Supplementary Information

A Novel Single-Side Azobenzene-Grafted Anderson-Type Polyoxometalate for Recognition-Induced Chiral Migration

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Materials

Methylene blue (MB) trihydrate, *trans*-4-hydroxyazobenzene and 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) were purchased from Sinopharm Chemical Reagent Co, Ltd. (SCRC). α-Cyclodextrin was the product of TCI. All these chemicals were used without further purification. $[(C_4H_9)_4N]_3[AlMo_6O_{18}(OH)_3\{(OCH_2)_3CNH_2\}]\cdot 7H_2O$ (NH_2-$AlMo_6$) was synthesized according to the literature.[S1] The remaining chemicals and solvents were purchased from Beijing Chemical Reagent Company. Acetonitrile was dried over P_2O_5 and distilled prior to use. Doubly distilled water was used in the experiments.

Measurements

FT-IR spectra were carried out on a Bruker Vertex 80V FT-IR spectrometer equipped with a DTGS detector (32 scans) at a resolution of 4 cm^{-1} on a KBr pellet. The UV-Vis spectra were taken on a spectrometer (Varian CARY 50 Probe). ^1H NMR spectra were recorded on a Bruker AVANCE 500 and 600 MHz spectrometer. Chemical shifts were referenced to the solvent values ($\delta = 2.50$ ppm for DMSO-d_6 and $\delta = 4.79$ ppm for D_2O). Organic elemental analysis was carried out on a Flash EA1112 from Thermo-Quest Italia S.P.A. Circular dichroism spectra (CDS) were performed on a Bio-Logic MOS-450 spectropolarimeter in water with a step size of 1-nm and speed of 1 nm s^{-1} at 25 °C. Single-crystal X–ray diffraction data were collected on a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo K_α ($\lambda = 0.71073$ Å) at 293 K.

Synthesis

Ethyl (4-azophenyl)phenoxylacetate (1). The compound was synthesized according to the procedures in literature.[S2]

(4-azophenyl)acetic acid (2). A mixture of **1** (1.00 g 3.52 mmol) and potassium hydroxide (0.40 g, 7.04 mmol) in ethanol (80 ml) mixed solvent with distilled water (20 ml) was refluxed for 24 h with stirring. The reaction solution was then adjusted to pH 2 by the addition of HCl aqueous solution (5 % in w/w). An orange precipitate was collected by filtration, washed with acidic solution (pH 2) and dried (0.84 g 92%). ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C, δ = ppm): 13.13 (s, 1H, COOH), 7.90 (d, 2H, Ar H), 7.58 (t, 2H, Ar H), 7.53 (t, 1H, Ar H), 7.13 (d, 2H, Ar H), 4.82 (s, 2H, CH_2).

$[(C_4H_9)_4N]_3[AlMo_6O_{18}(OH)_3\{(OCH_2)_3CNHCOCH_2C_6H_4NNC_6H_5\}]$ (TBA-Azo-POM). The Anderson-type polyoxometalate, TBA-Azo-AlMo$_6$, was synthesized according to the literature.[S3] A mixture of **2** (0.34 g 1.33 mmol), NH_2-AlMo$_6$ (2.592 g 1.45 mmol) and EEDQ (0.39 g 1.58 mmol) in CH_3CN (25 ml) was stirred at 50 °C for 24 h. The solvent was removed under vacuum and the residue was washed by ethyl acetate (20 ml) three times. The resulting precipitate was dissolved in $CHCl_3$ (50 ml), then a large amount of Et_2O (150 ml) added to the solution. TBA-Azo-AlMo$_6$ was isolated as an orange solid (1.32 g 49%). ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C, δ = ppm): 7.86 (m, 4H, Ar H), 7.56 (t, 2H, Ar H), 7.51 (t, H, Ar H), 7.42 (s, 1H, CONH), 7.08 (d, 2H, Ar H), 4.66 (s, 4H, CH_2), 4.53 (s, 2H, CH_2), 3.55 (s, 3H, OH), 3.16 (t, 24H, CH_2), 1.57 (m, 24H, CH_2), 1.31 (m, 24H, CH_2), 0.94 (m, 36H, CH_3). IR (KBr, cm^{-1}): ν = 3421, 2960, 2933, 2870, 1731, 1697, 1598, 1481, 1460, 1382, 1238, 1058, 1029, 1006, 939, 919, 902, 840, 789, 663 cm^{-1}. Elemental analysis calcd. (%) for $(C_{16}H_{36}N)_3C_{18}H_{18}O_{23}N_3AlMo_6(OH)_3$ (2025.38 g mol^{-1}): C 39.14, H 6.42, N 4.15; found C 40.05, H 6.74, N 4.20.

