Supplementary Information

Controlled Chiral Electrochromism of Polyoxometalates Incorporated in Supramolecular Complexes

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Materials

1-adamantanamine hydrochloride (AdH) was purchased from J&K Chemical Co, Ltd. and was used without any further purification. β-Cyclodextrin (CD) was the product of Sinopharm Chemical Reagent Co, Ltd. (SCRC) and was recrystallized three times before use. $H_4[PMo_{11}VO_{40}]\cdot 32.5H_2O$ ($PMo_{11}V$) was synthesized according to the literature[1]. $H_3PMo_{12}O_{40}$ (PMo_{12}) and the remaining chemicals were purchased from Beijing Chemical Reagent Company. 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} by using KBr pellet. The UV-Vis spectra were recorded on a spectrometer (Varian CARY 50 Probe). ^1H NMR spectra were taken on a Bruker AVANCE 500 and 600 MHz spectrometer. Chemical shifts were referenced to the solvent values (δ = 4.79 ppm for D_2O). Circular dichroism spectra (CDS) were performed 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. Solid CDS was collected with the same spectropolarimeter on a KBr pellet. Optical rotation values were obtained with a WZZ-3 automtic polarimeter equipping with sodium lamp (λ = 589.44 nm). Electrochemical measurements were tested by CHI 660C electrochemical workstation at room temperature under nitrogen atmosphere. A three electrode electrochemical cell containing a platinum wire as the counter electrode, an Ag/AgCl as reference electrode and a glassy carbon electrode (GCE) as the working electrode was used in the measurement. ITC data was collected by TAM III microcalorimetric (TA) system with a stainless steel sample cell.

Sample Preparations

β-CD: β-CD (100 mg, 0.088 mmol) was dissolved in 10 ml water with stirring at room temperature for 6 h, then let the resulting solution stand 2 h for test.

β-CD–AdH: β-CD (100 mg, 0.088 mmol) and AdH (16.54 mg, 0.088 mmol) in 10 ml water was stirred at room temperature for 6 h, then the solution aged 2 h for further experiments.

β-CD–AdH–$PMo_{11}V$: β-CD (63.56 mg, 0.056 mmol) and AdH (10.52 mg, 0.056 mmol)

dissolving in 4 ml distilled water was stirred at room temperature for 2 h. Then $PMo_{11}V$ (3.31 mg, 0.014 mmol) in 6 ml distilled water was added dropwise into the β-CD−AdH solution by continually stirring at room temperature for 2 h. The resulting solution (β-CD:AdH:$PMo_{11}V$ at molar ratio 4:4:1) was allowed to stand for 4 h for measurement.

Solid sample of β-CD−AdH−$PMo_{11}V$: The solid sample was prepared by freeze-drying the aqueous sample of β-CD−AdH−$PMo_{11}V$.

β-CD−AdH−PMo_{12}: The sample with β-CD:AdH:PMo_{12} molar ratio at 3:3:1 was prepared similar as that of β-CD−AdH−$PMo_{11}V$.

β-CD−PMo_{12}: The sample was prepared according to the literature.[2]

Characterizations

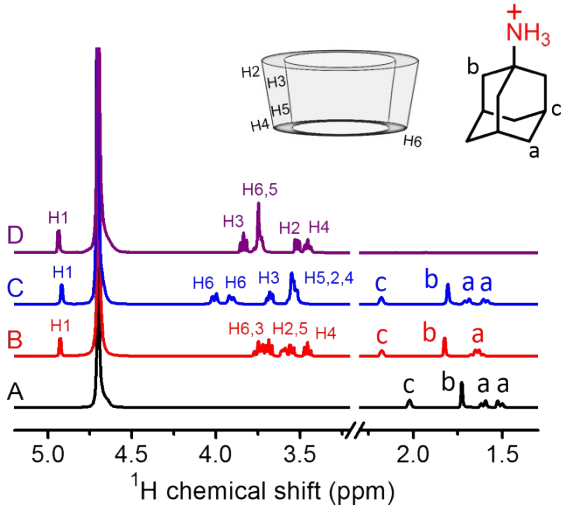

Fig. S1 ^1H NMR spectra of (A) AdH, (B) β-CD−AdH (1:1 molar ratio), (C) β-CD−AdH−$PMo_{11}V$ (4:4:1 molar ratio), and (D) β-CD in D_2O at 25 °C.

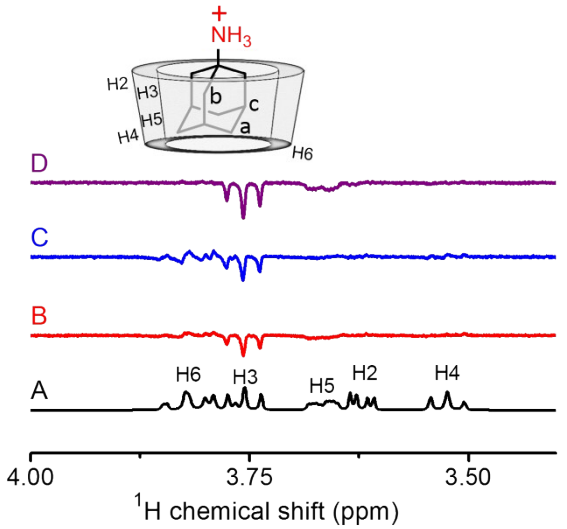

Fig. S2 ^1H NMR spectrum of (A) β-CD in β-CD−AdH inclusion complex D_2O solution at 25 °C and corresponding 1D selective Gradient NOESY spectra, irradiated with the frequency belonging to

AdH at (B) 1.712 ppm for H_a, (C) 1.914 for H_b, and (D) 2.260 ppm for H_c.

