Supplementary Information

Induced Chirality and Reversal of Phosphomolybdate Cluster via Modulating Its Interaction with Cyclodextrins

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Materials

1-adamantane carboxylic acid (AdCOOH) was purchased from J&K Chemical Co, Ltd. and was used without any further purification. β-Cyclodextrin (β-CD) was the product of Sinopharm Chemical Reagent Co, Ltd. (SCRC) and was recrystallized three times before use. α-CD and γ-CD were the product of Aladdin. $H_3PMo_{12}O_{40}$ (PMo_{12}) and the remaining chemicals were purchased from Beijing Chemical Reagent Company and used as received. Doubly distilled water was used in the experiments.

Measurements

The UV-Vis spectra were recorded on a spectrometer (Varian CARY 50 Probe). ^{1}H NMR spectra were performed on a Bruker AVANCE 500 MHz spectrometer. The chemical shifts were referenced to the solvent values (δ = 4.79 ppm for D_2O). Circular dichroism spectra (CDS) were carried out on a Bio-Logic MOS-450 spectropolarimeter in water with a step size of 0.5 nm and speed of 4 nm s^{-1} at 25 °C.

Sample Preparations

PMo_{12} (10 mM): 18.25 mg (0.01 mM) of PMo_{12} solid powder was dissolved in 0.3 mL water. The solution was transferred to a 1-mL volumetric flask and diluted to the marked volume.

α-CD–PMo_{12} (100:1): 97.3 mg (0.1 mM) of α-CD was dissolved in 0.9 mL water, then to the solution was added slowly 0.1 mL of PMo_{12} (10 mM) with continually stirring at room temperature for 2 h. The resulting solution was allowed to stand for 16 h for measurement.

β-CD–PMo_{12} (14:1) and γ-CD–PMo_{12} (100:1): The preparation procedure for them is similar with α-CD–PMo_{12}, β-CD (16 mg, 0.014 mM) and γ-CD (129.7 mg, 0.1 mM) were dissolved in 0.9 mL water, respectively. Then 0.1 mL PMo_{12} (10 mM) was added to both solutions to get the samples for measurements.

AdCS (AdCOONa): AdCOOH was dispersed in 5 mL water, and then NaOH (0.1 mM) was added dropwise with stirring until a transparent solution in pH 8.5 was obtained. The sodium salt was obtained after evaporating the water to dryness.

α-CD–AdCOOH–PMo_{12} (10:10:1): α-CD (9.73 mg, 0.01 mM) and AdCS (2.02 mg, 0.01 mM) were dissolved into 0.9 mL water with stirring for 2 h. Then 0.1 mL PMo_{12} (10 mM) was added and the three-component system was obtained.

β-CD–AdCOOH–PMo_{12} (10:10:1) and γ-CD–AdCOOH–PMo_{12} (10:10:1): The preparation process for β-CD–AdCOOH–PMo_{12} (11.35 mg, 0.01 mM), γ-CD (12.97 mg, 0.01 mM) was similar to that of α-CD–AdCOOH–PMo_{12}, and the sample solutions with concentration of 0.01 mM were prepared.

The preparation of other samples at different concentrations and molar ratios that were not mentioned here just followed the same procedures.

