Electronic Supplementary Information

Counterion-Dominating Chirality Transfer between Chiral and Achiral Polyoxometalates

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Experimental Section

Reagents and materials: The chiral D,L-POMs and Na-D,L-POMs were synthesized according to published method[S1] except that a slight modification was adopted in the prepration procedure of Na-D,L-POMs. Achiral POMs, $PMo_{10}V_2$, $PMo_{11}V^{IV}$, PMo_{12}, and $PW_{11}V$ were prepared following other published procedures.[S2-S5] D-tartaric acid was the products of Aladdin. L-tartaric acid and dimethylamine hydrochloride were purchased from Sinopharm Chemical Reagent Co., Ltd. Water in high purity (18.2 MΩ resistivity) prepared from a Millipore® Direct-Q water purification system was used.

Measurements. FT-IR spectra were collected on a Bruker Vertex 80v spectrometer equipped with a deuterated triglycine sulfate detector (32 scans) at a resolution of 4 cm^{-1}. UV-Vis and CD spectra were recorded on a Bio-Logic MOS-450 spectropolarimeter. XPS data were acquired on an ESCALAB-250 spectrometer with a monochromic X-ray source (Al Kα line, 1486.6 eV). ^1H, and ^{51}V NMR spectra were recorded on a Bruker Ultra-Shield TM 500 MHz spectrometer. Optical rotation values were obtained with a WZZ-3 automtic polarimeter equipped with sodium lamp (λ = 589.44 nm). ITC measurements were performed on a MicroCal ITC_{200} (GE) instrument, and a program of Origin 7.0 was used for nonlinear least-squares fitting. Aqueous solution of D-POM (or Na-D-POM) in a concentration of 50 μM was dropped in a sample cell, and 4.5 mM NaCl (or dimethylamine hydrochloride) aqueous solution was injected into the cell under stirring (1000 rpm) with an interval of 120 s.

Preparation of Na-D,L-POMs: To a water solution (15 mL) dissolving $ZrO(NO_3)_2 \cdot 6H_2O$ (0.24 g, 0.7 mmol) was added D-Tartaric acid (0.105 g, 0.7 mmol) with stirring, forming a slurry mixture. Solid $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}] \cdot 18H_2O$ (1.00 g, 0.23 mmol) was then added in one portion with vigorous stirring for 30 min at room temperature, forming a clear solution. To the reaction was added 100 mL acetonitrile, and the POM precipitates were obtained after centrifugation (12000 r/min) for 10 min and drying in air, giving the final product Na-D-POM in glassy state (yield 0.54g). The

Na-L-POM was synthesized by similar procedure except that L-Tartaric acid was used to modulate the chirality of POM.

Preparation of mixed aqueous solutions of chiral and achiral POMs: D,L-POM (9.1 mg, 1 μmol) and $PMo_{10}V_2$ (1.1 mg, 0.5 μmol) were dissolved in pure water (0.5 mL). The concentration of chiral POM and achiral POM was controlled at 2.0 and 1.0 mM, respectively. After 5 min of sonication, uniform aqueous solutions were ready for subsequent UV-Vis and CD measurements. Different amounts of D,L-POM, for example, 1.0 and 1.5 mM, were used to study the influence of chiral POMs' concentration on the chirality transfer. Similarly, NaCl salts were gradually added to detect the change of the induced CD of achiral POMs.

Preparation of water and acetone mixture solution of chiral and achiral POMs: D,L-POM (9.1 mg, 1 μmol) and $PMo_{10}V_2$ (1.1 mg, 0.5 μmol) were dissolved in pure water (0.45 mL), and then acetone (0.05 mL) was added. The concentration of chiral and achiral POM was controlled at 2.0 and 1.0 mM, respectively, while acetone was controlled at 10% in volume ratio. After 5 min of sonication, the uniform aqueous solutions were ready for the subsequent spectral measurements.

Characterization of chiral and achiral POMs

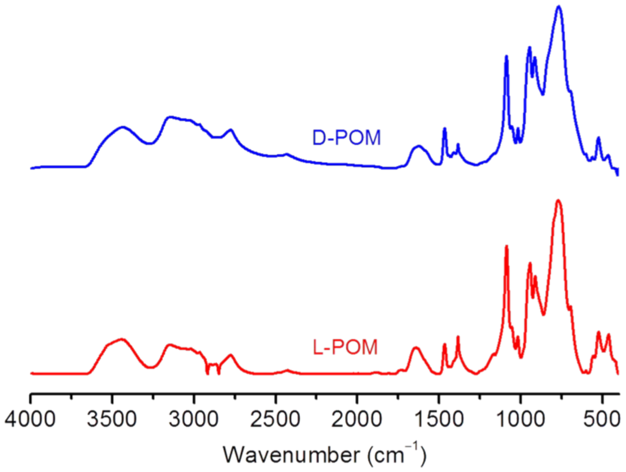

Figure S1. FT-IR spectra of D, L-POM solids in KBr pellets.