$Na_3[AlMo_6O_{18}(OH)_3\{(OCH_2)_3CNHCOCH_2C_6H_4NNC_6H_5\}]$ (Na-Azo-POM). TBA-Azo-POM (0.2 g, 0.1 mmol) in acetonitrile (5 mL) was added dropwise into a vigorously stirred acetonitrile solution (5 mL) of $NaClO_4$ (0.25 g, 0.2 mmol), and then the mixed solution was kept stirring for 30 min to obtain an orange precipitation. The precipitate was washed twice with acetonitrile, giving a product Na-Azo-POM (0.106 g, 76%). ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C, δ = ppm): 7.86 (t, 4H, Ar H), 7.57 (t, 2H, Ar H), 7.52 (t, H, Ar H), 7.43 (s, 1H, CONH), 7.09 (d, 2H, Ar H), 4.68 (s, 4H, CH_2), 4.53 (s, 2H, CH_2), 3.68 (s, 3H, OH). Elemental analysis calcd. (%) for

$Na_3C_{18}H_{18}O_{23}N_3AlMo_6(OH)_3$ (1402.99 g mol^{-1}): C 15.41, H 1.80, N 3.00; found C 15.24, H 1.81, N 3.38.

Structural Characterizations

Table 1. Summary of Elemental analysis data of TBA-Azo-POM, crystal sample of TBA-Azo-POM, Na-Azo-POM and MB-Azo-POM.

Element	C (%)	H (%)	N (%)
TBA-Azo-POM			
Calculate	39.14	6.42	4.15
Found	40.05	6.74	4.20
Formula : $[(C_4H_9)_4N]_3C_{18}H_{18}O_{23}N_3AlMo_6(OH)_3$ (2025.38 g mol^{-1})			
Crystalline TBA-Azo-POM			
Calculate	33.66	5.31	3.93
Found	33.52	5.21	3.98
Formula : $[(C_4H_9)_4N]_2HC_{18}H_{18}O_{23}N_3AlMo_6(OH)_3$ (1783.92 g mol^{-1})			
Na-Azo-POM			
Calculate	15.41	1.80	3.00
Found	15.24	1.81	3.38
Formula : $Na_3C_{18}H_{18}N_3O_{23}AlMo_6(OH)_3{\cdot}2H_2O$ (1402.99 g mol^{-1})			
MB-Azo-POM			
Calculate	36.85	3.51	7.81
Found	36.54	3.41	7.88
Formula : $(C_{16}H_{18}N_3S)_3C_{18}H_{18}N_3O_{23}AlMo_6(OH)_3$ (2151.19 g mol^{-1})			

Table 2. Crystal analysis data and structure refinements of crystalline TBA-Azo-POM.

