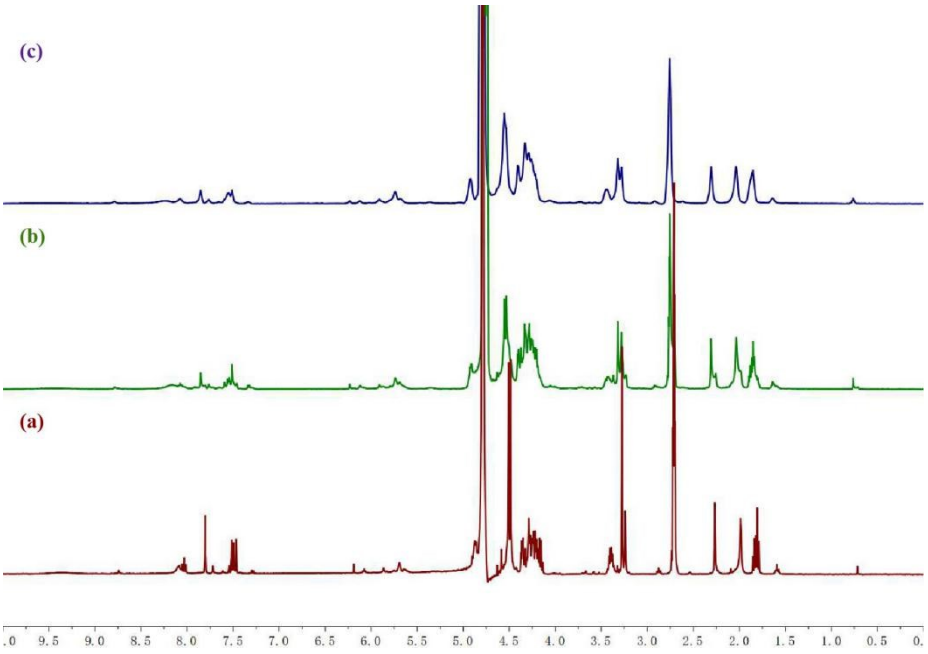


Figure S9. ^{1}H NMR spectra of (a) BDP/Azo/*β*-CD-C (molecular ratio 1:2:1, C_{BDP} = 4 mM), (b) under 530 nm irradiation for 2 h, and (c) further 450 nm irradiation for 2 h in D_2O/CD_3CN (1:2, v/v).

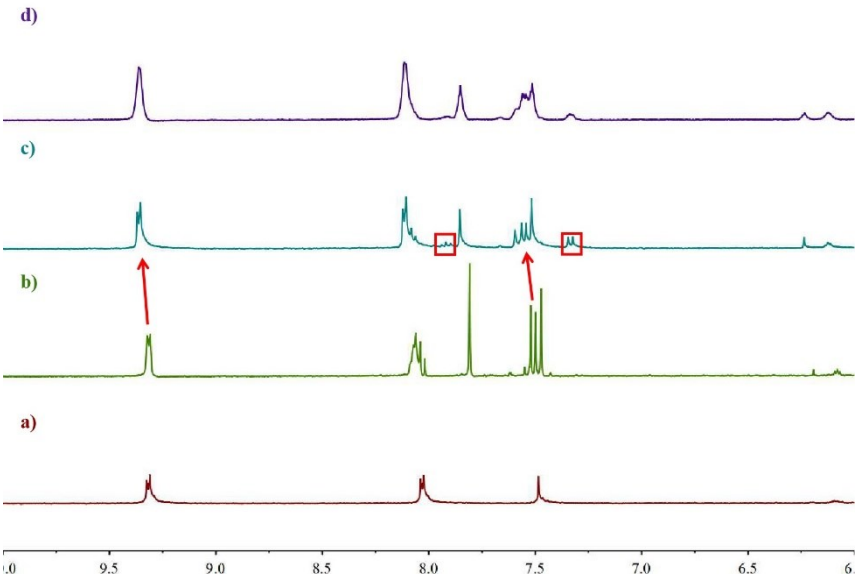


Figure S10. Partial enlargement ^{1}H NMR spectra of (a) BDP monomer (C_{BDP} = 4 mM), (b) BDP/Azo complex (molecular ratio 1:2, C_{BDP} = 4 mM); (c) under 530 nm irradiation for 2 h, and (d) further 450 nm irradiation for 2 h in D_2O/CD_3CN (1:2, v/v).