Characterizations

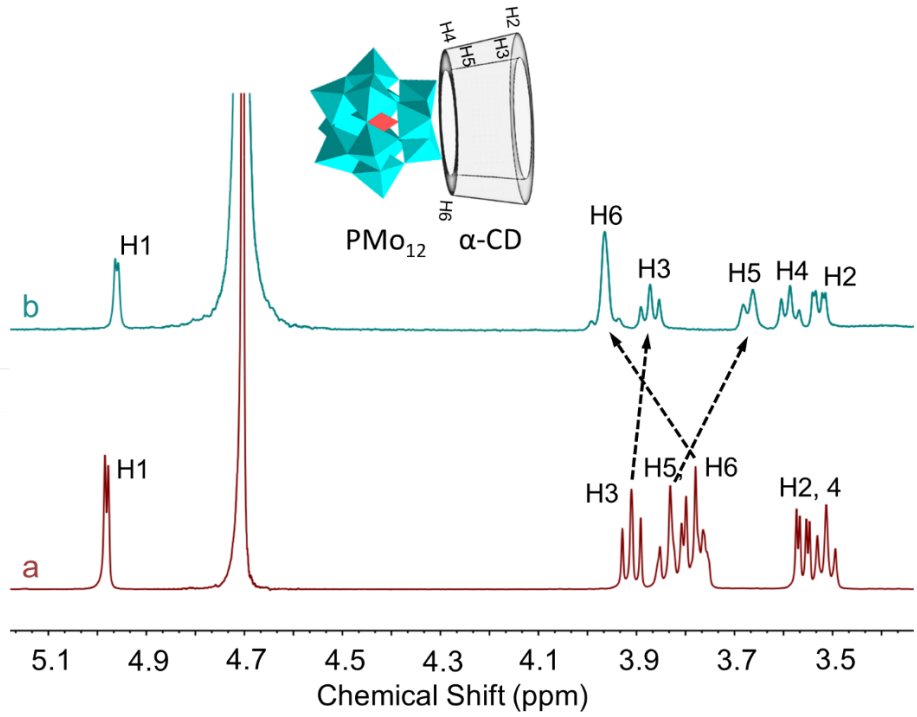

Fig. S1. ^{1}H NMR spectra of (a) α-CD (0.1 mM) and (b) its mixture with PMo_{12} (1.0 mM) in D_2O at 25 °C. To ensure the clear assignment to the proton chemical shifts of α-CD, excess PMo_{12} was used in the measurement.

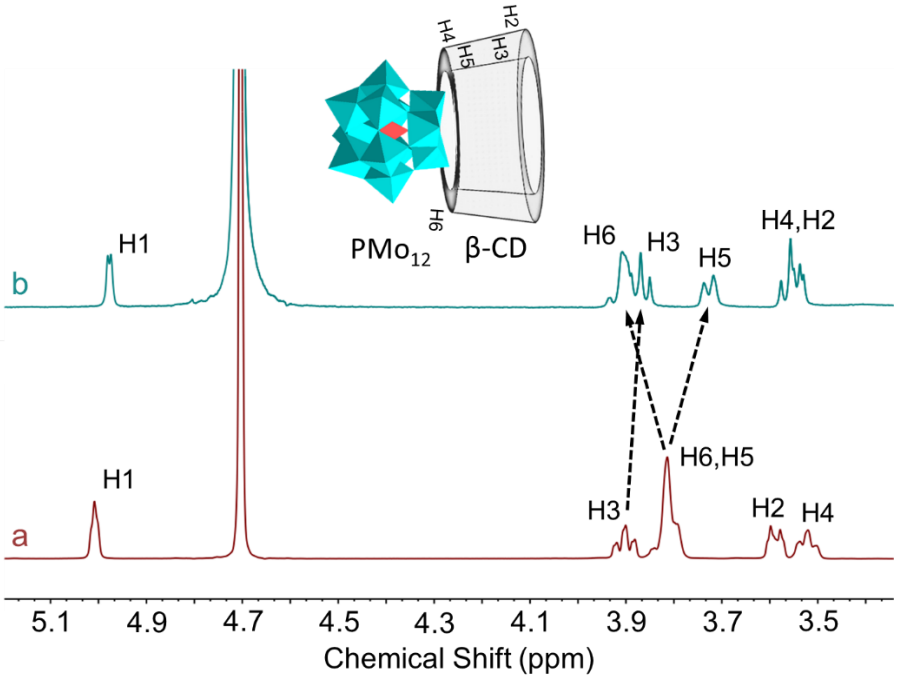

Fig. S2. ^{1}H NMR spectra of (a) β-CD (0.1 mM) and (b) its mixture with PMo_{12} (1.0 mM) in D_2O at 25 °C. To ensure the clear assignment to the proton chemical shifts of β-CD, excess PMo_{12} was used in the measurement.