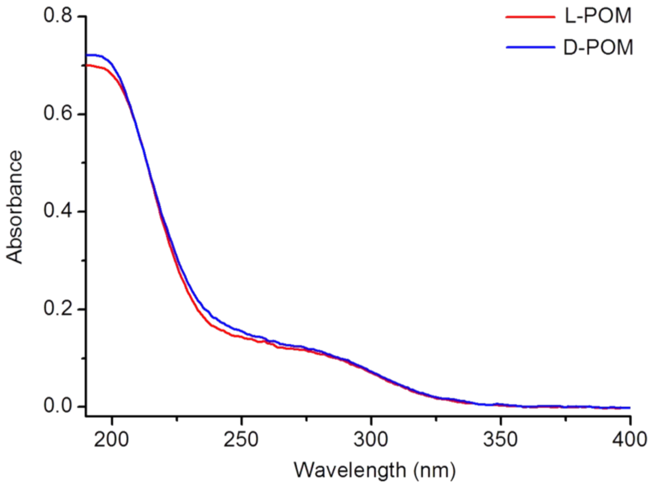

Figure S2. UV-Vis spectra of D,L-POM in aqueous solution at concentration of 2.0 × 10^{-5} mol L^{-1}.

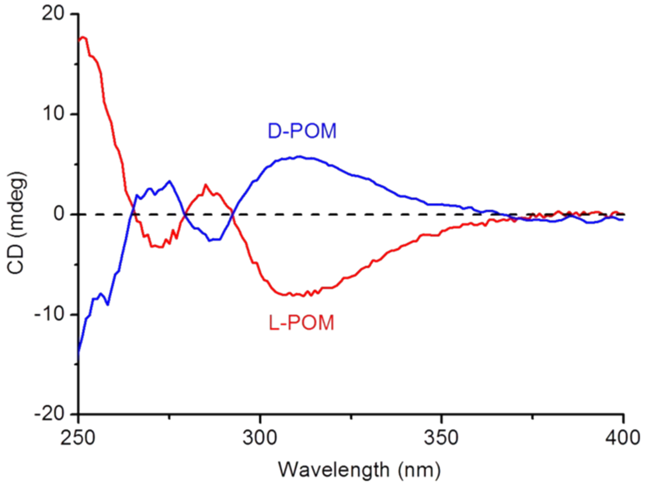

Figure S3. CD spectra of D,L-POM in aqueous solution at concentration of 2.2 × 10^{-4} mol L^{-1}.

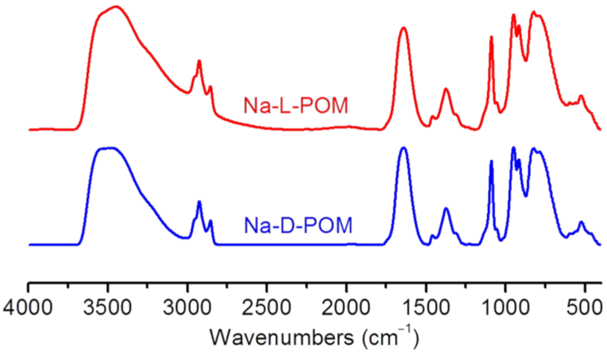

Figure S4. FT-IR spectra of the Na-D,L-POM solids in KBr pellets.

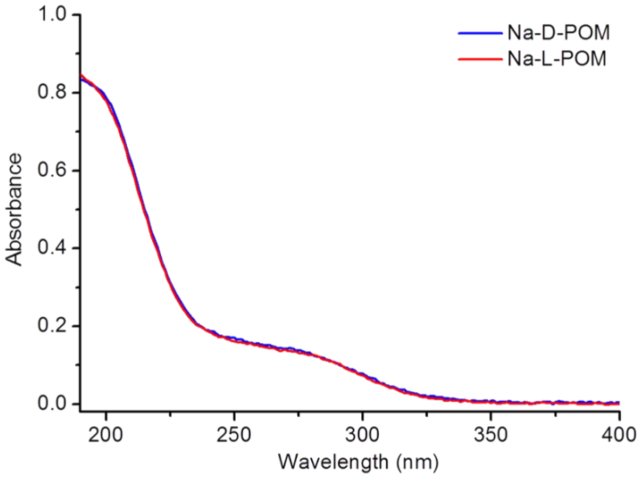

Figure S5. UV-Vis spectra of Na-D,L-POM in aqueous solution at concentration of 2.0 × 10^{-5} mol L^{-1}.