12. NMR spectra of BDP/γ-CD.

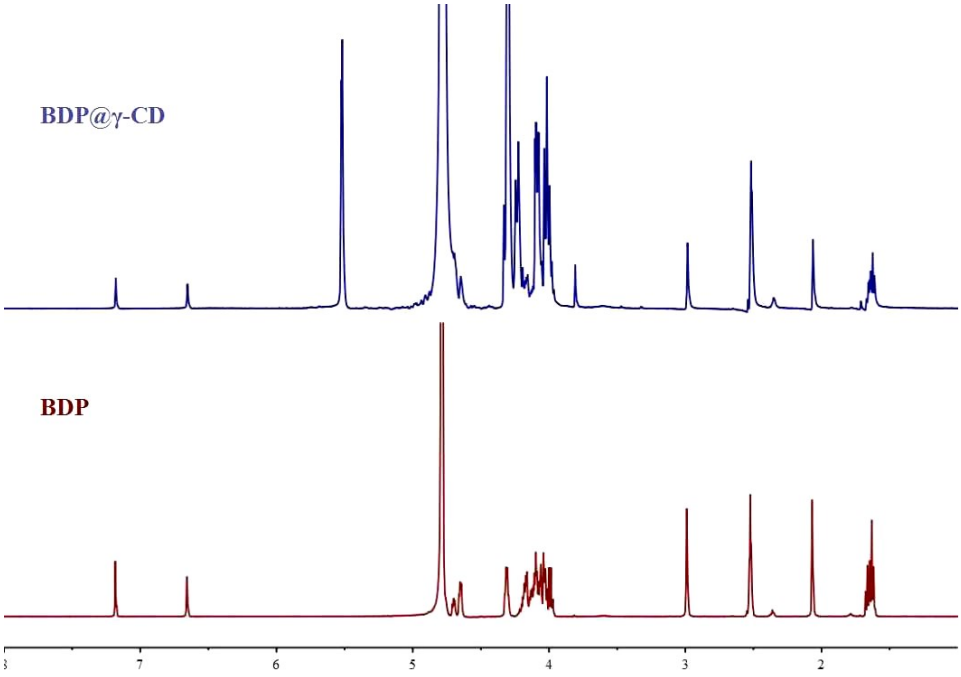


Figure S11. ^{1}H NMR spectra of BDP (red) and mixture of BDP and γ-CD (1:1, blue) in D_2O

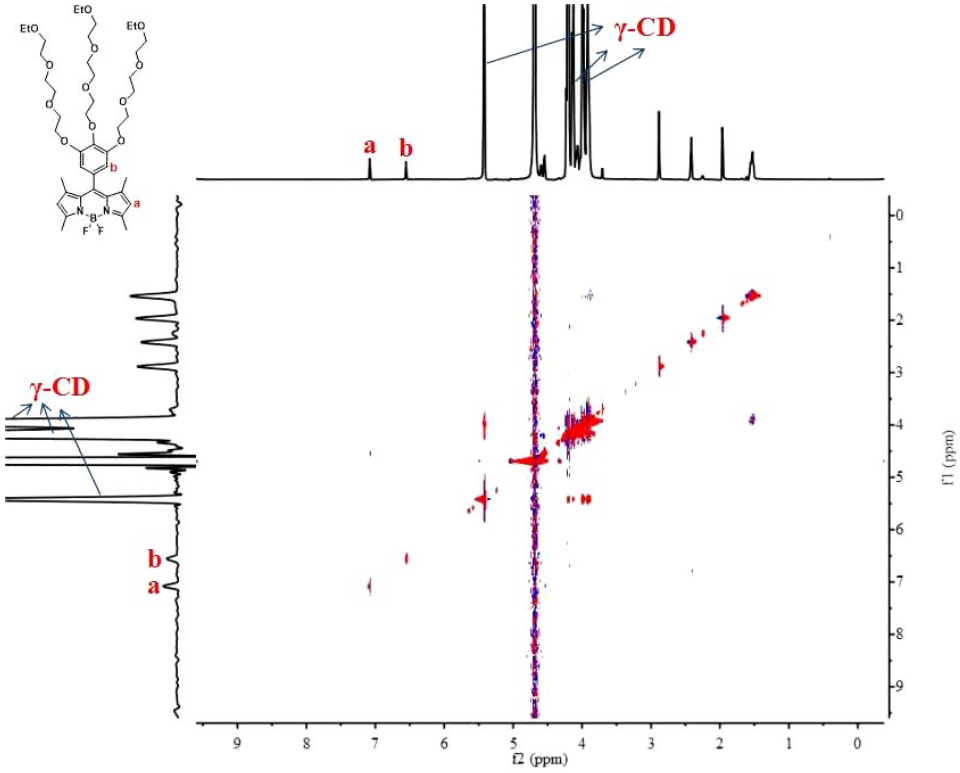


Figure S12. The NOESY spectrum (500 MHz) of BDP/γ-CD in D_2O.