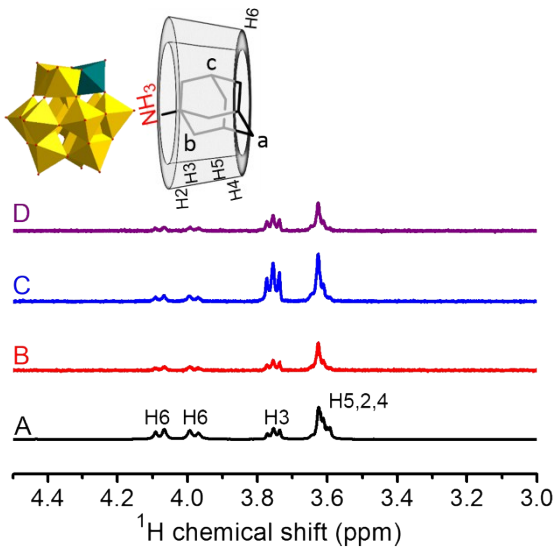

Fig. S3 ^{1}H NMR spectra of (A) β-CD−AdH−$PMo_{11}V$ in D_2O at 25 °C and corresponding 1D selective Gradient NOESY NMR spectra, irradiated with the frequency belonging to AdH at (B) 1.610−1.719 ppm for H_a, (C) 1.835 for H_b, and (D) 2.200 ppm for H_c.

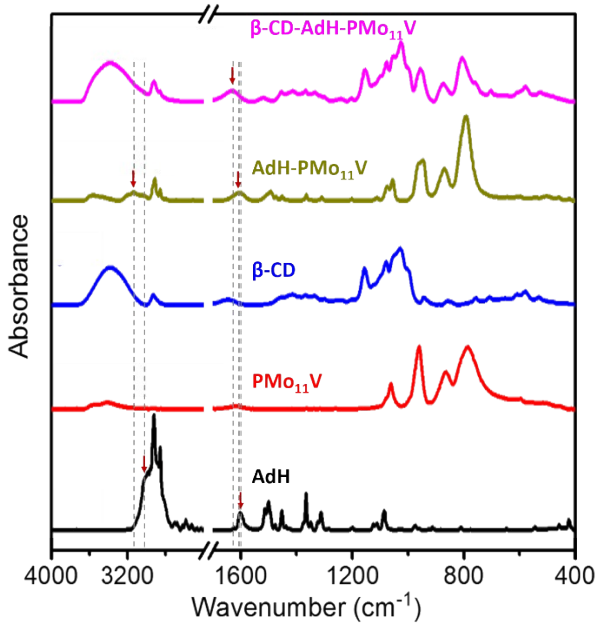

Fig. S4 FT-IR spectra of AdH, $PMo_{11}V$, β-CD, AdH−$PMo_{11}V$ and β-CD−AdH−$PMo_{11}V$ in KBr pellets.

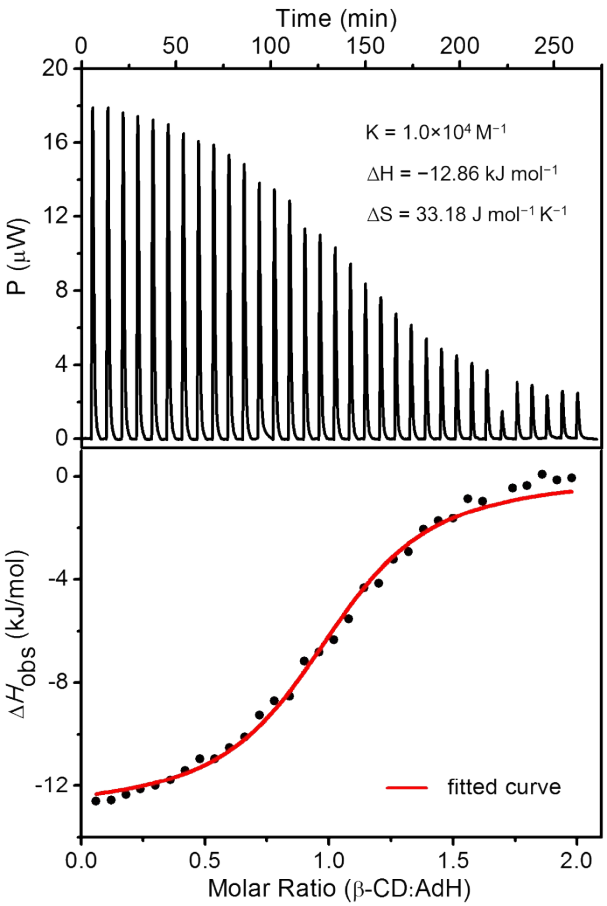

Fig. S5 ITC curve and corresponding plot of observed enthalpy changes (Δ_{obs}) against β-CD:AdH molar ratio by titrating 9.0 mM β-CD into 2.5 mM AdH aqueous solution, where Δ_{obs} values are expressed in terms of kJ mol^{-1} of β-CD and the dilution enthalpy of β-CD has been deducted.

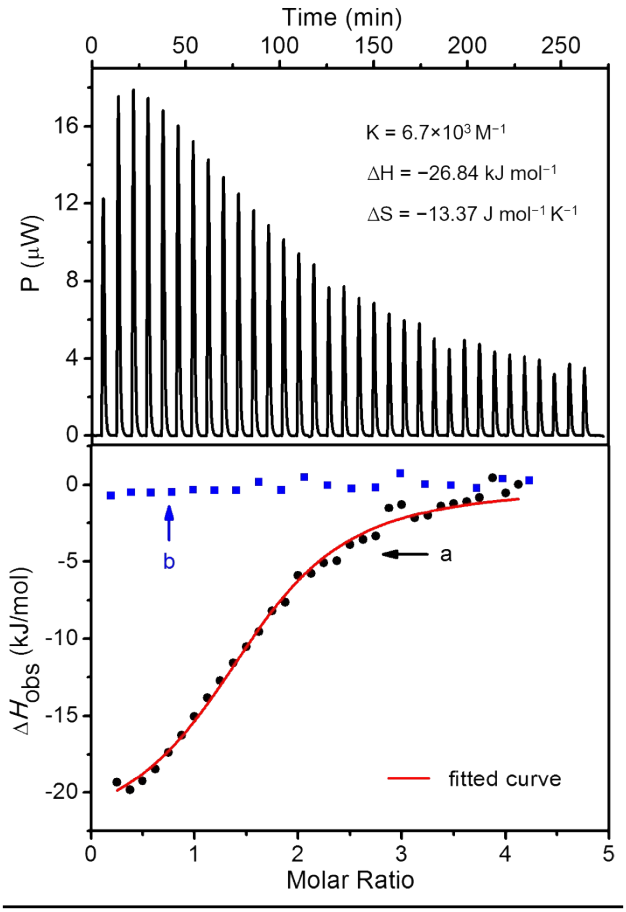

Fig. S6 ITC curve and corresponding plots of observed enthalpy changes (Δ_{obs}) against (a) β-CD−AdH:$PMo_{11}V$ by titrating 6.0 mM β-CD−AdH into 0.8 mM $PMo_{11}V$ aqueous solution and (b) β-CD:$PMo_{11}V$ by titrating 6.0 mM β-CD into 0.8 mM $PMo_{11}V$ aqueous solution. The Δ_{obs} values are in terms of kJ mol^{-1} of β-CD−AdH and the dilution enthalpy of β-CD−AdH has been deducted.