Empirical formula	C54 H110 Al Mo6 N5 O30
Formula weight	1912.09
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P−1
a (Å)	14.995(3)

b (Å)	15.608(3)
c (Å)	17.555(3)
α (°)	86.98(3)
β (°)	75.31(3)
γ (°)	82.81(3)
V ($Å^3$)	3942.1(13)
Z	2
$D_{calc.}$($g\ cm^{-3}$)	1.611
Abs. coeff. (mm^{-1})	1.014
F(000)	1948
R(int)	0.0408
GOOF on F^2	1.104
Final R indices [I>2sigma(I)]	$^{a}R1 = 0.0573$, $^{b}R_w = 0.1677$
R indices (all data)	$^{a}R1 = 0.0674$, $^{b}R_w = 0.1743$

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[a] $R1 = ||F_o| - |F_c||/|F_o|$; [b] $R_w = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

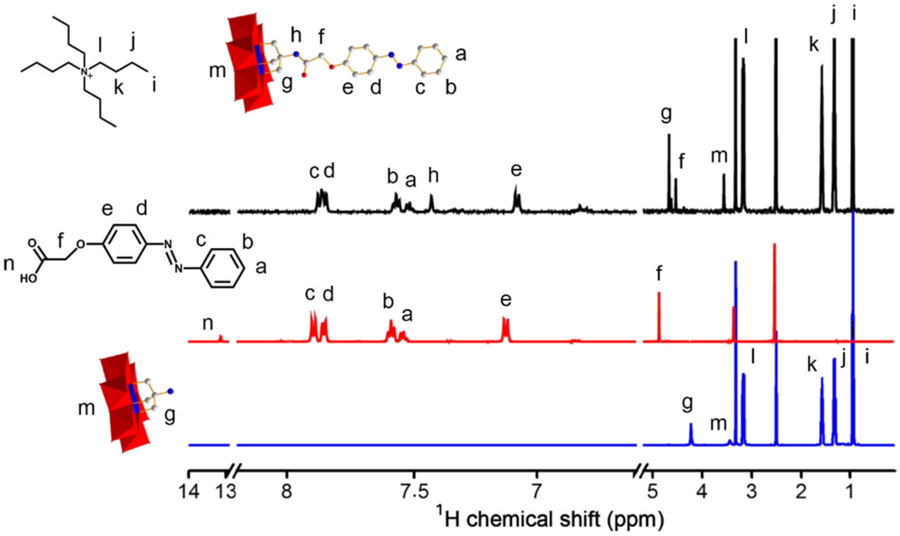

Fig. S1 ^{1}H NMR spectra of NH_2-POM, (4-azophenyl)acetic acid and TBA-Azo-POM in DMSO-d_6 at 25 °C.

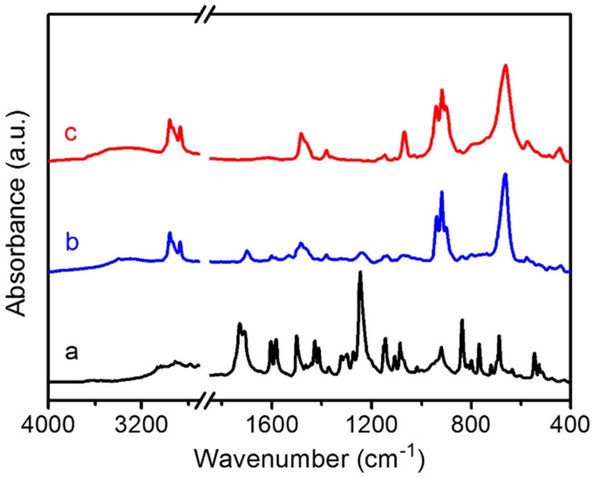

Fig. S2 FT-IR spectra of (a) (4-azophenyl)acetic acid; (b) TBA-Azo-POM and (c) NH_2-POM in KBr pellets.

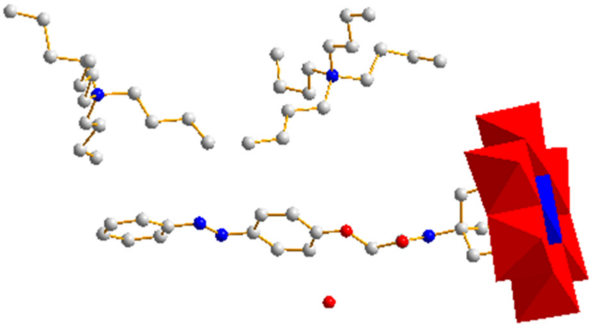

Fig. S3 Crystal structure of TBA-Azo-POM with two TBA counterions.