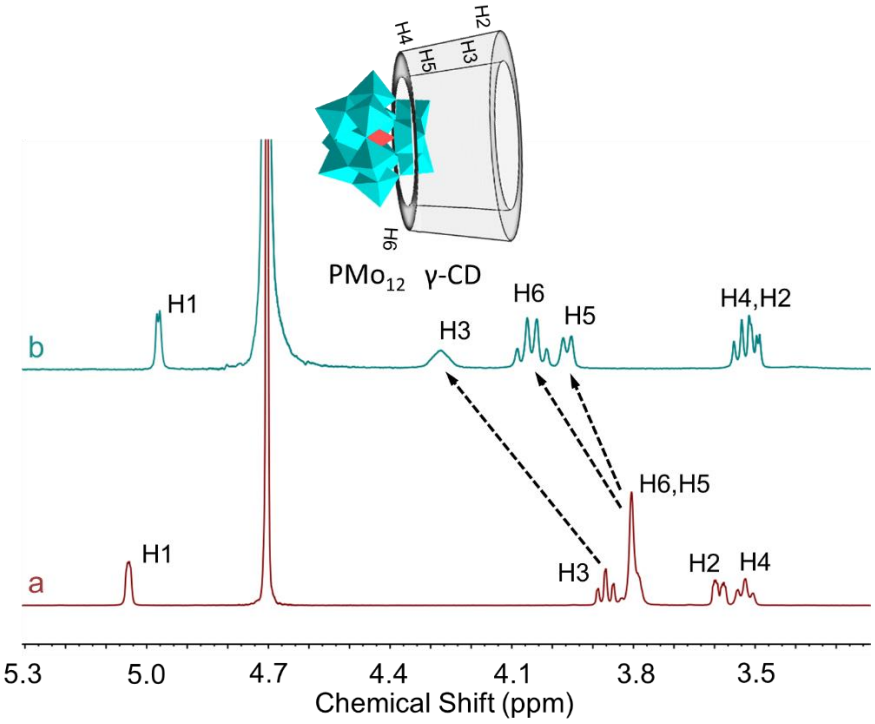

Fig. S3. ^{1}H NMR spectra of (a) γ-CD (0.1 mM) and (b) its mixture with PMo_{12} (1.0 mM) in D_2O at 25 °C. To ensure the clear assignment to the proton chemical shifts of γ-CD, excess PMo_{12} was used in the measurement.

Table S1. The summary of chemical shifts of three cyclodextrins and their mixtures with PMo_{12} from Fig. S1–S3.

	H1 (ppm)	H2 (ppm)	H3 (ppm)	H4 (ppm)	H5 (ppm)	H6 (ppm)
α-CD	4.98	3.56	3.91	3.51	3.83	3.78
α-CD–PMo_{12}	4.96	3.53	3.87	3.58	3.67	3.96
Δδ	0.02	0.03	0.04	−0.07	0.16	−0.16
β-CD	5.01	3.59	3.90	3.52	3.81	3.81
β-CD–PMo_{12}	4.98	3.54	3.87	3.56	3.73	3.90
Δδ	0.03	0.05	0.03	−0.04	0.04	−0.09
γ-CD	5.05	3.59	3.87	3.52	3.81	3.81
γ-CD–PMo_{12}	4.87	3.50	4.27	3.53	3.96	4.05
Δδ	0.08	0.09	−0.4	−0.01	−0.15	−0.24

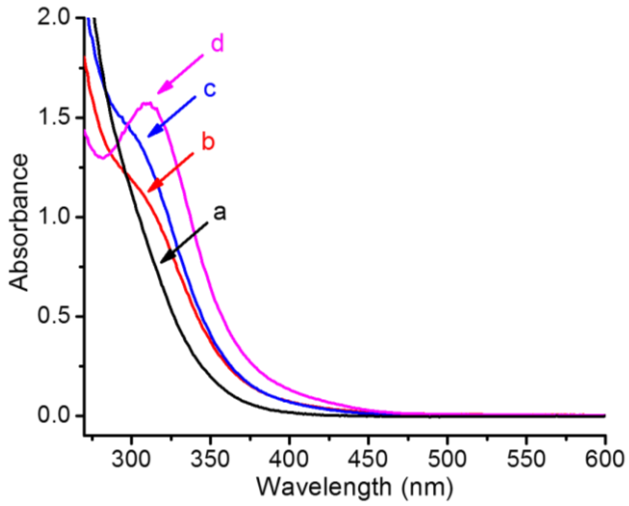

Fig. S4. UV-Vis spectra of (a) PMo_{12} (fixed at 1.0 mM) mixing with (b) α-CD (100 mM); (c) β-CD (14 mM) and (d) γ-CD (100 mM) in aqueous solution at room temperature. Excess CDs were used to ensure their distinct influence on the electronic absorption of PMo_{12} in the measurement.

