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Supporting Information

Cyclodextrin-/Photoisomerization- Modulated Assembly and Disassembly of An Azobenzene-Grafted Polyoxometalate Cluster

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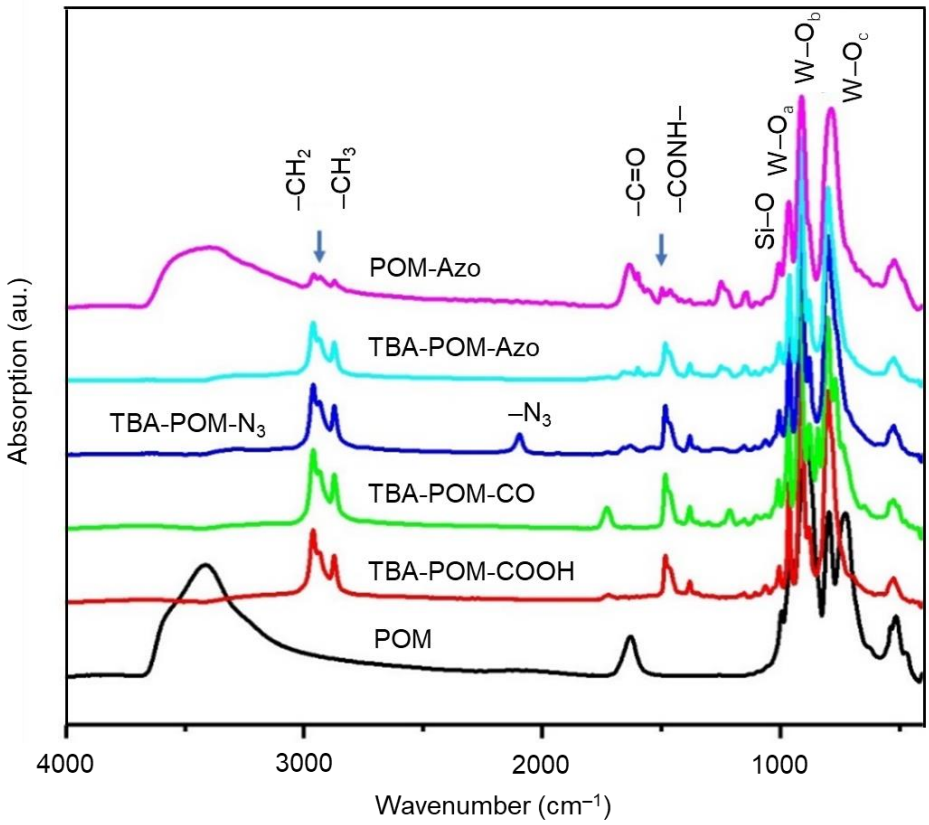

Fig S1. FT-IR spectra of Keggin POM, organic grafted intermediates, the inclusion complexes, and final product in KBr pellets.