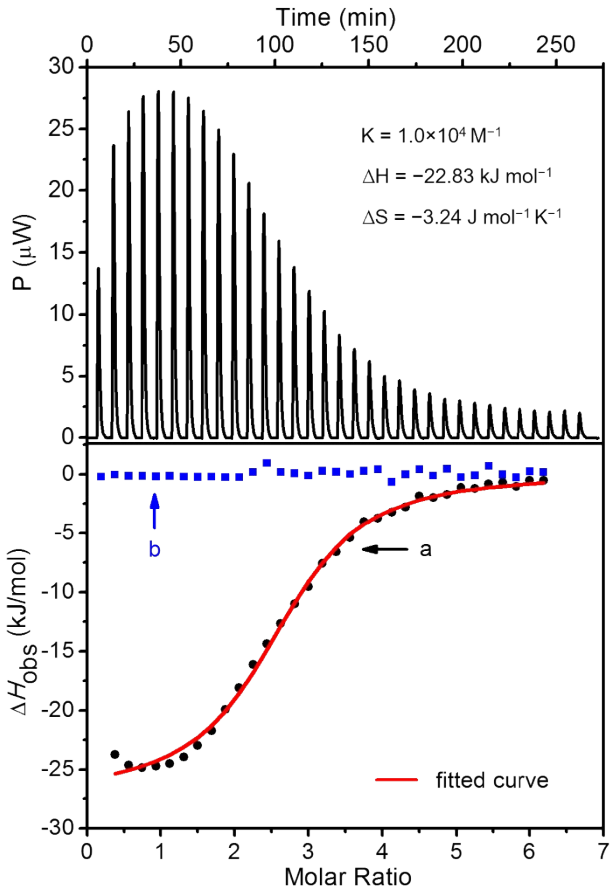

Fig. S7 ITC curve and corresponding plots of observed enthalpy changes (Δ_{obs}) against (a) β-CD−AdH:PMo_{12} by titrating 9.0 mM β-CD−AdH into 0.8 mM PMo_{12} aqueous solution and (b) β-CD:PMo_{12} by titrating 9.0 mM β-CD into 0.8 mM PMo12 aqueous solution. The Δ_{obs} values are in terms of kJ mol^{-1} of β-CD−AdH and the dilution enthalpy of β-CD−AdH has been deducted.

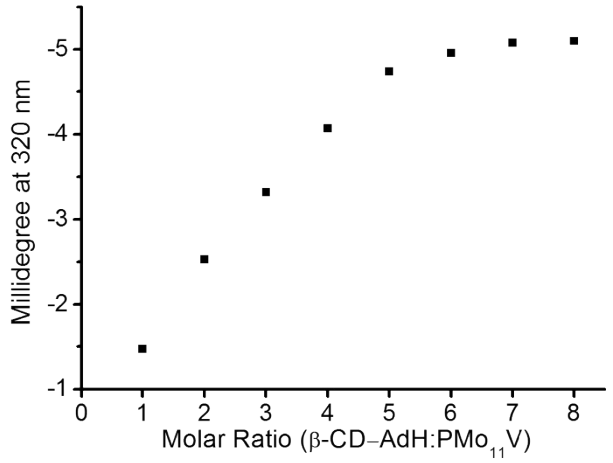

Fig. S8 Plot of millidegree value in CDS of β-CD−AdH−$PMo_{11}V$ at 320 nm versus the molar ratio of $PMo_{11}V$ (concentration fixing at 1.4×10^{-3} mmol ml^{-1}) gradually increasing in order of β-CD:AdH:$PMo_{11}V$ at 1:1:1, 2:2:1, 3:3:1, 4:4:1, 5:5:1, 6:6:1, 7:7:1 and 8:8:1.

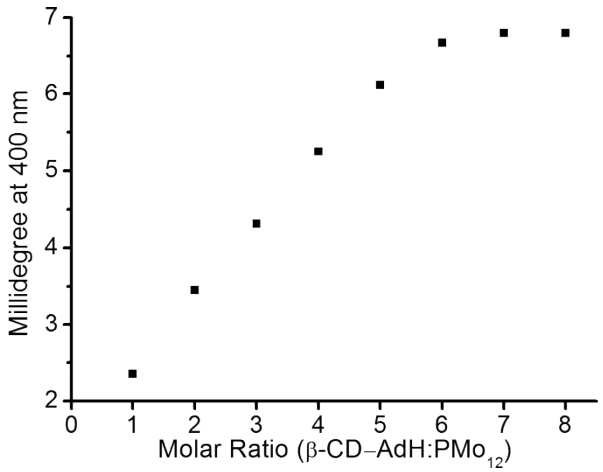

Fig. S9 Plot of millidegree values in CDS of β-CD−AdH−PMo_{12} at 400 nm versus the molar ratio of PMo_{12} (concentration fixing at 1.11×10^{-3} mmol ml^{-1}) gradually increasing in order of β-CD:AdH:PMo_{12} at 1:1:1, 2:2:1, 3:3:1, 4:4:1, 5:5:1, 6:6:1, 7:7:1 and 8:8:1.