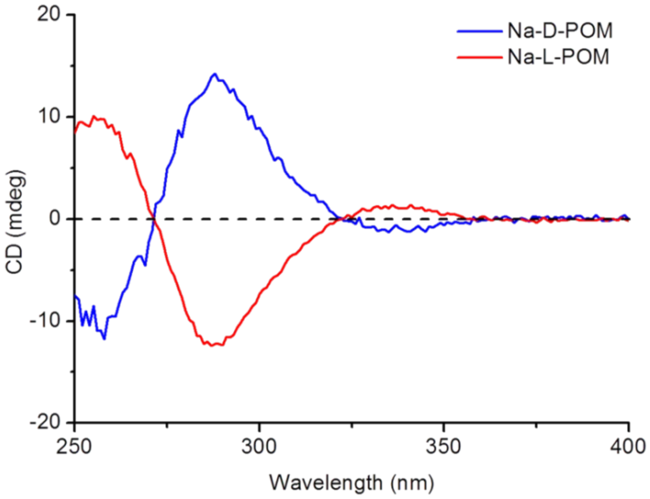

Figure S6. CD spectra of Na-D,L-POM in aqueous solution at concentration of 2.2 × 10^{-4} mol L^{-1}.

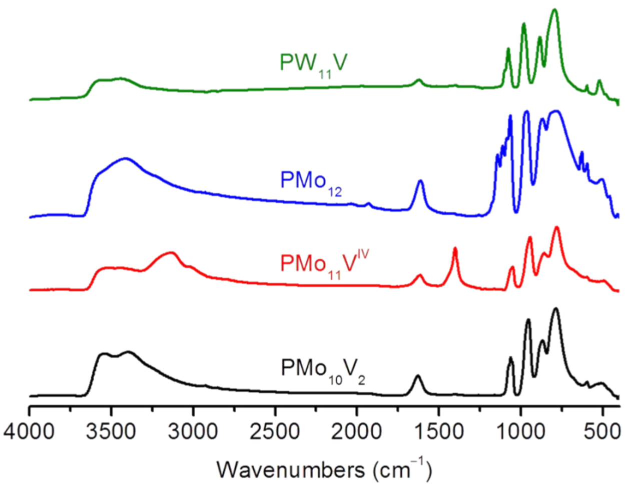

Figure S7. FT-IR spectra of $PMo_{10}V_2$, $PMo_{11}V^{IV}$, PMo_{12}, and $PW_{11}V$ solids in KBr pellets.

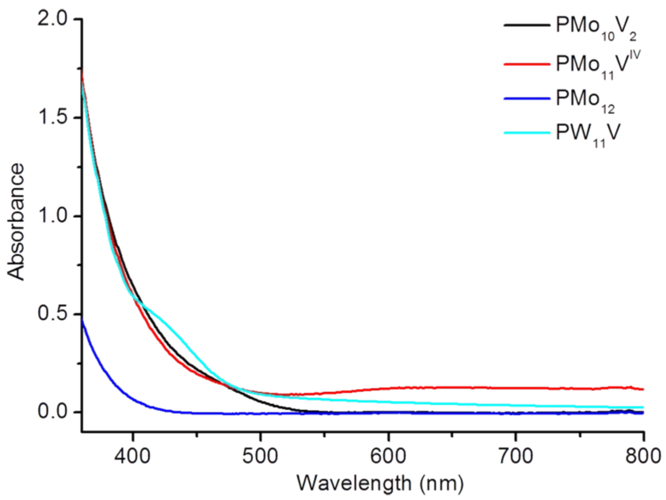

Figure S8. UV-Vis spectra of $PMo_{10}V_2$, $PMo_{11}V^{IV}$, PMo_{12}, and $PW_{11}V$ in aqueous solution at the same concentration of 1.0×10^{-3} mol L^{-1}.

Characterization for chirality transfer and electron transfer

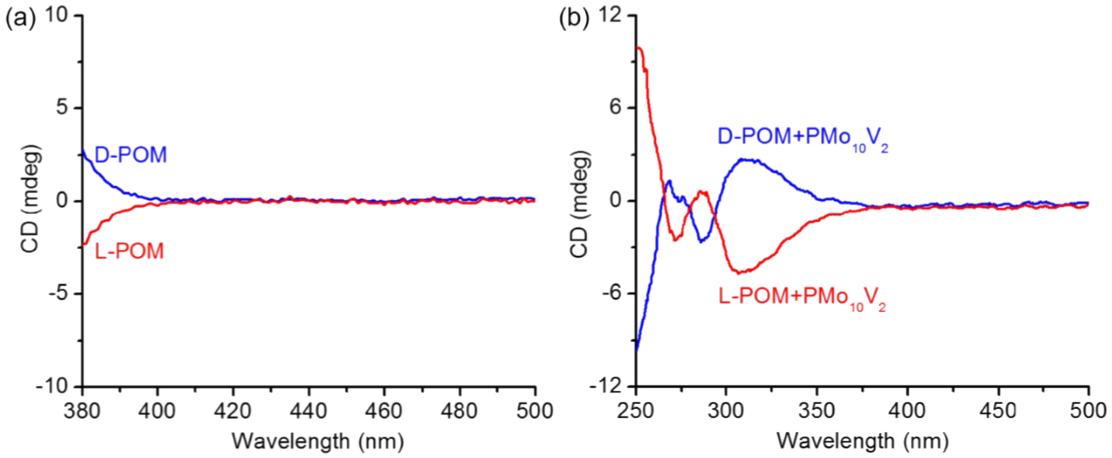

Figure S9. CD spectra of the D,L-POM aqueous solution (c = 2.0×10^{-3} mol L^{-1}) (a) without and (b) with the addition of $PMo_{10}V_2$ (c = 1.0×10^{-3} mol L^{-1}) which are diluted 10-folds when the measurement is performed.