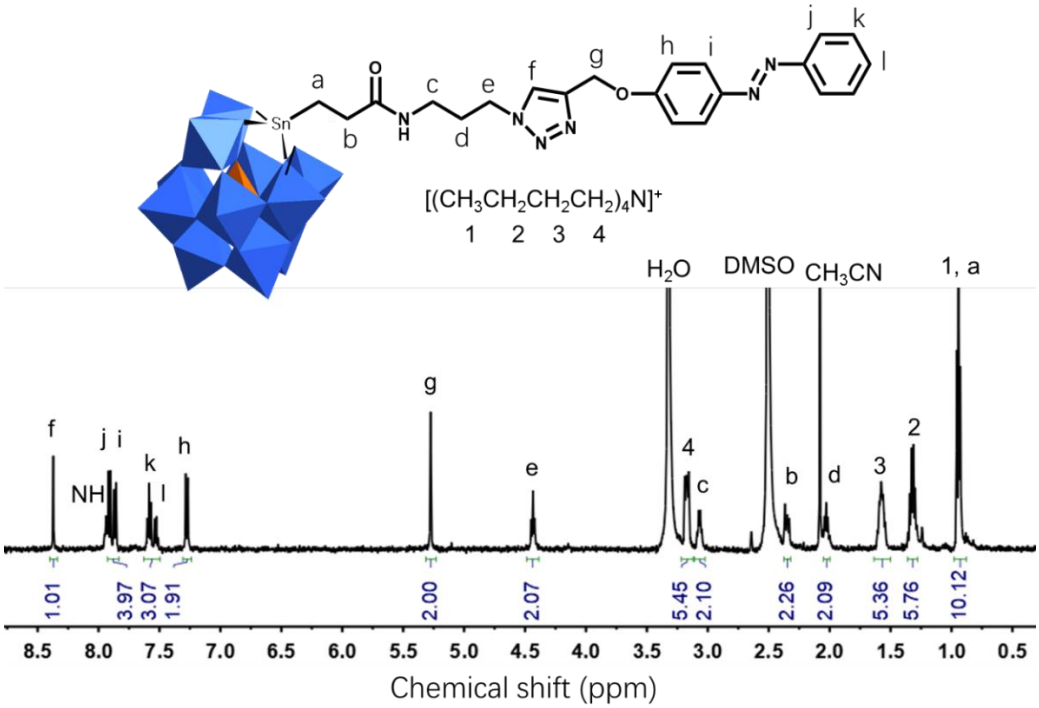

Fig S2. ^{1}H NMR spectrum of POM-Azo complex. (DMSO-d_6, 25 °C, 0.15 mM)

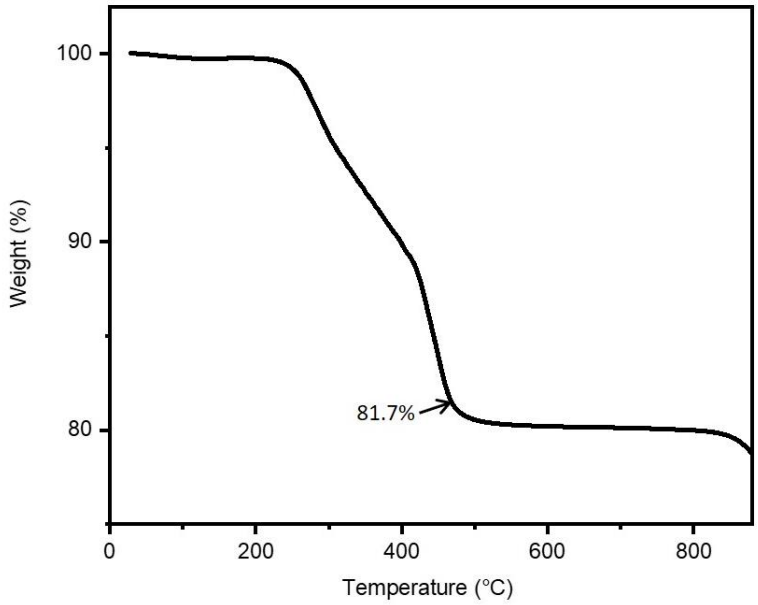

Fig S3. TGA curve of POM-Azo complex.

Table S1. The elemental analysis result of prepared POM-Azo in a chemical formula of $H_{4.3}TBA_{0.7}[SiW_{11}O_{39}Sn(C_6H_{11}ON)(C_2HN_3)CH_2O(C_{12}H_9N_2)]$.

	C	H	N	Si	W	Sn
Calcd. (%)	11.52	1.58	2.79	0.84	60.21	3.54
Found (%)	11.48	1.61	2.80	0.84	60.25	3.55