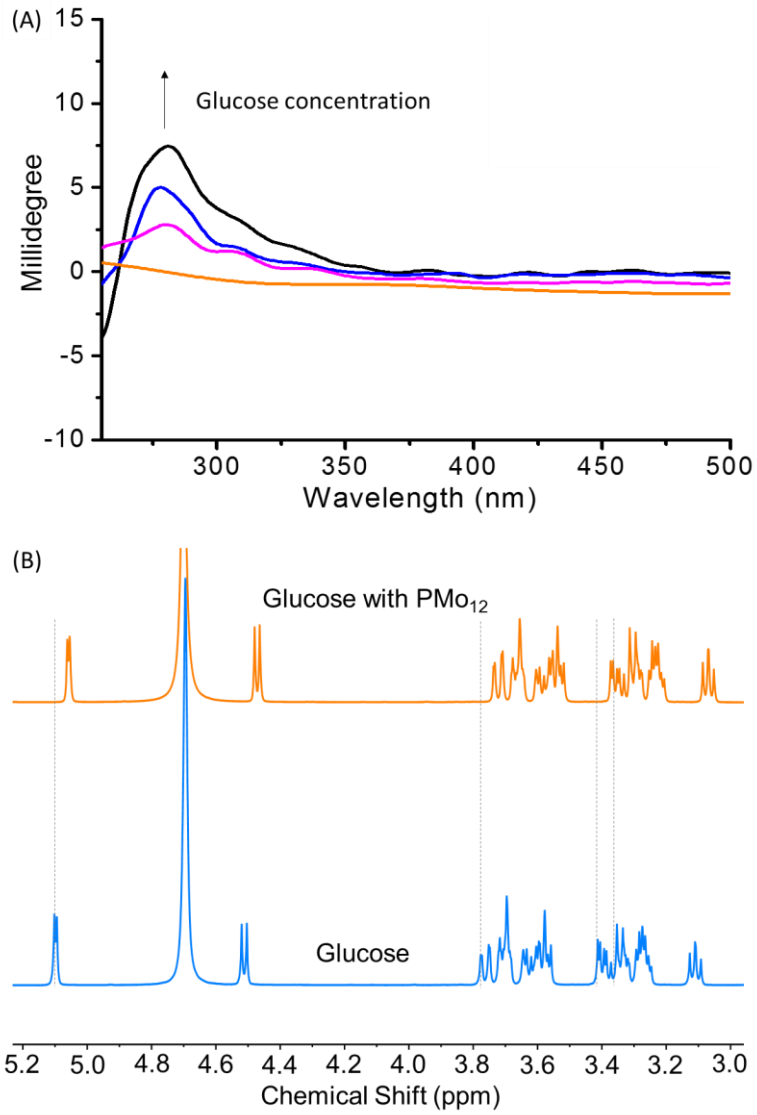

Fig. S5. CDS spectra of PMo_{12} (0.011 M) mixing with different conentration (0.21, 0.41, 0.83 and 3.30 M) of D-glucose in aqueous solution at room temperature and ^{1}H NMR spectra of D-glucose with and without addition of PMo_{12} in D_2O.