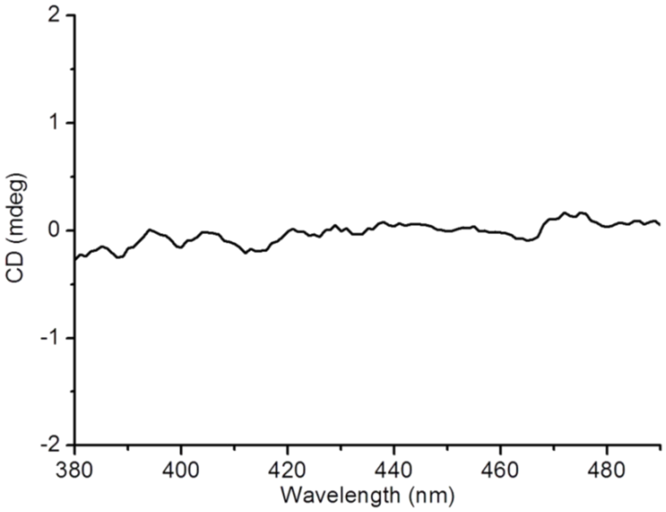

Figure S10. CD spectrum of $PMo_{10}V_2$ aqueous solution (c = 1.0 × 10^{-3} mol L^{-1}) mixed with racemate D,L-POM (c = 2.0 × 10^{-3} mol L^{-1}).

Table S1. The summary of optical rotation values of $PMo_{10}V_2$, D- and L-POM, and their mixed aqueous solution.[a]

Sample	Optical Rotation ($[\alpha]20$ D/ deg cm^2 g^{-1})[b]	Variance (σ_{n-1})[c]
$PMo_{10}V_2$	0.00	–
D-POM	+2.92	0.041
D-POM+$PMo_{10}V_2$	+1.08	0.067
L-POM	–2.88	0.158
L-POM+$PMo_{10}V_2$	–1.06	0.090

[a] The sample solutions were prepared with constant concentration of 18.2 and 2.1 mg mL^{-1} for D,L-POM (2 mM) enantiomers and $PMo_{10}V_2$ (1 mM) respectively; [b] Each of optical rotation values is an average of six parallel tests; [c] The variance indicates the dispersion degree corresponding to the six parallel tests.

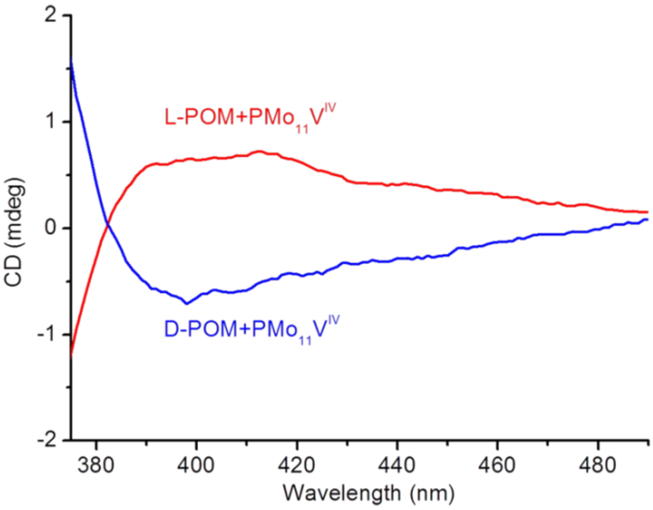

Figure S11. CD spectra of $PMo_{11}V^{IV}$ aqueous solution ($c = 1.0 \times 10^{-3}$ mol L^{-1}) mixed with D- and L-POM ($c = 2.0 \times 10^{-3}$ mol L^{-1}) respectively.

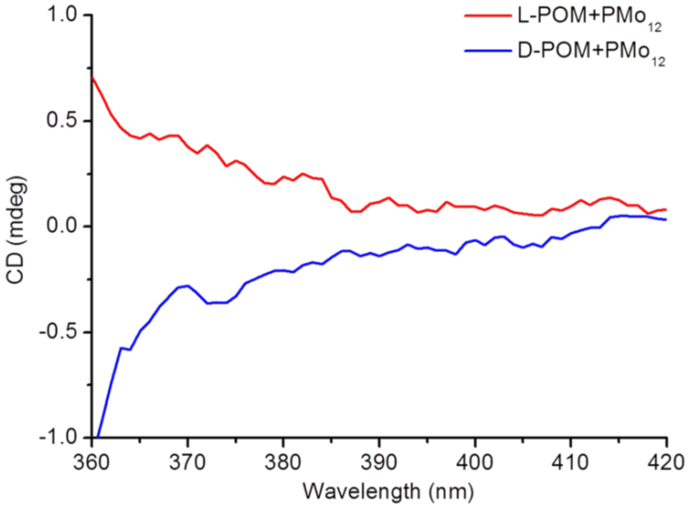

Figure S12. CD spectra of PMo_{12} aqueous solution ($c = 2.0 \times 10^{-3}$ mol L^{-1}) mixed with D- and L-POM ($c = 2.0 \times 10^{-3}$ mol L^{-1}) respectively.