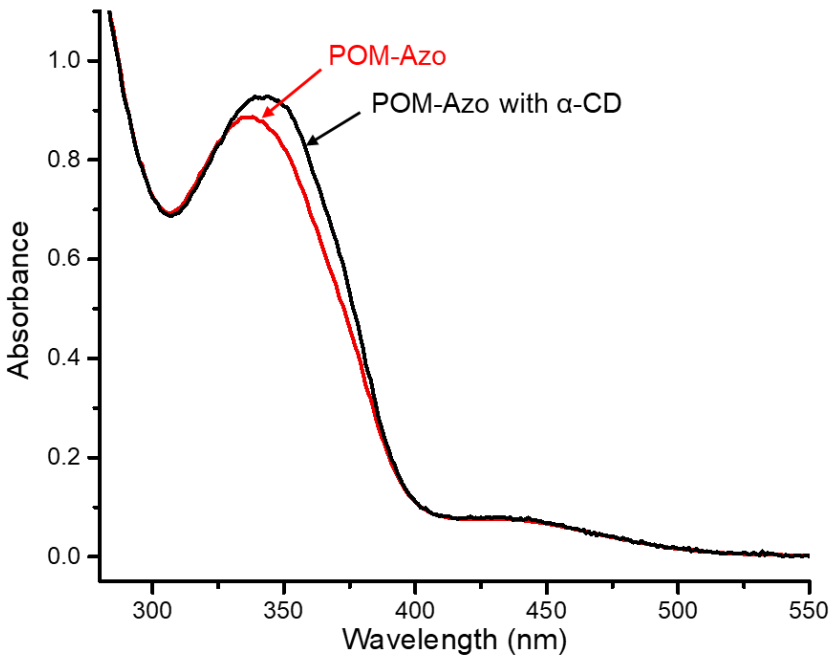

Fig. S4. UV-Vis spectra of POM-Azo in water with and without addition of α-CD (10 molar ratio) at 25 ºC.

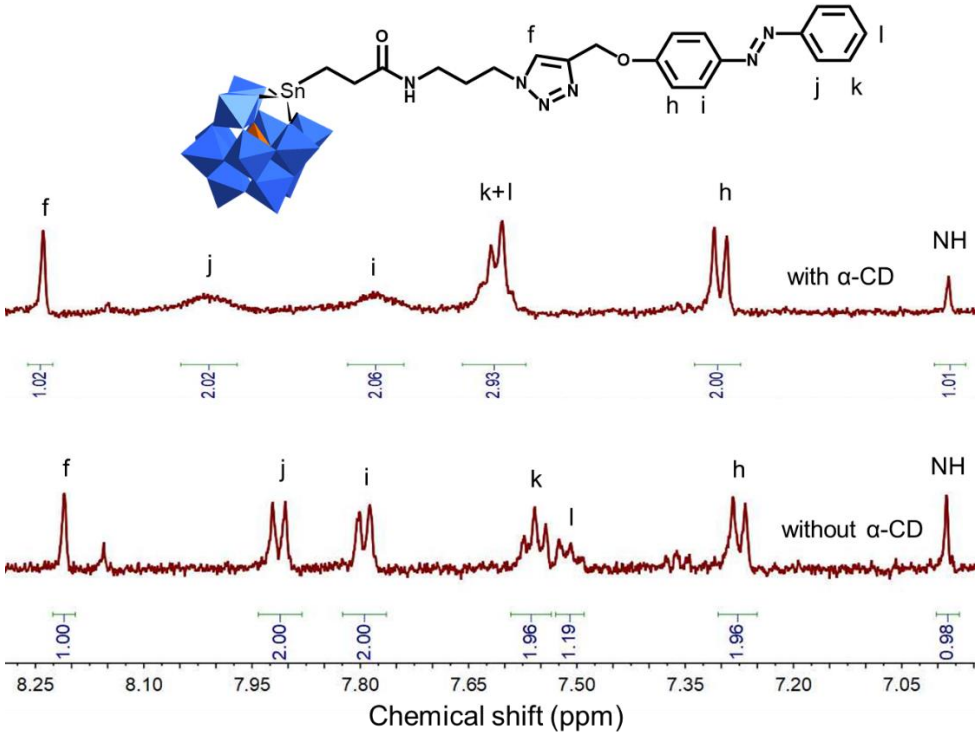

Fig S5. ^{1}H NMR spectra of POM-Azo with and without addition of α-CD in D_2O (0.15 mM, 25 °C).