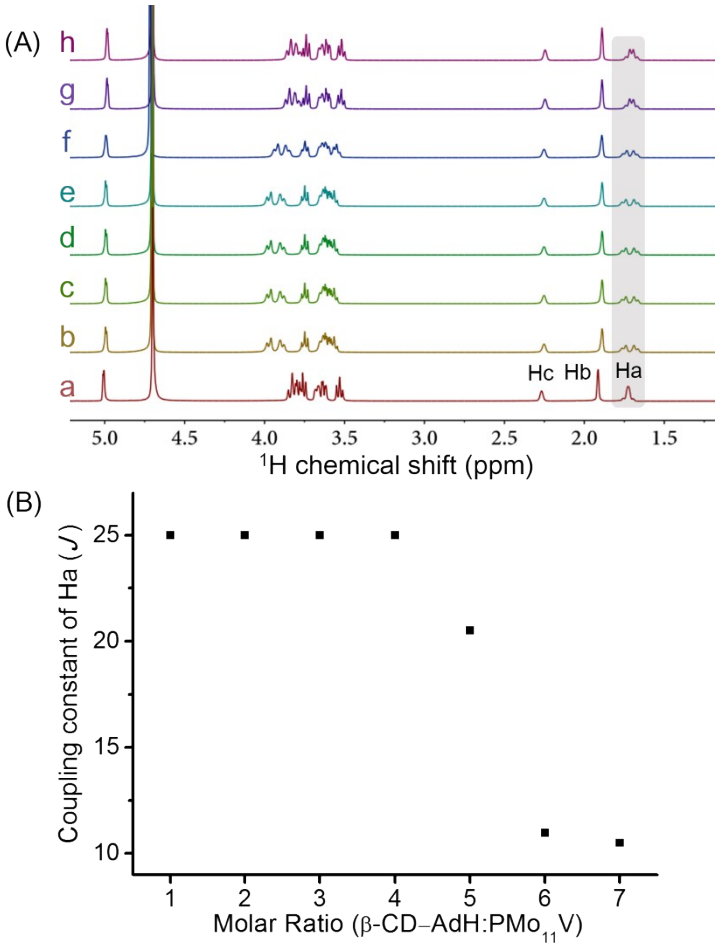

Fig. S10 (A) ^1H NMR spectra of β-CD−AdH−$PMo_{11}V$ in D_2O with a certain concentration of AdH at 4.1×10^{-2} mmol ml^{-1} with the molar ratio of β-CD:AdH:$PMo_{11}V$ at (a) 1:1:0, (b) 1:1:1, (c) 2:2:1, (d) 3:3:1, (e) 4:4:1, (f) 5:5:1, (g) 6:6:1 and (h) 7:7:1, and (B) corresponding plot of Ha coupling constant versus the above molar ratio changes.

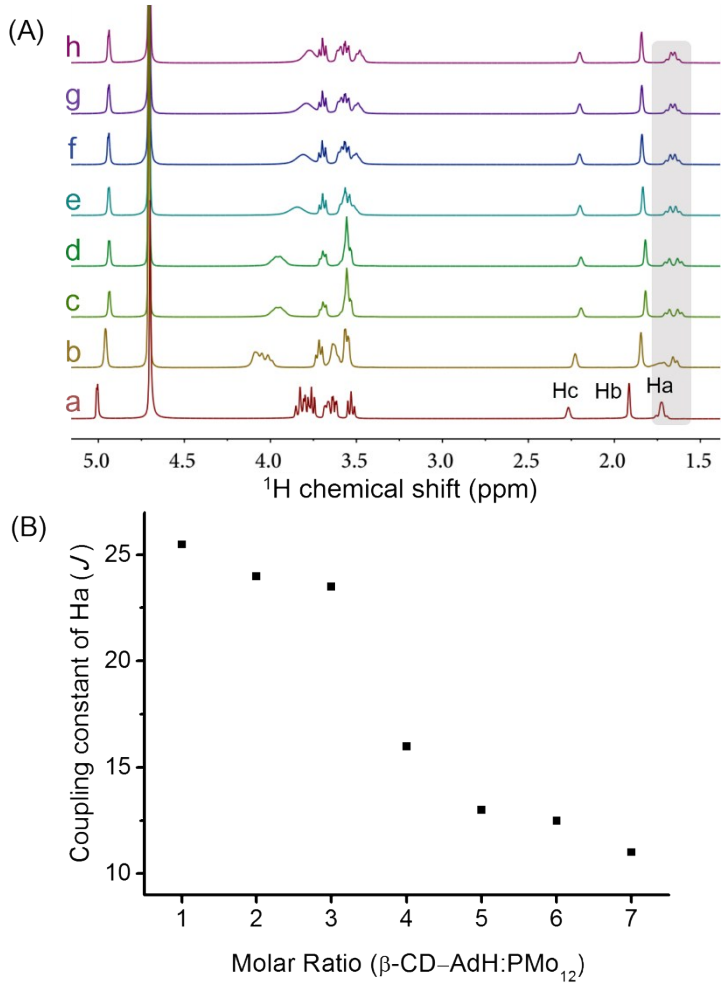

Fig. S11 (A) ^{1}H NMR spectra of β-CD–AdH–PMo_{12} in D_2O with a certain concentration of AdH at 4.1×10^{-2} mmol ml^{-1} except (b) 1×10^{-2} mmol ml^{-1} used considering the solubility, and the molar ratio of β-CD:AdH:PMo_{12} set at (a) 1:1:0, (b) 1:1:1, (c) 2:2:1, (d) 3:3:1, (e) 4:4:1, (f) 5:5:1, (g) 6:6:1 and (h) 7:7:1, and (B) corresponding plot of Ha coupling constant versus the above molar ratio changes.

Chiral migration characterization

Table S1. The summary of optical rotation values of β-CD, β-CD–AdH, β-CD–AdH–$PMo_{11}V$ and β-CD–AdH–PMo_{12}.[a]

Sample	Optical Rotation ($[\alpha]^{20}_{D}$)[b]	Variance (σ_{n-1})[c]
β-CD	161.62	0.286
β-CD–AdH (1:1 molar ratio)	129.15	0.187
β-CD–AdH–$PMo_{11}V$ (4:4:1 molar ratio)	99.48	0.232
β-CD–AdH–PMo_{12} (3:3:1 molar ratio)	71.95	0.187

[a] All sample solutions were prepared under a constant β-CD concentration of 10 mg ml^{-1} (8.8 mM), and the variable concentrations of other components depending on their molar ratio to β-CD.

[b] Each of optical rotation values is an average of six parallel tests.

[c] The variance is the dispersion degree of tests.