13. NMR and Mass spectra

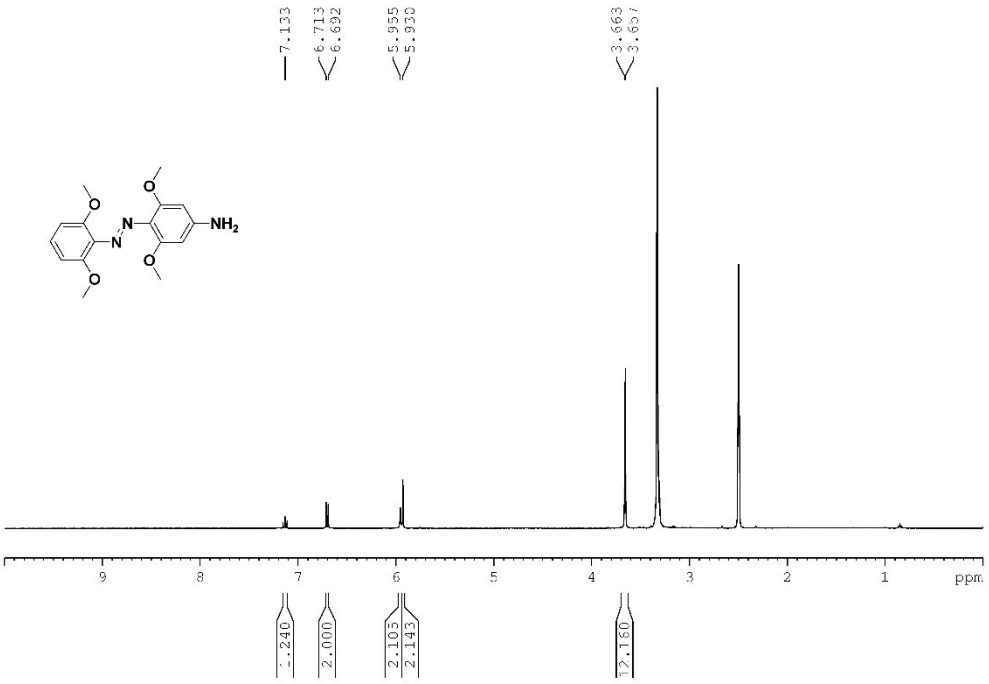


Figure S13. ^{1}H NMR spectrum of tetramethoxy azoaniline in DMSO-d_6

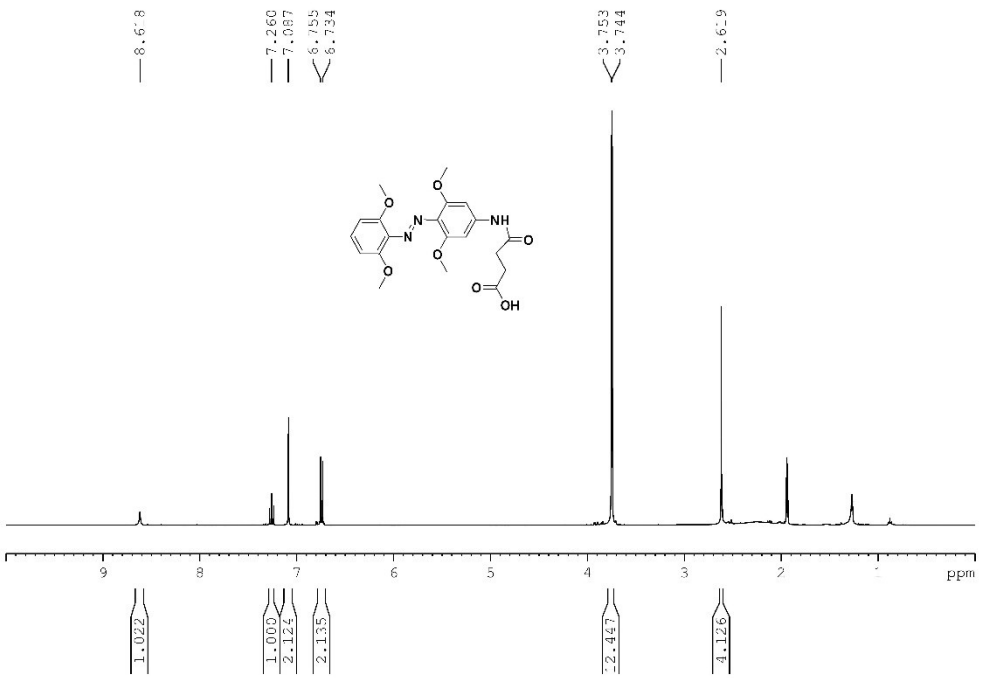