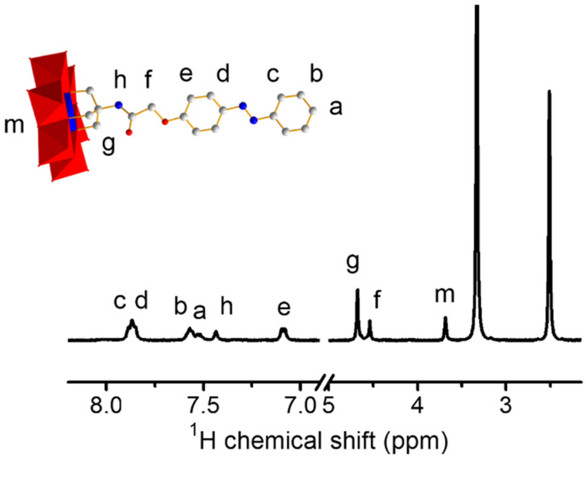

Fig. S4 ^{1}H NMR spectrum of Na-Azo-POM in DMSO-d_6 at 25 °C.

Chiral Migration

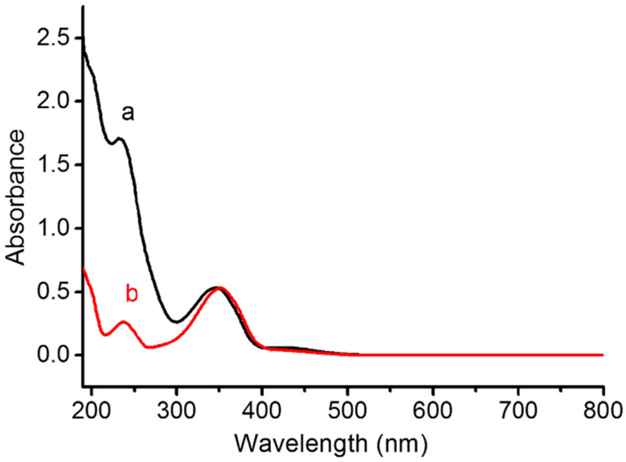

Fig. S5 UV-Vis spectra of (a) Na-Azo-POM mixed with α-CD and (b) Azo-COOH mixed with α-CD in aqueous solution.

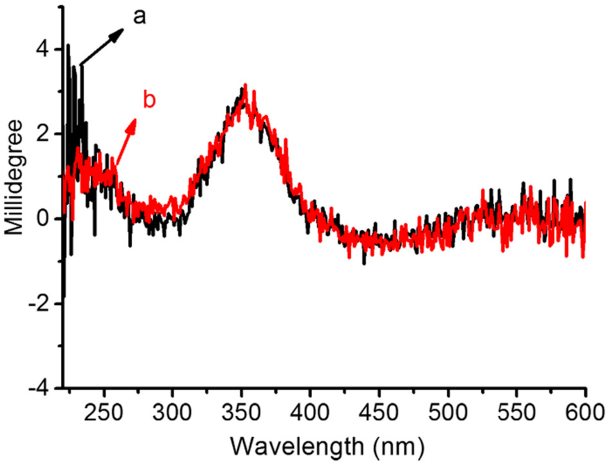

Fig. S6 CDS of (a) Na-Azo-POM mixed with α-CD and (b) Azo-COOH mixed with α-CD in aqueous solution.