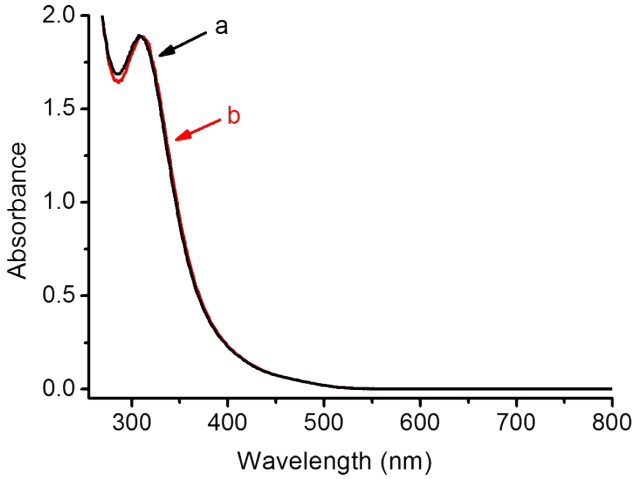

Fig. S12 UV-Vis spectra of (a) β-CD−$PMo_{11}V$ and (b) β-CD−AdH−$PMo_{11}V$ in aqueous solution at room temperature.

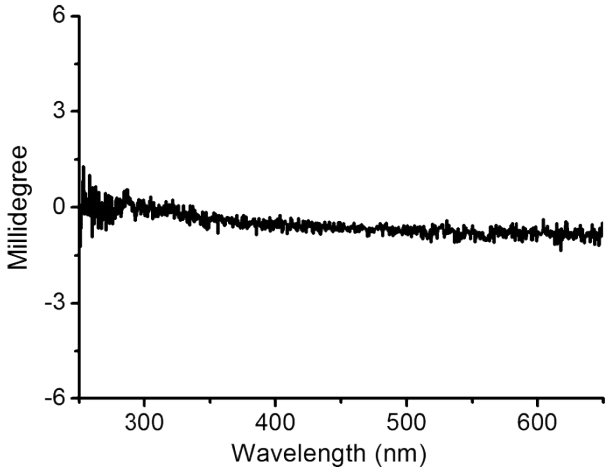

Fig. S13 Solid CDS of β-CD−PMo_{12} in KBr pellet.

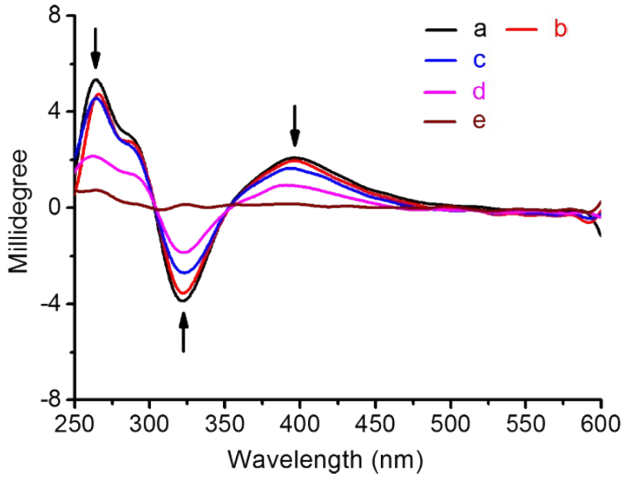

Fig. S14 CDS of β-CD−AdH−$PMo_{11}V$ in aqueous solution with a certain concentration of $PMo_{11}V$ at 1.4×10^{-3} mmol ml^{-1} versus the molar ratio of β-CD:AdH:$PMo_{11}V$ at (a) 4:4:1, (b) 4:3:1, (c) 4:2:1, (d) 4:1:1, and (e) 4:0:1.

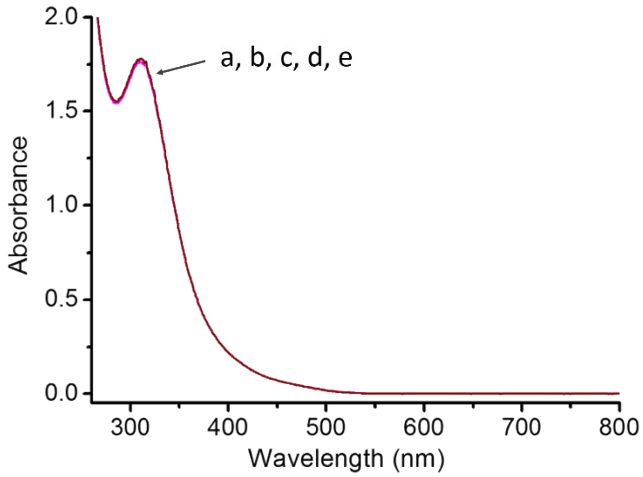

Fig. S15 UV-Vis spectra of β-CD−AdH−$PMo_{11}V$ in aqueous solution used in corresponding to CDS in Fig S7, and there is no change of the absorption value because of the same concentration of $PMo_{11}V$ in the experiments.

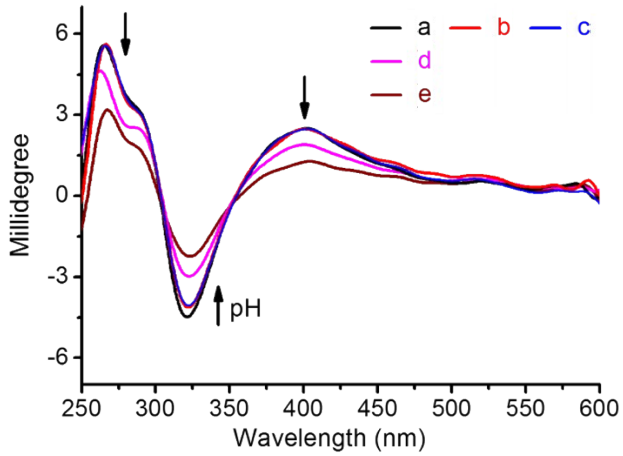

Fig. S16 CDS of β-CD−AdH−$PMo_{11}V$ (4:4:1 molar ratio) in aqueous solution ($PMo_{11}V$ concentration fixing at 1.4×10^{-3} mmol ml^{-1}) with gradually increasing pH from (a) 2.65, to (b) 2.86, (c) 3.48, (d) 5.36, and (e) 5.80, by adding dilute NaOH aqueous solution.