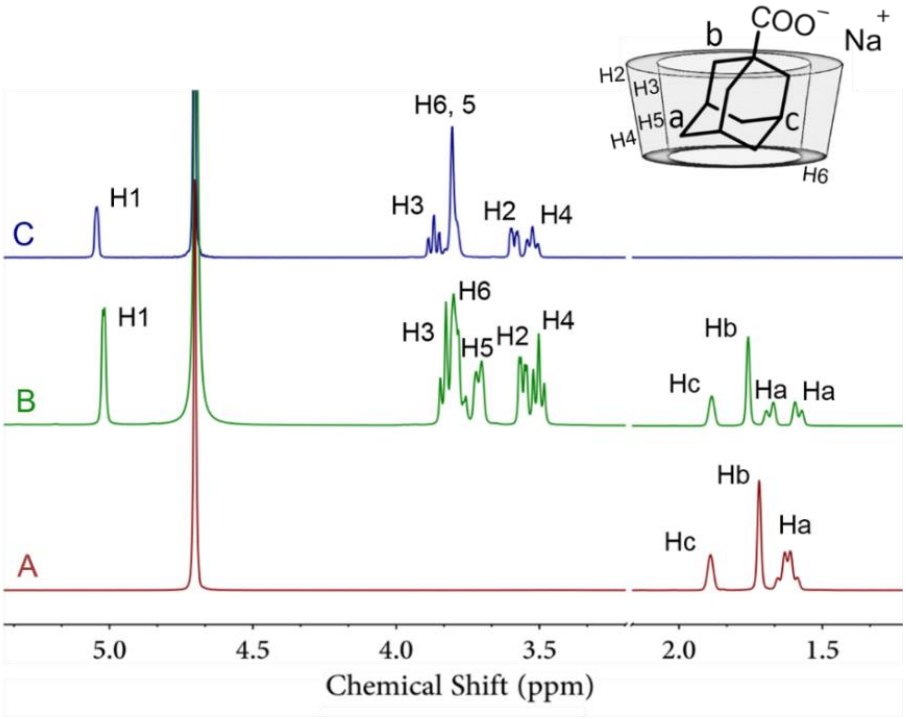

Fig. S6. ^{1}H NMR spectra of (A) AdCOONa, (B) γ-CD and AdCOONa mixture (1:1 in molar ratio, where the concentration of γ-CD fixing at 0.042 mM), and (C) isolated γ-CD in D_2O at 25 °C.

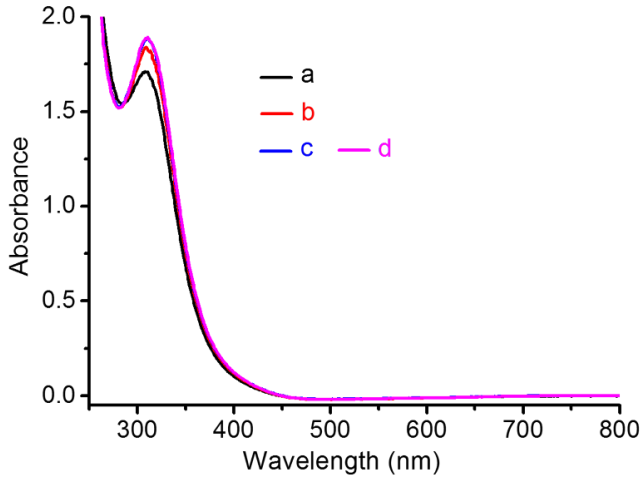

Fig. S7. UV-Vis spectra of PMo_{12} (1.0 mM) aqueous solution under the concentration of γ-CD at (a) 3.0, (b) 8.0, (c) 16.0 and (d) 24.0 mM.

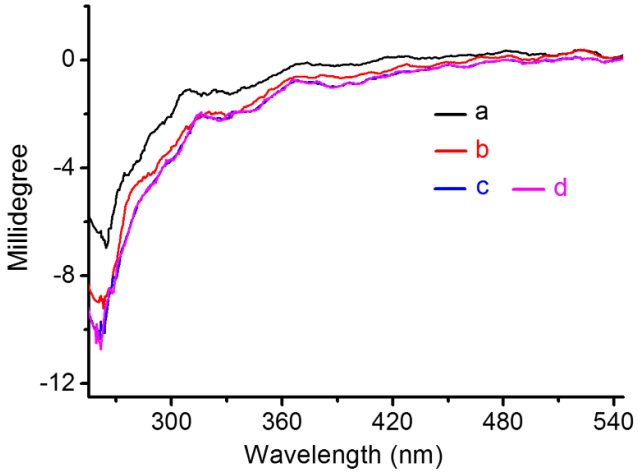

Fig. S8. CDS of PMo_{12} (1.0 mM) aqueous solution in the presence of γ-CD at (a) 3.0, (b) 8.0, (c) 16.0, and (d) 24.0 mM, corresponding to the UV-Vis spectra in Figure S8.