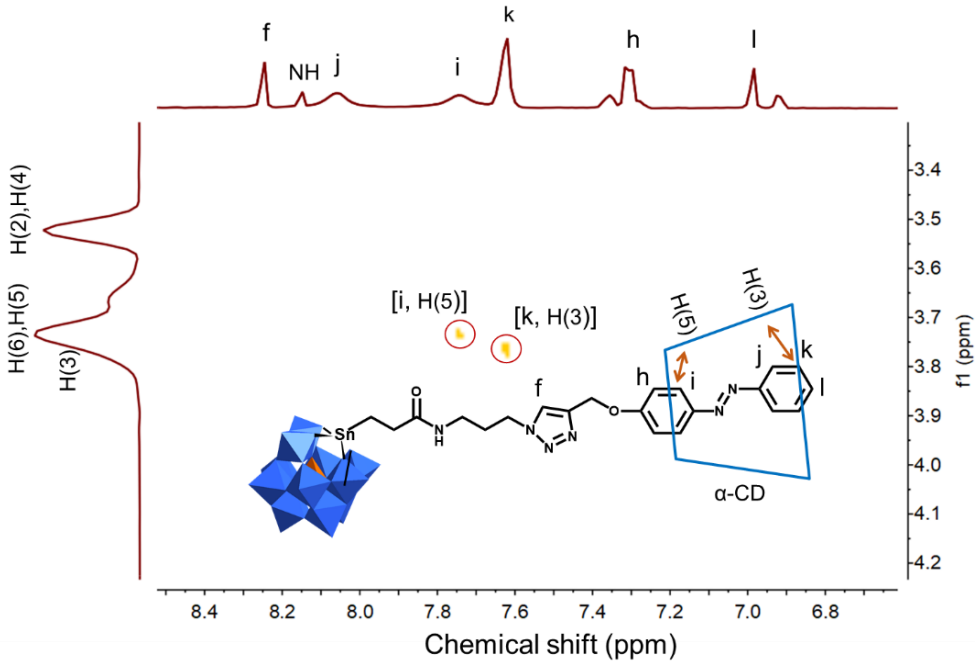

Fig S6 2D NOESY NMR spectrum of POM-Azo (*trans*) with α-CD in D_2O (25 °C, 0.15 mM). Two cross-correlation points appear and are marked in yellow.