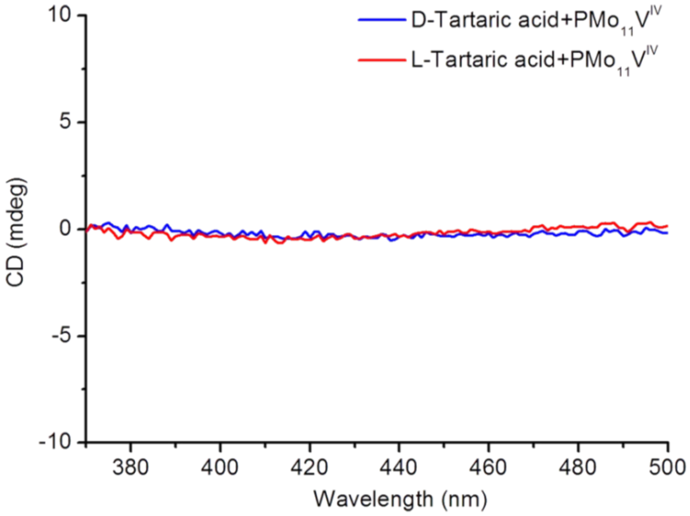

Figure S13. CD spectra of $PMo_{11}V^{IV}$ aqueous solution ($c = 1.0 \times 10^{-3}$ mol L^{-1}) mixed with D- and L-tartaric acid ($c = 3.0 \times 10^{-2}$ mol L^{-1}) respectively.

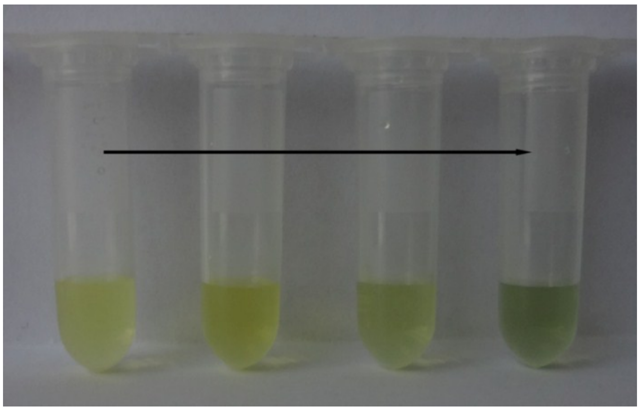

Figure S14. Photographs of mixed aqueous solution of $PMo_{10}V_2$ (1 mM) and D-POM, in which the concentration of D-POM is 0, 0.5, 1.0, and 2.0 mM in samples (from left to right).

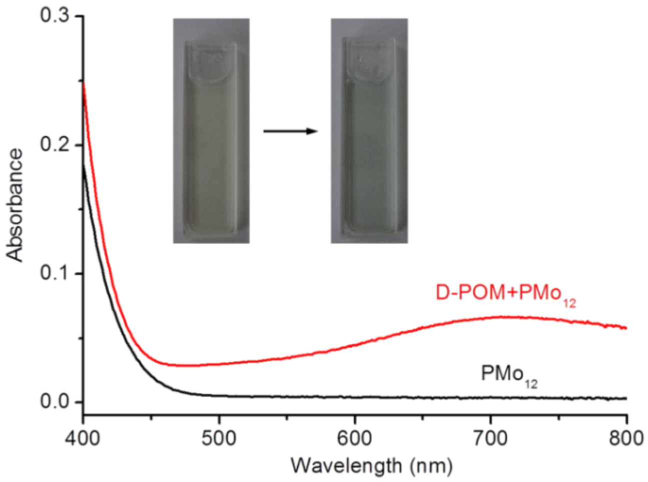

Figure S15. UV-Vis spectra of individual PMo_{12} aqueous solution and its mixed solution with D-POM after aging 2 days. The inset shows corresponding photographs of the two solutions, indicating the color changing from yellow to light green.