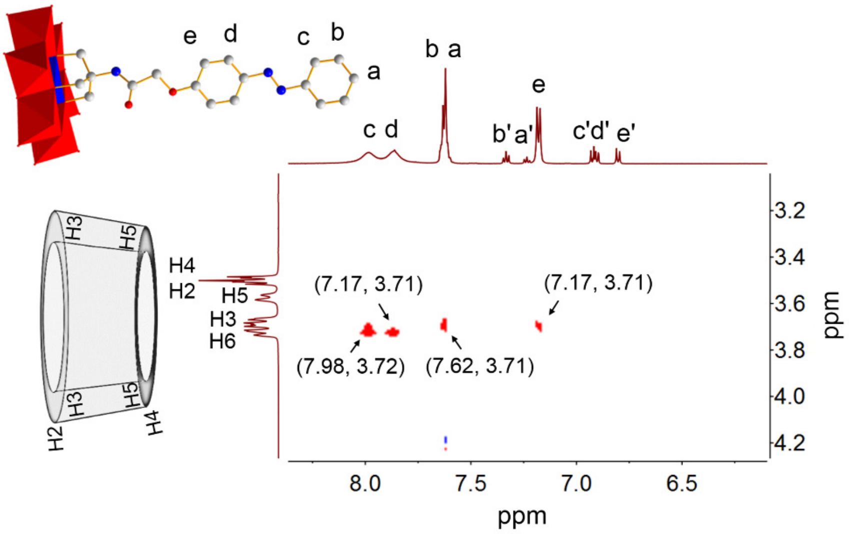

Fig. S7 2D ROESY NMR spectrum of Na-Azo-POM mixed with equivalent mole of α-CD in D_2O at 25 °C. Four cross-correlation peaks appear in the spectrum, implying the formation of the inclusion complex between Na-Azo-POM and α-CD.

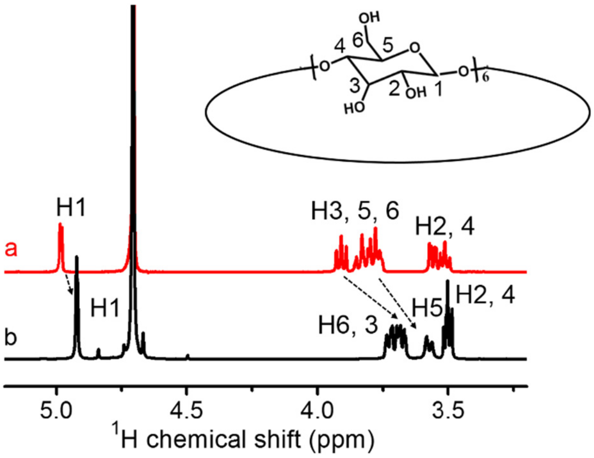

Fig. S8 (a) ^{1}H NMR spectrum of α-CD alone and (b) corresponding 1D selective ROESY spectrum in the mixture solution with equivalent mole of Na-Azo-POM in deuterated water. In this 1D selective ROESY NMR experiment,the peaks belonging to α-CD shift to the high field, especially the peaks come from the cavity microenvironment (δ_{H3} = 3.91–3.68 ppm, δ_{H5} = 3.78–3.57 ppm), indicating the existence of intramolecular inclusion interaction between Na-Azo-POM and α-CD.

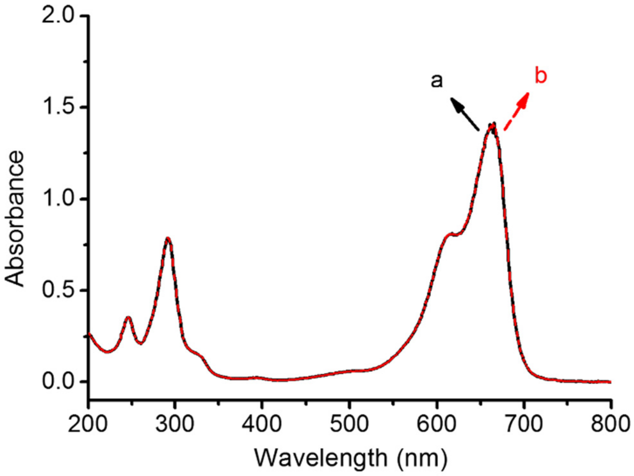

Fig. S9 UV-Vis spectra of isolated MB in water solution at (a) RT and (b) 80 °C after 30 min standing for each measurement.