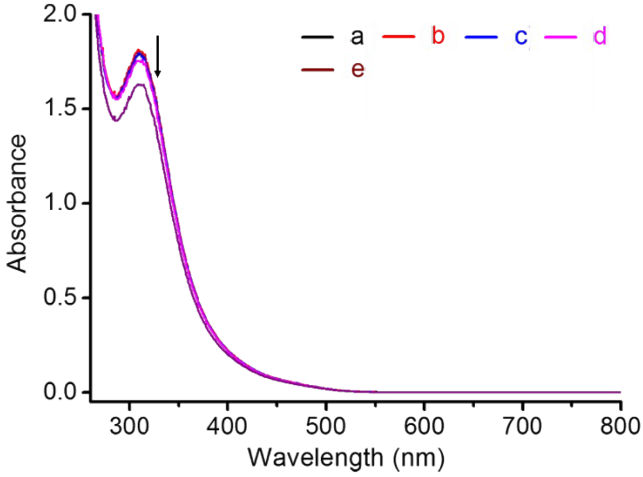

Fig. S17 UV-Vis spectra of β-CD−AdH−$PMo_{11}V$ (4:4:1 molar ratio) in water at a fixed $PMo_{11}V$

concentration of 1.4×10^{-3} mmol ml^{-1} accompanied by gradually increasing pH from (a) 2.65, to (b) 2.86, (c) 3.48, (d) 5.36, and (e) 5.80, by adding dilute NaOH (5.6×10^{-1} mmol ml^{-1}).

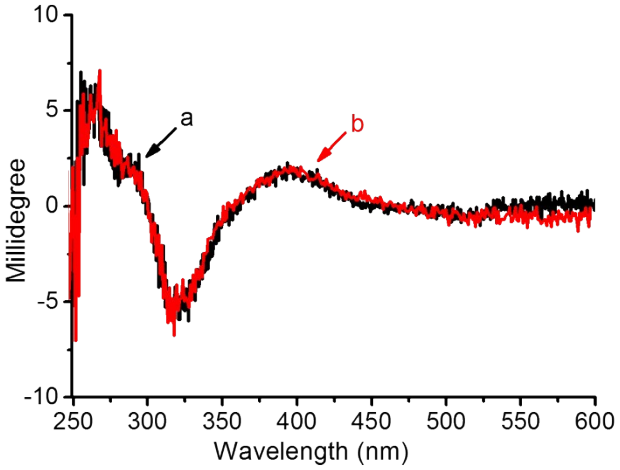

Fig. S18 CDS of β-CD−AdH−$PMo_{11}V$ with the cluster concentration of 1.4×10^{-3} mmol ml^{-1} in water prepared (a) freshly and (b) encountered several tens of days at 4 °C.

Chiral Electrochromism Characterization

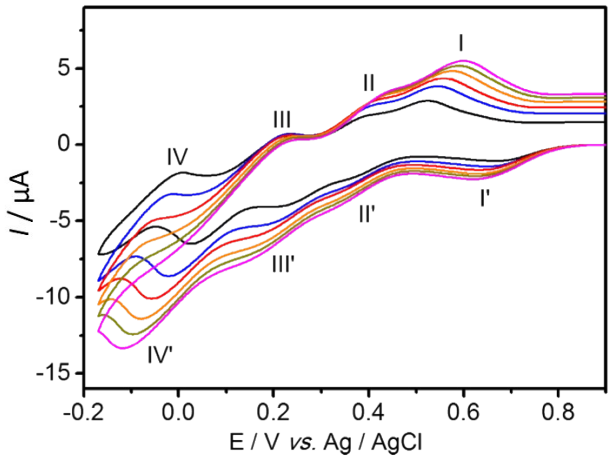

Fig. S19 CVs of β-CD−AdH−$PMo_{11}V$ (4:4:1 molar ratio) aqueous solution with fixed $PMo_{11}V$ concentration (1.15×10^{-2} mmol ml^{-1}) at scan rate of 50, 100, 150, 200, 250 and 300 mV s^{-1} (from inner to outer) without adding any other electrolytes.

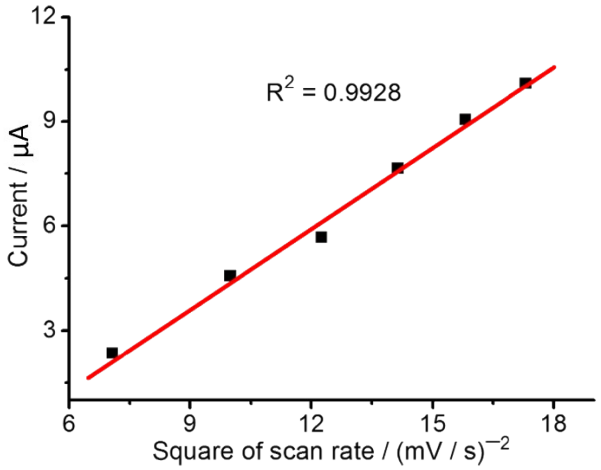

Fig. S20 The plot of peak current of V^{IV}/V^{V} versus square root of scan speed (*vs.* Ag/AgCl), according to the CVs in Fig S12.

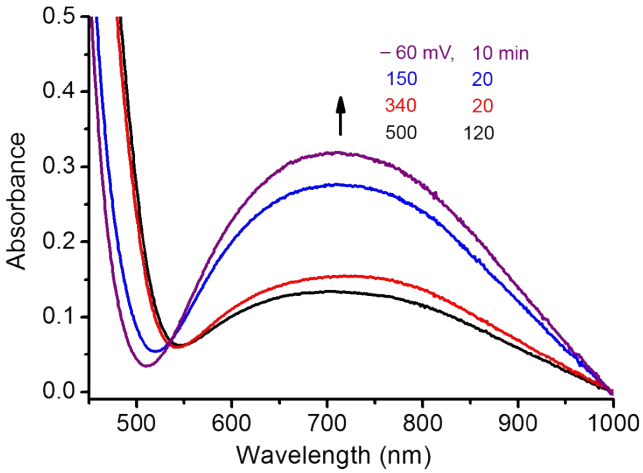

Fig. S21 UV-Vis spectra of β-CD–AdH–$PMo_{11}V$ (4:4:1 molar ratio) with $PMo_{11}V$ concentration of 1.15×10^{-2} mmol ml^{-1} at different reduction state in aqueous solution.