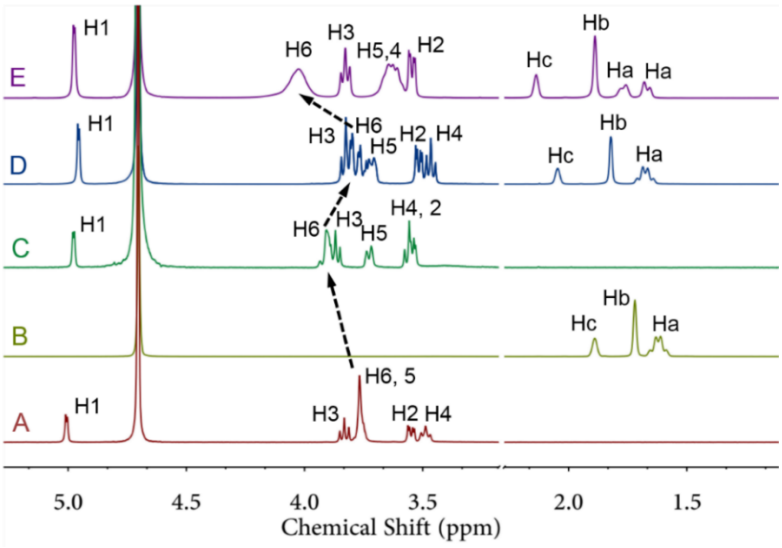

Fig. S9. ^{1}H NMR spectra of (A) β-CD, (B) AdCOONa, (C) β-CD−PMo_{12}, (D) β-CD−AdCOONa, and (E) β-CD−AdCOOH−PMo_{12} in D_2O at 25 °C.

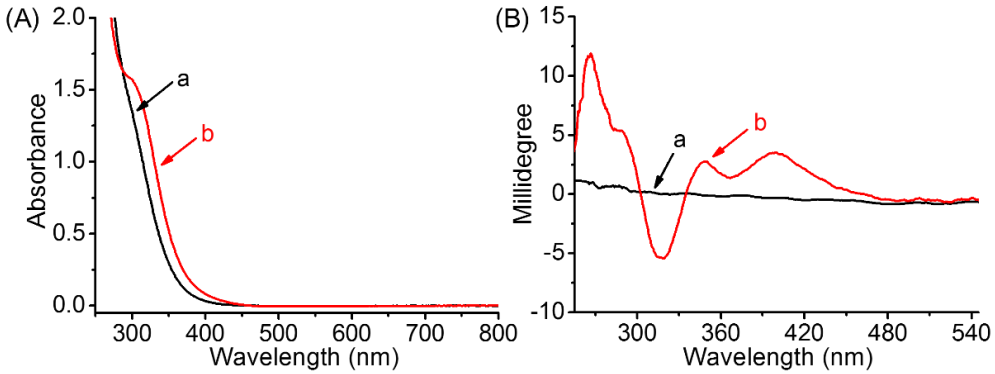

Fig. S10. (A) UV-Vis spectra of (a) β-CD−PMo_{12} (3:1 molar ratio) and (b) β-CD−AdCOOH−PMo_{12} (3:3:1 molar ratio), where PMo_{12} concentration is fixed at 1.0 mM; and (B) corresponding CDS of (a) β-CD−PMo_{12} and (b) β-CD−AdCOOH−PMo_{12} under the same concentration conditions.

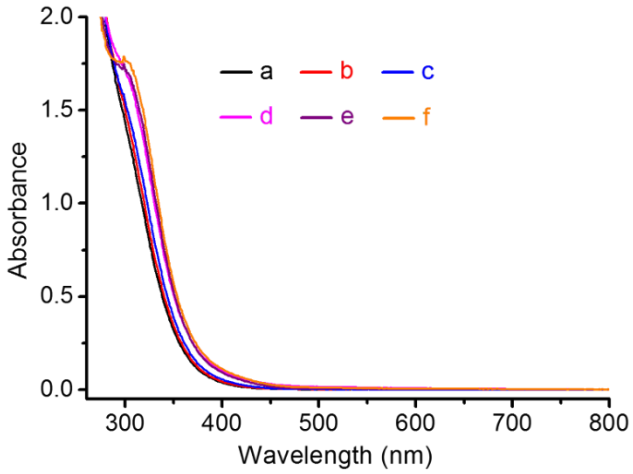

Fig. S11. UV-Vis spectra of PMo_{12} (fixing at 1.0 mM) in the presence of α-CD with gradually increasing concentration to (a) 3.0, (b) 5.0, (c) 10.0, (d) 20.0, (f) 30.0, and (e) 40.0 mM.