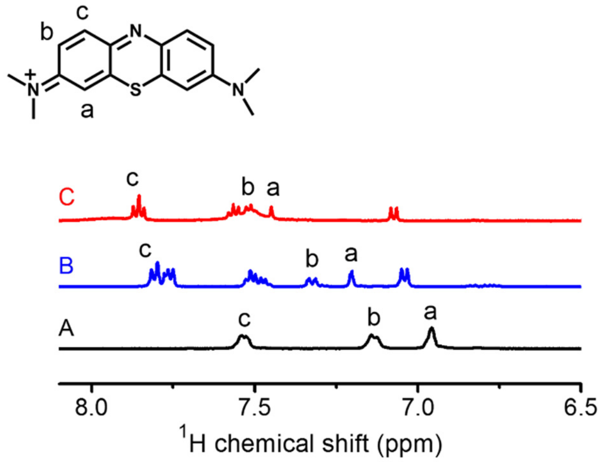

Fig. S10 ^{1}H NMR spectrum of (A) MB; (B) MB mixing with Na-Azo-POM in the mixed solution of D_2O/DMSO-d_6 (1:1 in v/v) and (C) MB-Azo-POM in DMSO-d_6.

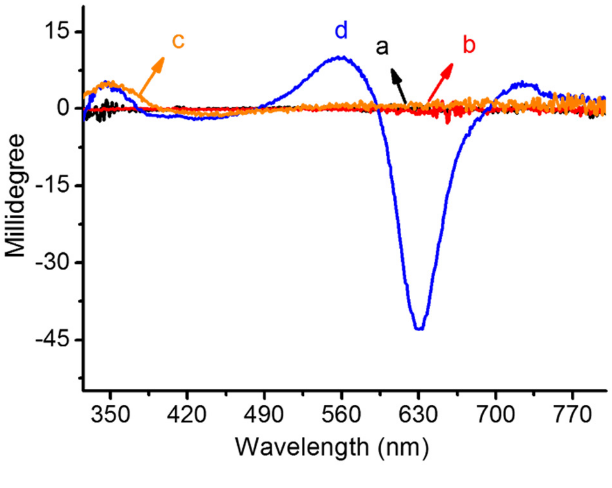

Fig. S11 CDS of (a) MB mixed with Na-Azo-POM; (b) MB mixed with α-CD; (c) Na-Azo-POM mixed with α-CD and (d) MB mixed with α-CD included Na-Azo-POM in aqueous solution.

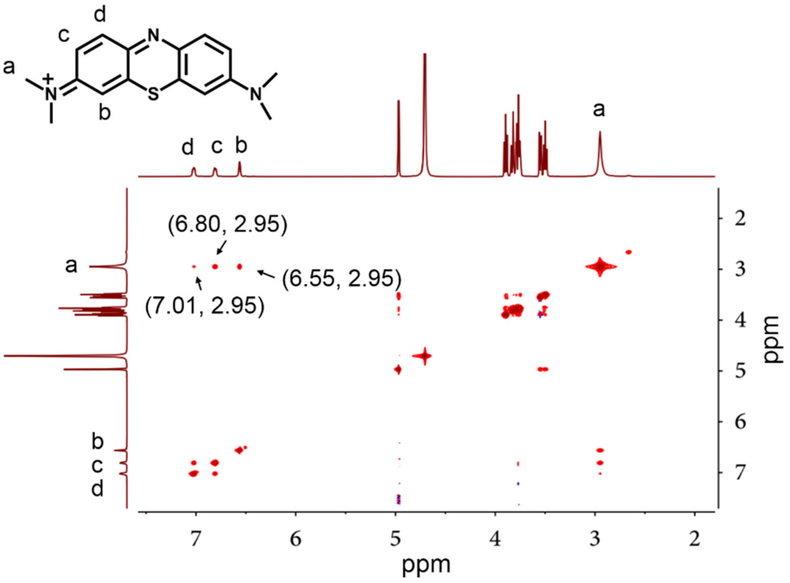

Fig. S12 2D ROESY NMR spectrum of MB with equivalent molar α-CD in D_2O at 25 °C. The three cross-correlation peaks appeared in the spectrum indicate the self cross-correlation of the MB and no inclusion interaction with α-CD.