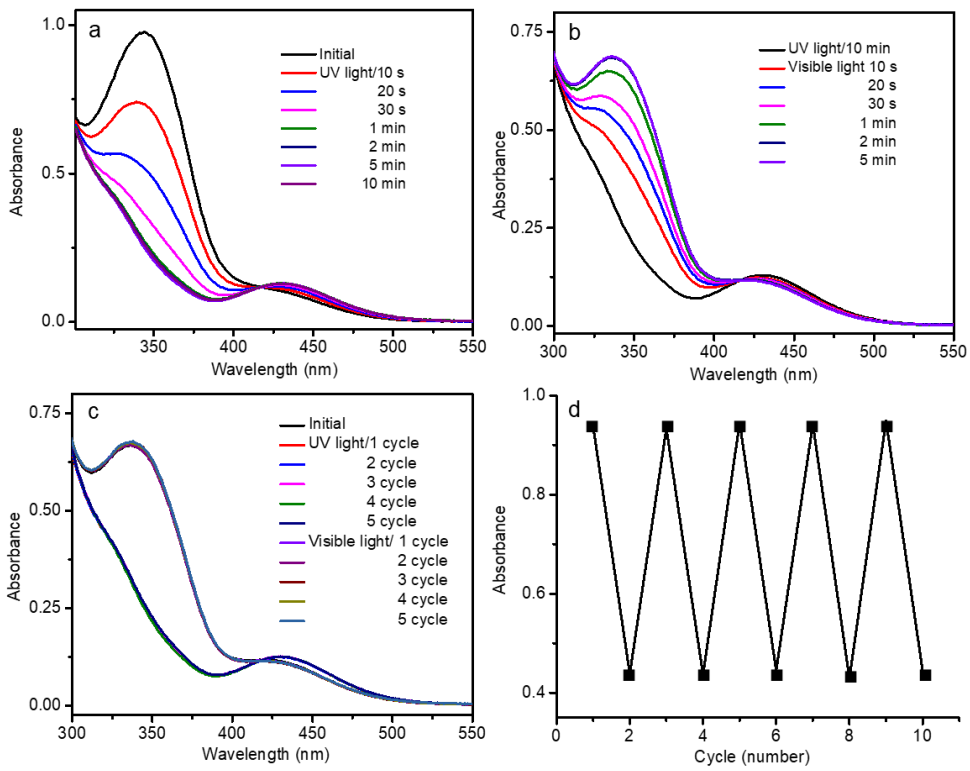

Fig S7. UV-vis spectra of POM-Azo in water (8.4 μM) under different irradiation time upon a) UV light irradiation, and b) visible light irradiation, and c) undergo 5 cycles of alternate UV light (365 nm) and visible light (450 nm) irradiation, d) Plots of (c) absorbance at λ = 344 nm.

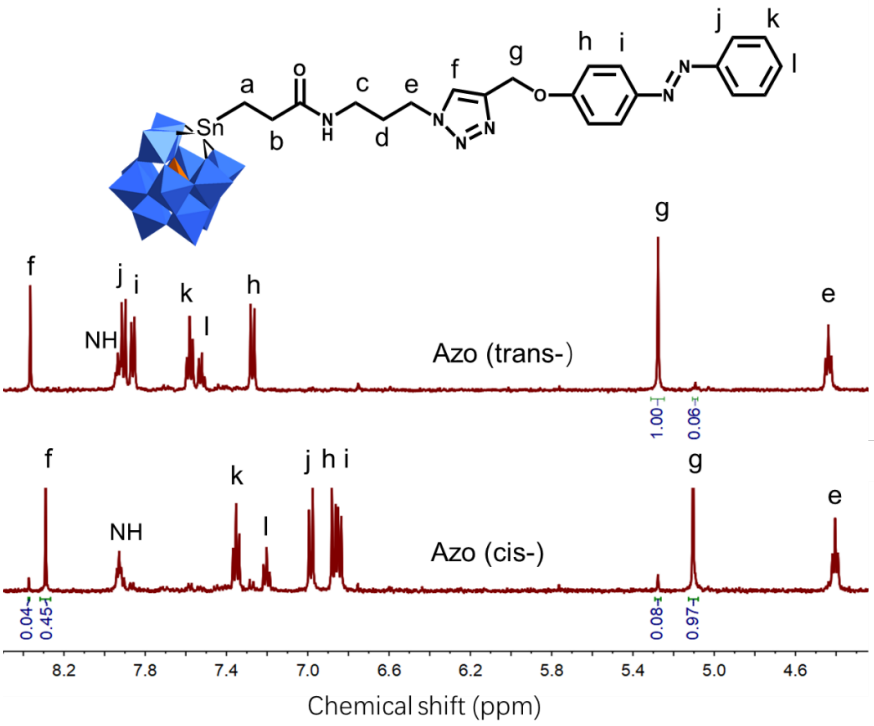

Fig S8. ^{1}H NMR spectra of POM-Azo in *trans* and *cis* states in DMSO-d_6 (25 °C, 0.15 mM).