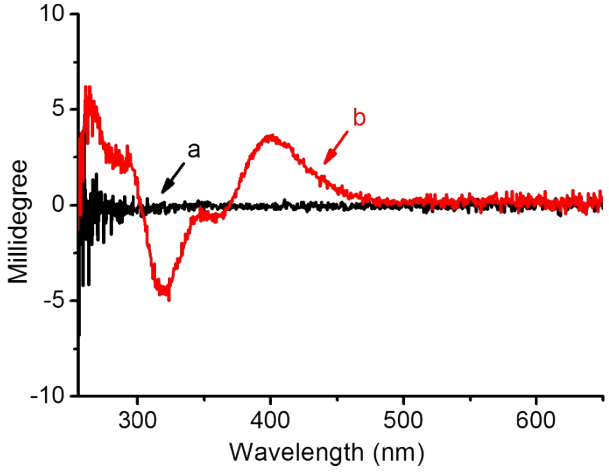

Fig. S22 CDS of (a) β-CD–PMo_{12} (3:1 molar ratio) and (b) β-CD–AdH–PMo_{12} (3:3:1 molar ratio) with PMo_{12} concentration of 1.11×10^{-3} mmol ml^{-1} in aqueous solution at room temperature.

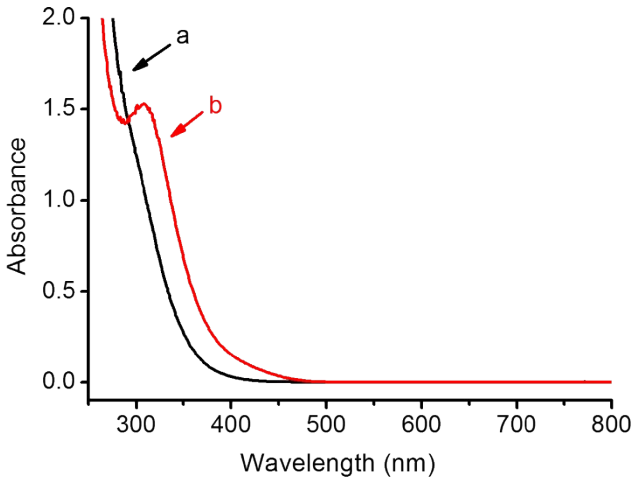

Fig. S23 UV-Vis spectra of (a) β-CD–PMo_{12} and (b) β-CD–AdH–PMo_{12} in aqueous solution at room temperature.

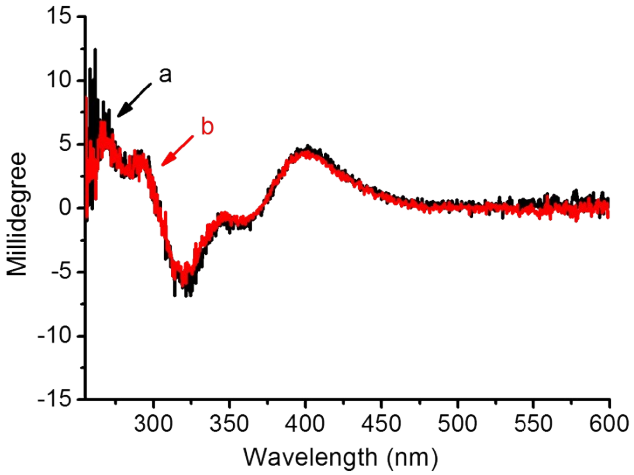

Fig. S24 CDS of β-CD–AdH–PMo_{12} (3:3:1 molar ratio) with PMo_{12} concentration of 1.11×10^{-3} mmol ml^{-1} in aqueous solution (a) prepared freshly and (b) preserved for several tens of days at 4 °C.

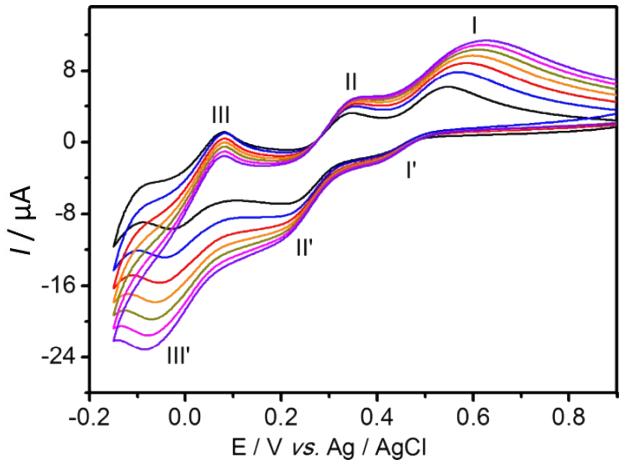

Fig. S25 CVs of β-CD–AdH–PMo_{12} (3:3:1 molar ratio) with PMo_{12} concentration of 1.5×10^{-2} mmol ml^{-1} at scan rates of 50, 100, 150, 200, 250, 300 and 350 mV s^{-1} (from inner to outer) without adding any other electrolyte.

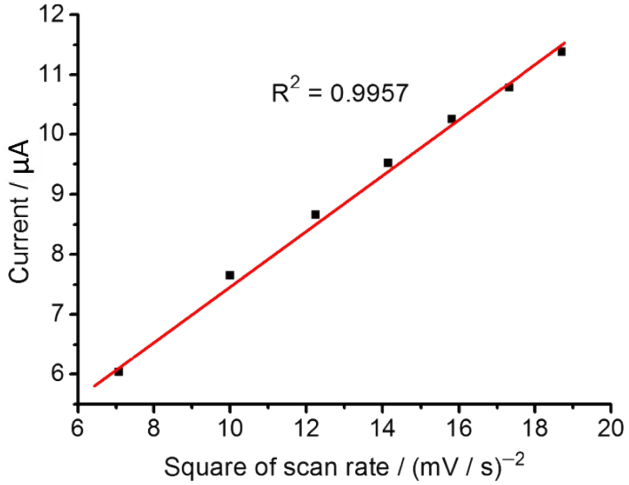

Fig. S26 The plot of peak currents of Mo^{V}/Mo^{VI} versus the square root of scan speeds (*vs.* Ag/AgCl) where the data were taken from Fig. S18.