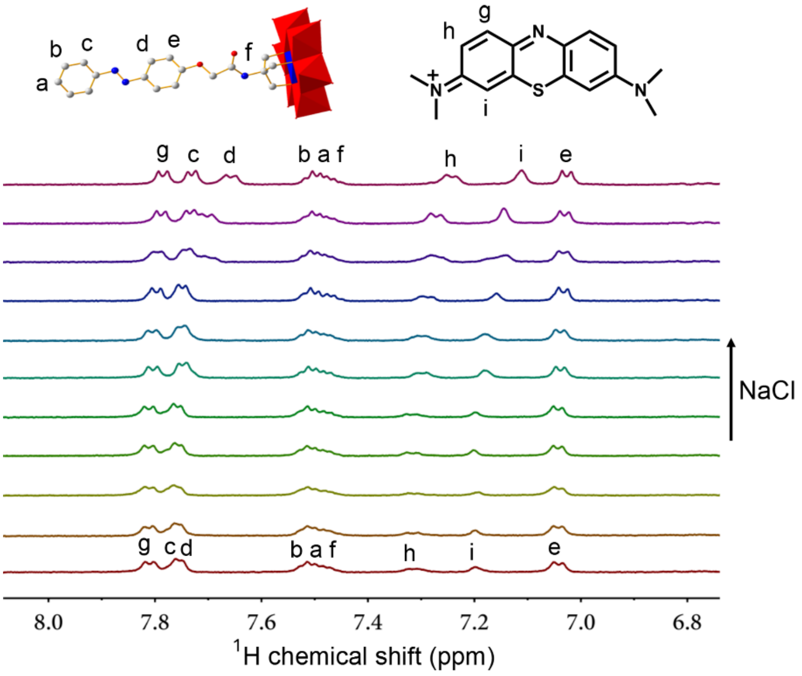

Fig. S13 ^{1}H NMR spectra of Na-Azo-POM mixed with MB by gradually increasing the concentration of NaCl (0, 0.043, 0.086, 0.128, 0.171, 0.214, 0.257, 0.342, 0.428, 0.599, 0.770 mmol ml^{-1}) in the mixed solution of D_2O/DMSO-d_6 (1:1 in v/v). The proton peaks belonging to both Na-Azo-POM and MB shift to the high field, implying the electrostatic interaction between MB and Azo-POM cluster becomes weaker.

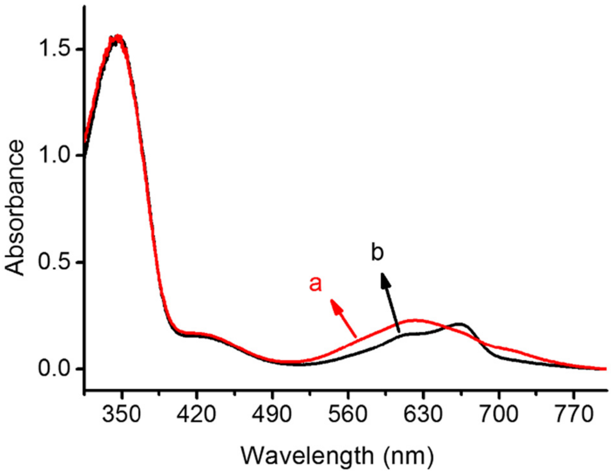

Fig. S14 UV-Vis spectra of MB and Na-Azo-POM mixing with α-CD (a) without and (b) with NaCl (1.454 mmol ml^{-1}).