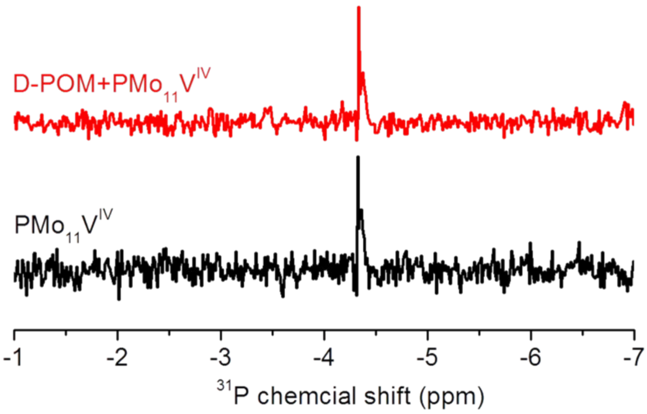

Figure S16. ^{31}P NMR spectra of individual $PMo_{11}V^{IV}$ (black line) and the mixed solution with D-POM (red line) in aqueous solution.

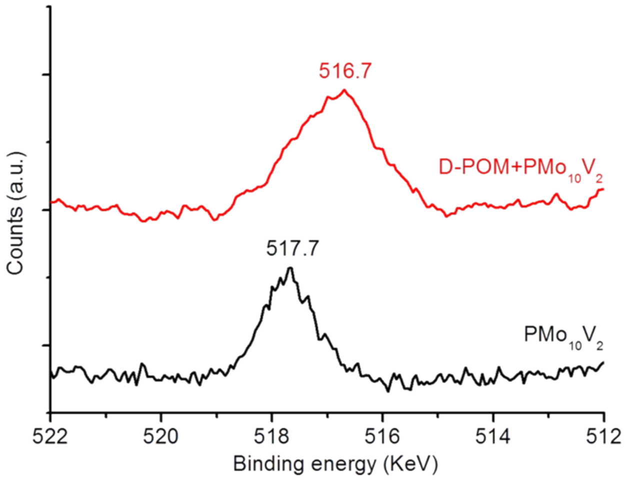

Figure S17. XPS spectra of V2p level of individual $PMo_{10}V_2$ and its mixture with D-POM, which are performed by casting their aqueous solution on silica wafer.

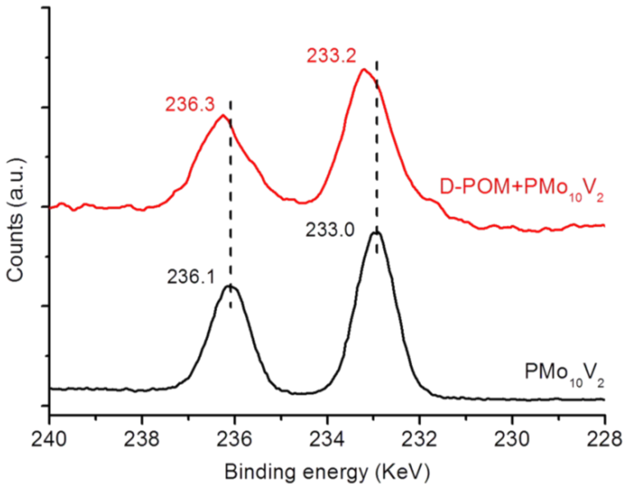

Figure S18. XPS spectra of Mo3d level of individual $PMo_{10}V_2$ and its mixture with D-POM, which are conducted by casting sample solutions on silica wafer.

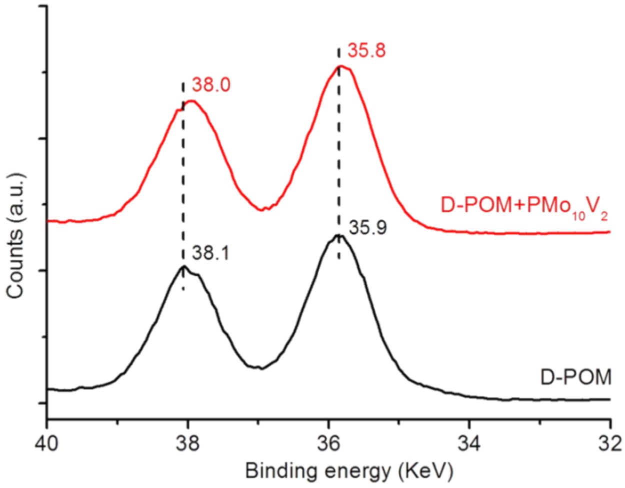

Figure S19. XPS spectra of W4f level of individual D-POM and its mixture with $PMo_{10}V_2$ which are carried out by casting sample solution in silica wafer.