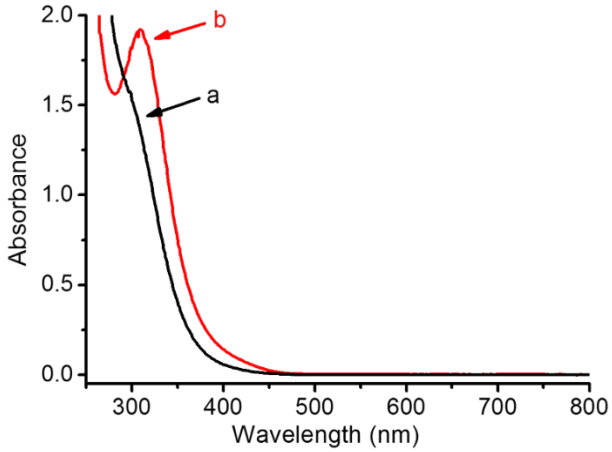

Fig. S12. UV-Vis spectra of (a) β-CD−PMo_{12} with the concentration ratio of β-CD to PMo_{12} at 16 mM to 1.0 mM) and (b) addition of γ-CD with the concentration of 16 mM.

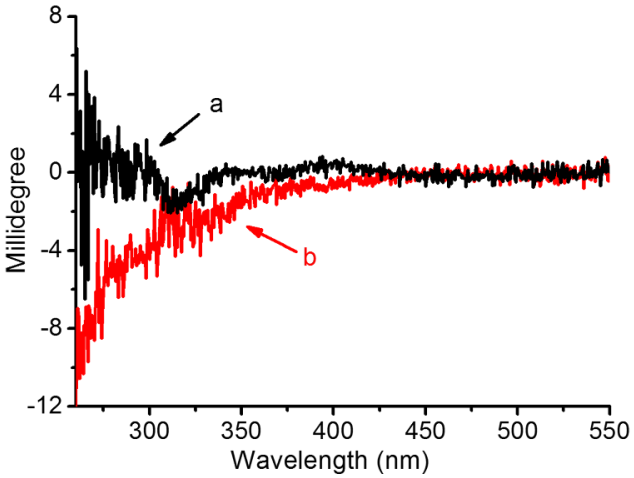

Fig. S13. CDS of (a) β-CD−PMo_{12} and (b) β-CD−PMo_{12} in the presence of γ-CD corresponding to the UV-Vis spectra in Fig. S13.

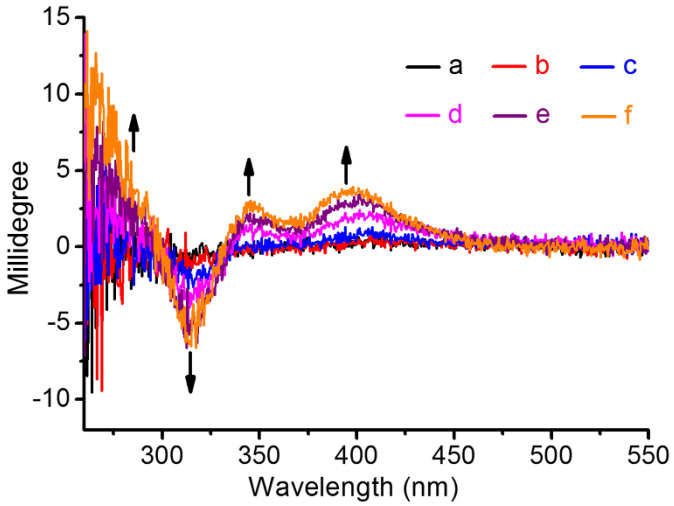

Fig. S14. CDS of α-CD–PMo_{12} with the concentration of α-CD increasing to (a) 3.0, (b) 5.0, (c) 10.0, (d) 20.0, (f) 30.0 and (e) 40.0 mM, corresponding to UV-Vis spectra in Fig. S12.