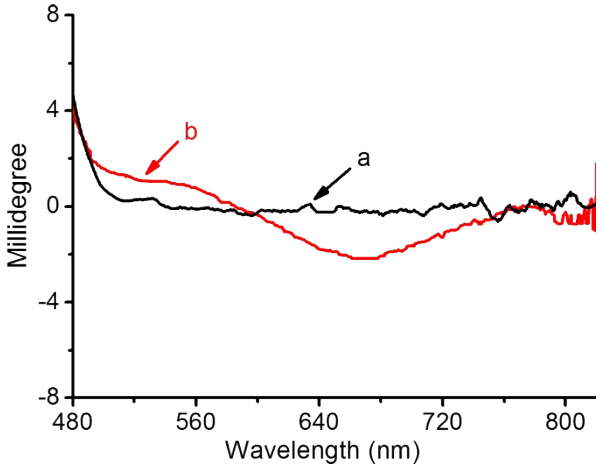

Fig. S27 CDS of β-CD−AdH−PMo_{12} (3:3:1 molar ratio) with PMo_{12} concentration of 1.5×10^{-2} mmol ml^{-1} in visible region at (a) initial state, and (b) after 120 min reduction under 340 mV.

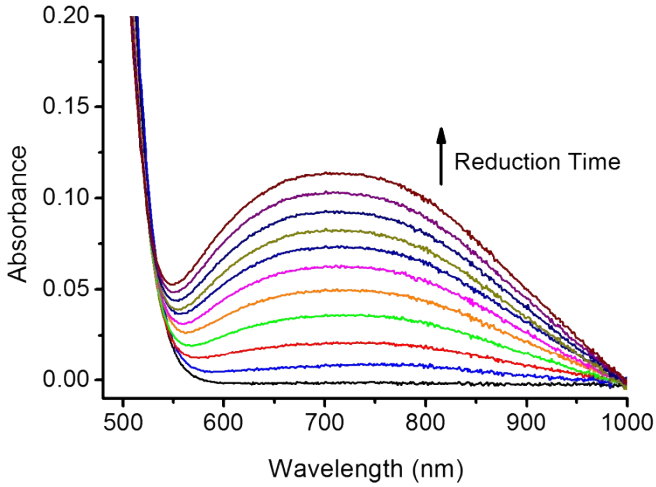

Fig. S28 UV-Vis spectra of β-CD−AdH−$PMo_{11}V$ in aqueous solution at different reduction time, measured in every 800 s under the reduction voltage 500 mV.

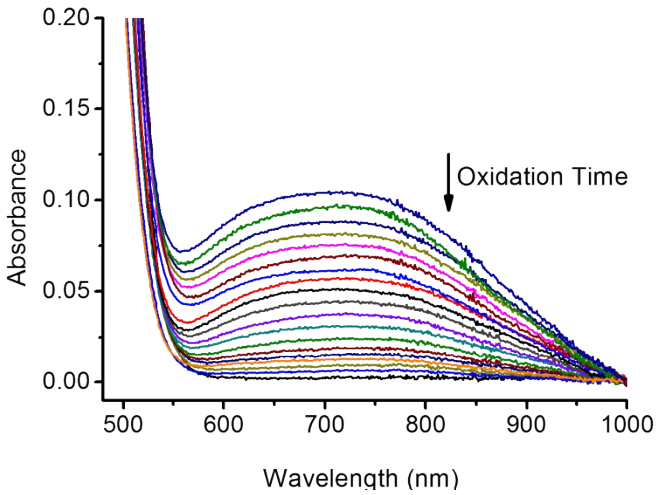

Fig. S29 UV-Vis spectra of β-CD−AdH−$PMo_{11}V$ in aqueous solution at different oxidation time, which are measured with an interval of 400 s under oxidation voltage at 900 mV.

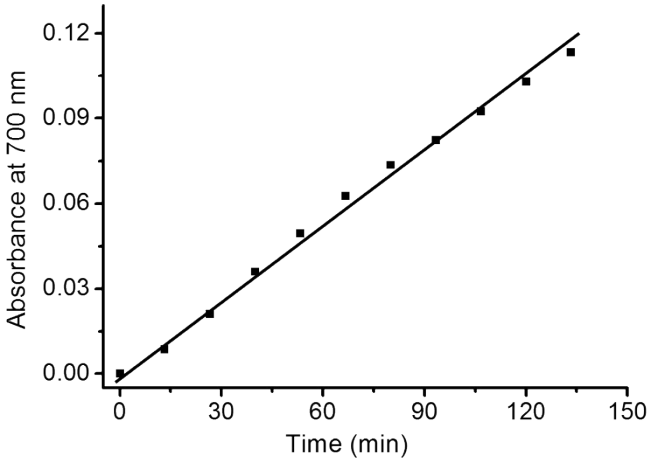

Fig. S30 The absorbance plot of β-CD−AdH−$PMo_{11}V$ in aqueous solution at 700 nm versus the reduction times in every 800 s under 500 mV.

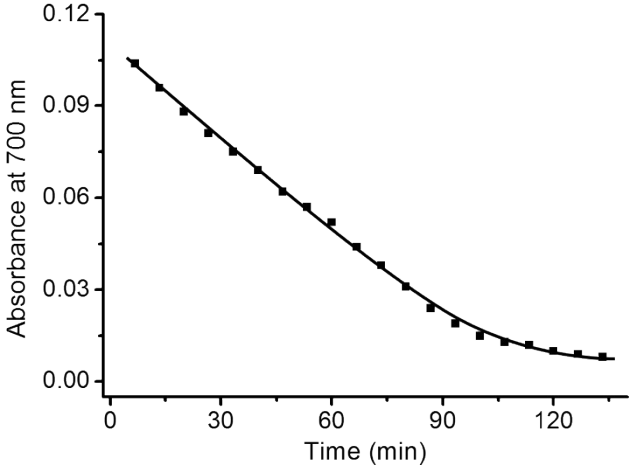

Fig. S31 The absorbance plot of β-CD−AdH−$PMo_{11}V$ in aqueous solution at 700 nm versus the oxidation time in every 400 s under 900 mV.

References

[1] G. A. Tsigdinos and C. J. Hallada, *Inorg. Chem*., 1968, **7**, 437.

[2] Y. L. Wu, R. F. Shi, Y. L. Wu, J. M. Holcroft, Z. C. Liu, M. Frasconi, M. R. Wasielewski, H. Li and J. F. Stoddart, *J. Am. Chem. Soc*., 2015, **137**, 4111.