Figure S14. ^{1}H NMR spectrum of Azo in CD_3CN

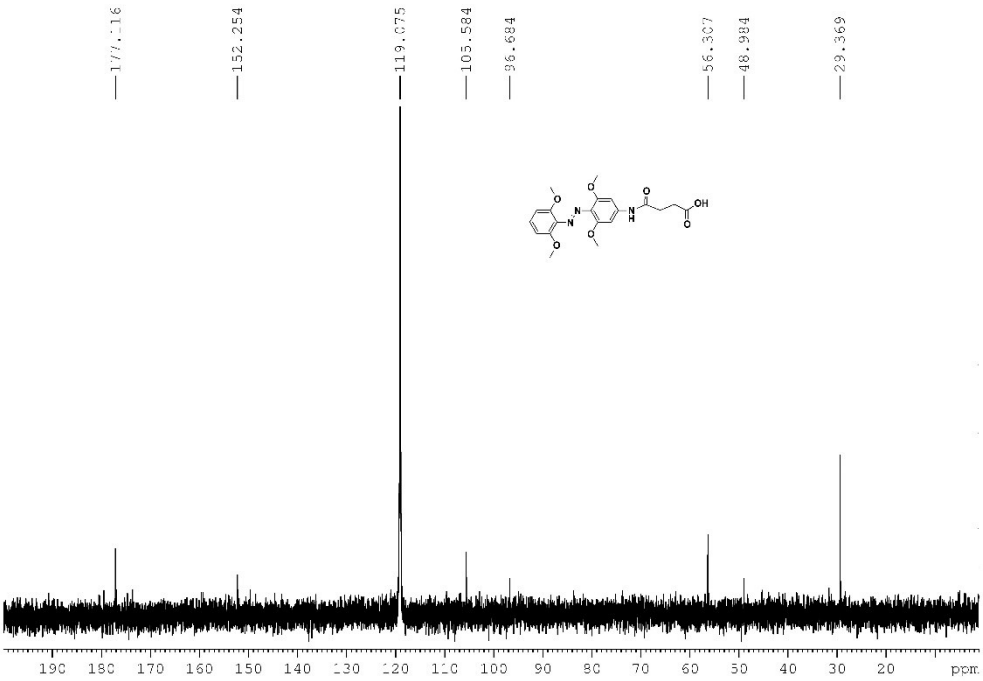


Figure S15. ^{13}C NMR spectrum of Azo in D_2O

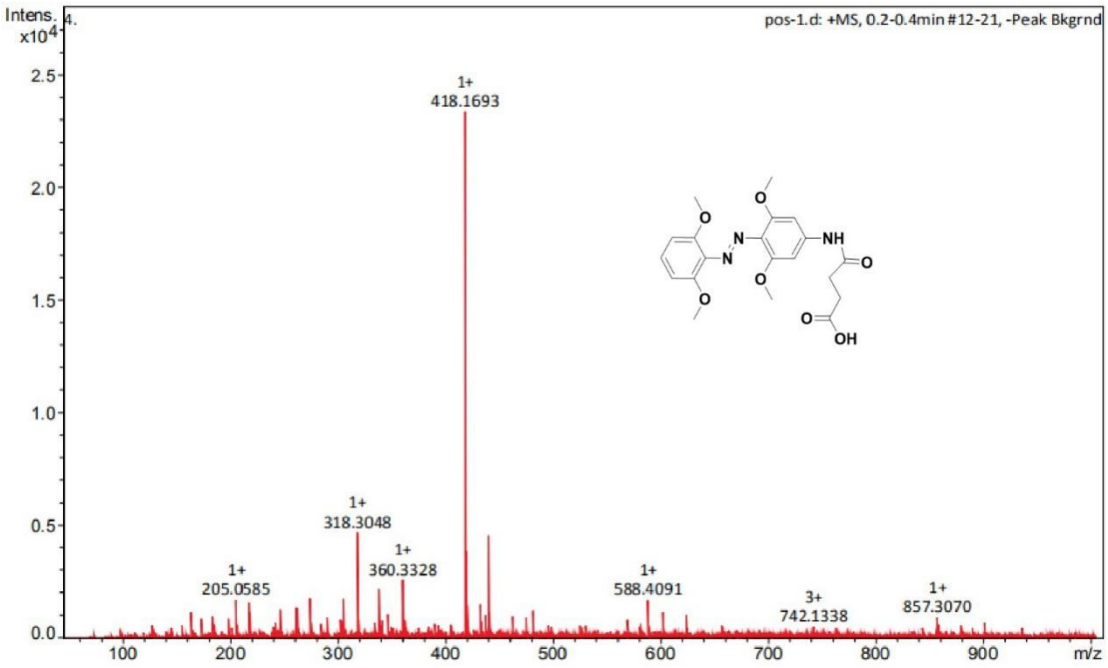


Figure S16. HR ESI-MS spectrum of Azo