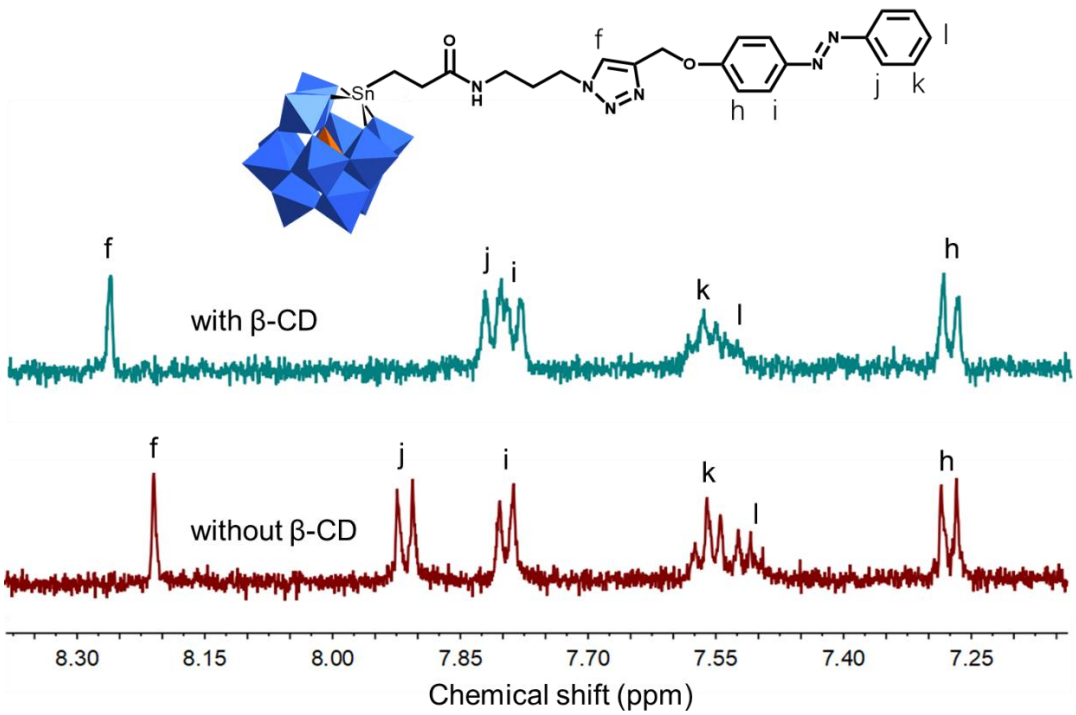

Fig S9. ^{1}H NMR spectra of POM-Azo with (top) and without (down) β-CD. (D_2O, 25 °C, 0.15 mM)

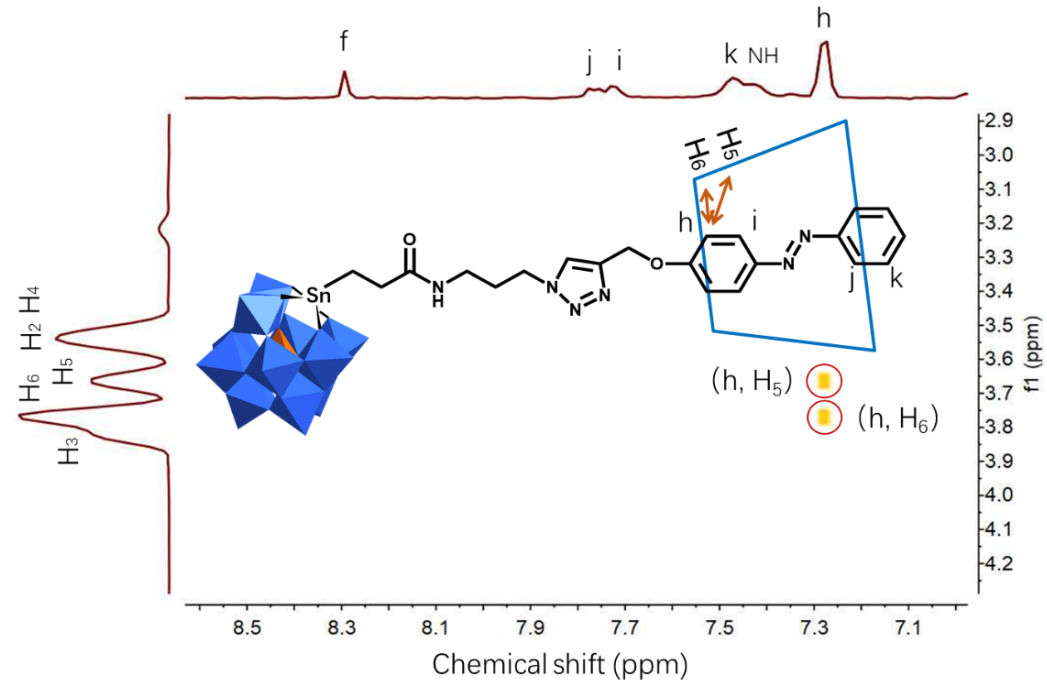

Fig S10. 2D NOESY NMR spectrum of POM-Azo (*trans*) with β-CD in water. (D_2O, 25 °C, 0.15 mM). Two cross-correlation peaks appear in NOESY NMR spectrum, implying the formation of the inclusion complex between POM-Azo (*trans*) and β-CD.