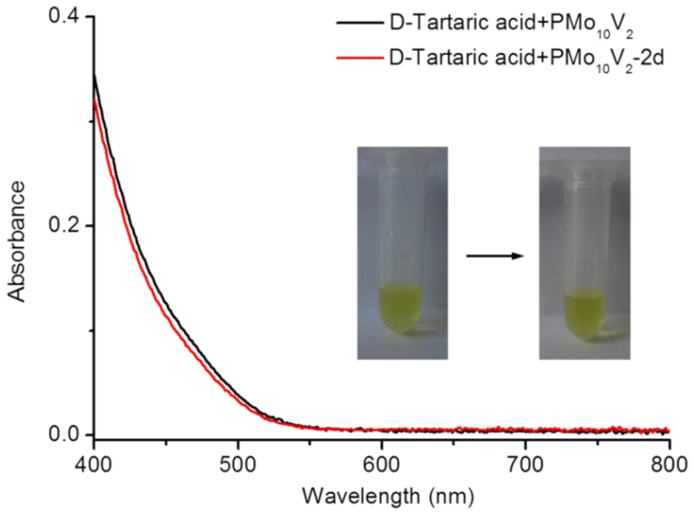

Figure S20. UV-Vis spectra of fresh mixture solution of D-tartaric acid and $PMo_{10}V_2$ and that after aging 2 days. The inset shows the corresponding photographs, in which the color presents little change.

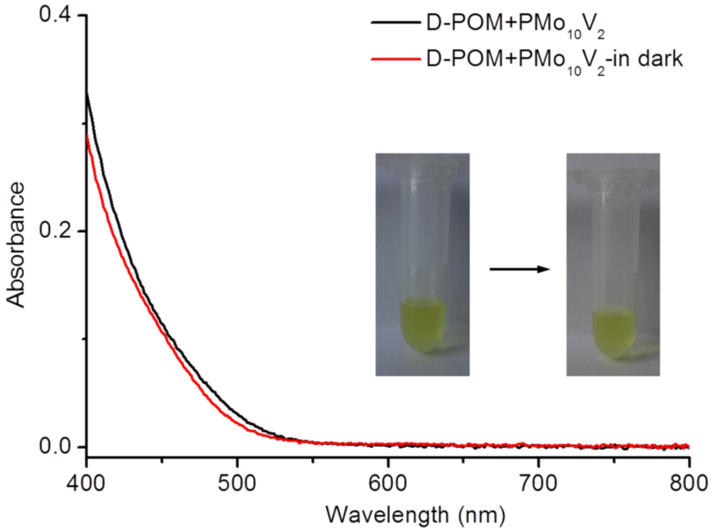

Figure S21. UV-Vis spectra of fresh mixture solution of D-POM and $PMo_{10}V_2$ and that after aging 2 days in dark. The inset shows corresponding photographs, where the color of aqueous solution experiences little change.

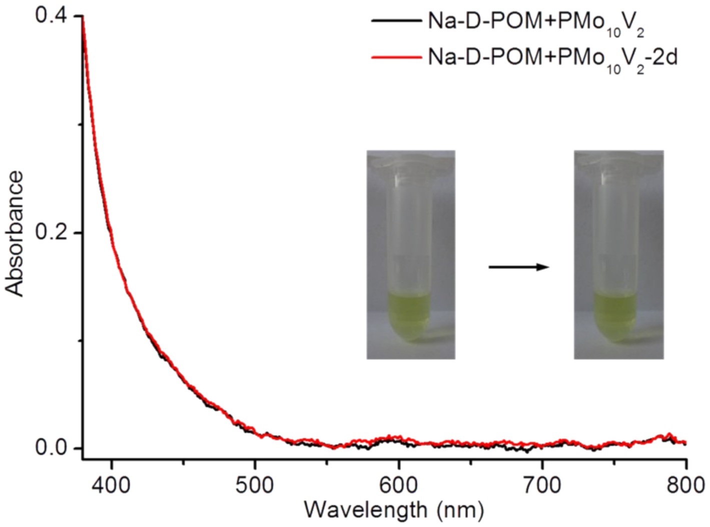

Figure S22. UV-Vis spectra of freshly prepared mixture solution of Na-D-POM and $PMo_{10}V_2$ and that after aging 2 days. The inset shows the corresponding photographs, where the color of aqueous solution shows little change.

Additional structural analysis of chiral POMs

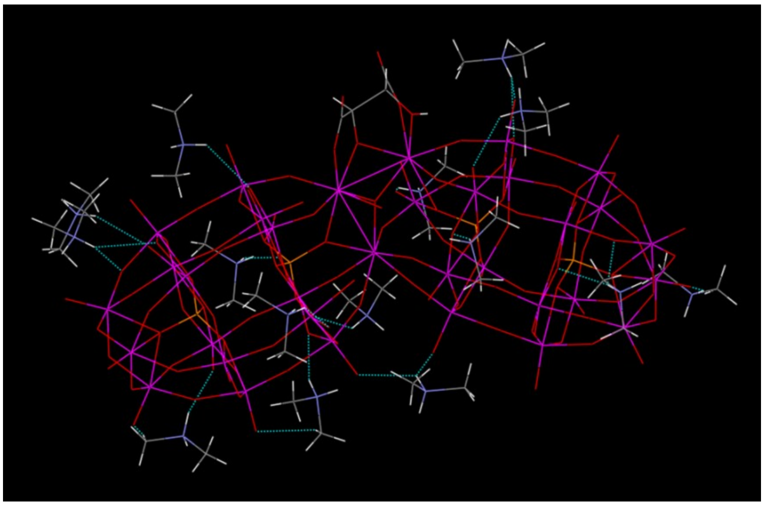

Figure S23. The crystal strucutre of L-POM, in which the hydrogen bonds between protonate dimethylammonium cations and oxygens at POM surface are marked with blue dotted lines that display the O–H distance.