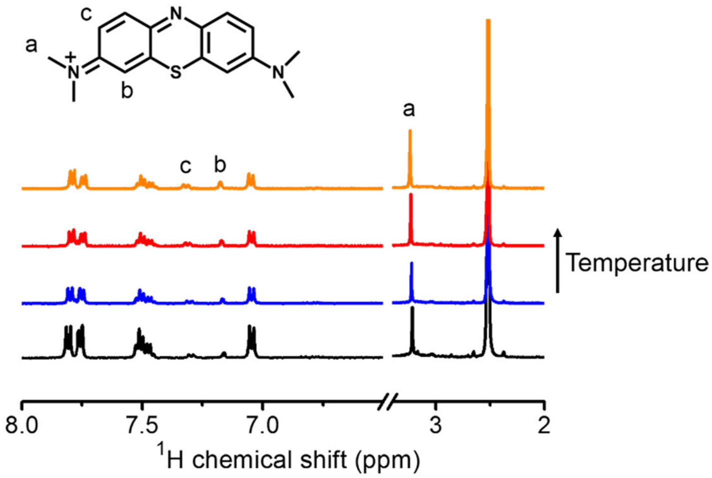

Fig. S15 ^{1}H NMR spectra of Na-Azo-POM mixed with MB at different temperature (30, 40, 50, and 60 °C) in the mixed solution of D_2O/DMSO-d_6 (1:1 in v/v). The proton peaks belonging to MB remain the same chemical shift during heating process, implying that the electrostatic interaction between MB and Azo-POM cluster has not changed with increasing the temperature.

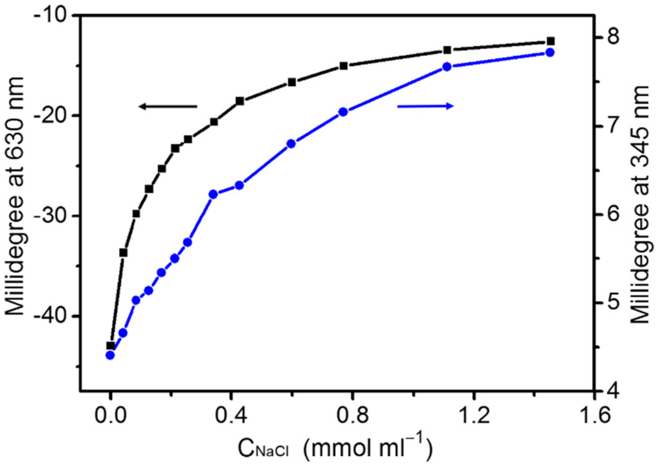

Fig. S16 Plots of Millidegree values of CDS at 630 nm and 345 nm versus the concentrations of NaCl (0, 0.043, 0.086, 0.128, 0.171, 0.214, 0.257, 0.342, 0.428, 0.599, 0.770, 1.112, and 1.454 mmol ml^{-1}).

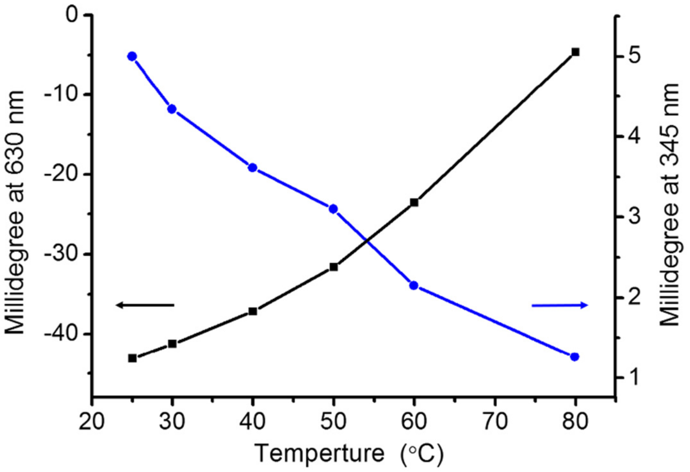

Fig. S17 Plot of Millidegree values of CDS at 630 nm and 345 nm versus the different temperature (RT, 30, 40, 50, 60, 80 °C).

References

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[2] Y. Yan, H. Wang, B. Li, G. Hou, Z. Yin, L. Wu and V. W. W. Yam, Angew. Chem. Int. Ed., 2010, **122**, 9419.

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