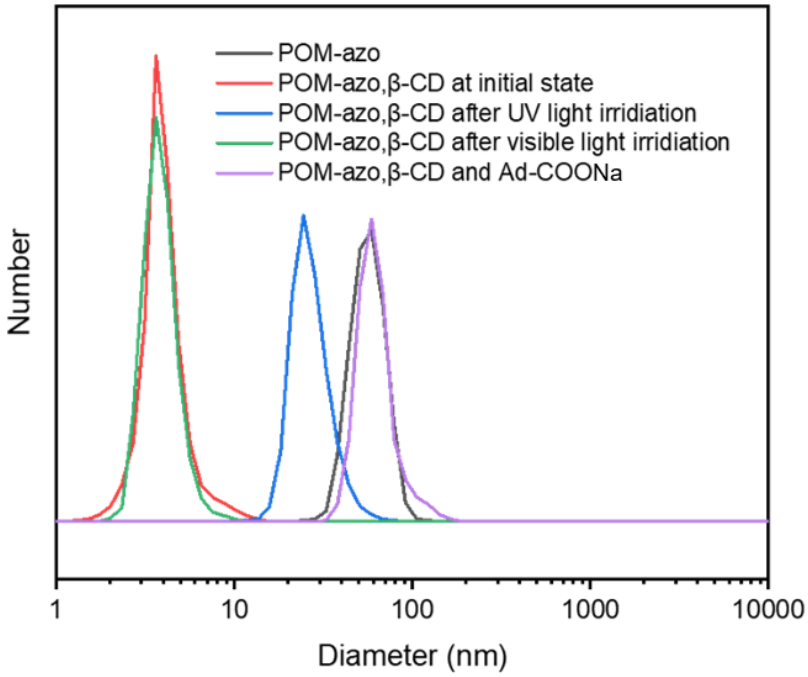

Fig S11. DLS curves in water, 25 °C for (black) pure POM-Azo complex, (red) POM-Azo interact with β-CD (1:1), (blue) POM-Azo with β-CD under 0.5 h UV light irradiation, (green) POM-Azo with β-CD under 0.5 h visible light irradiation, (purple) POM-Azo, β-CD and Ad-COONa with the ratio of 1:1:1.1.

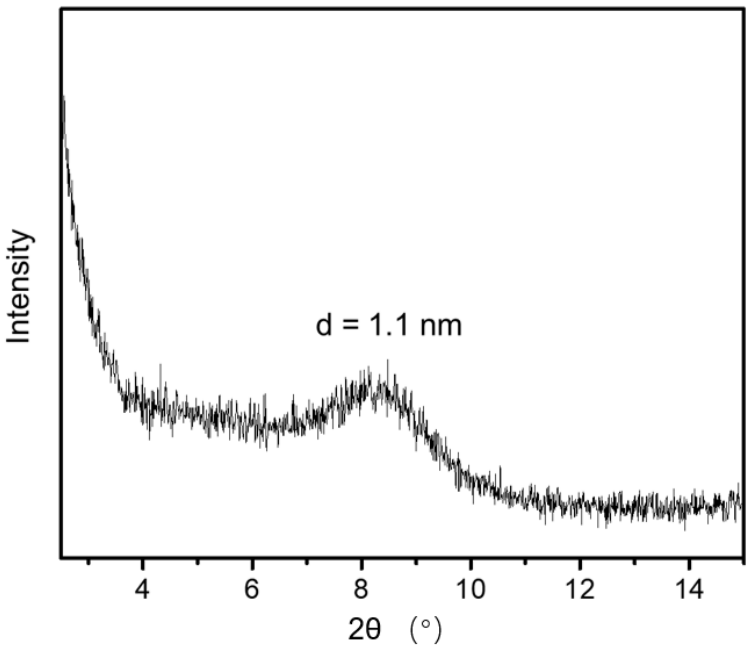

Fig S12. X-ray diffraction pattern of POM-Azo assembly prepared from water.