Table S2. The summary of O–H and P–N distance in L-POM crystal structure.[S1]

Entry	O–H distance (Å)	P–N distance (Å)	Entry	O–H distance (Å)	P–N distance (Å)
1	2.474	7.351	11	2.251	6.656
2	2.467	7.203	12	2.222	6.51
3	2.460	7.126	13	2.205	6.292
4	2.449	7.125	14	2.155	6.05
5	2.404	7.120	15	2.035	5.781
6	2.395	7.100	16	2.023	
7	2.380	7.060	17	1.990	
8	2.362	7.035	18	1.963	
9	2.360	6.919	19	1.836	
10	2.265	6.785			
Average	2.247	6.808			

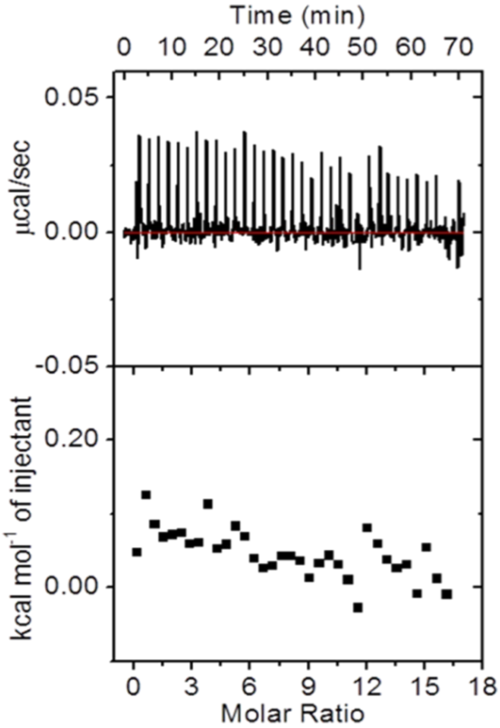

Figure S24. Titration isotherms (top panels) by adding NaCl (4.5 mM) into D-POM aqueous solution (50 μM, in a cell) at 25 °C. The integrated heat values and corresponding fittings are plotted in bottom panels.

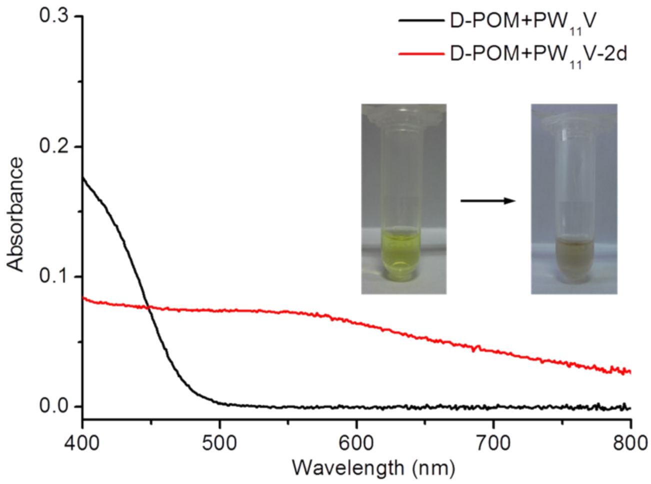

Figure S25. UV-Vis spectra of freshly prepared mixture solution of D-POM and $PW_{11}V$ and that after 2 days' aging. The inset shows the corresponding photographs, in which the color of aqueous solution changes from greenish yellow to brown.

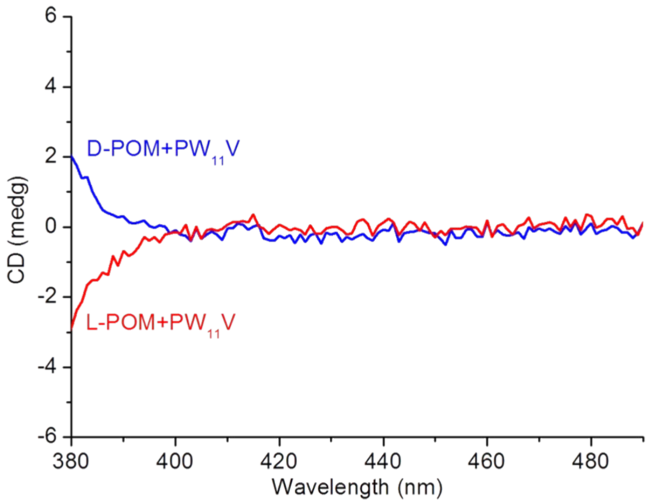

Figure S26. CD spectra of $PW_{11}V$ aqueous solution ($c = 1.0 \times 10^{-3}$ mol L^{-1}) mixing with D- and L-POM ($c = 2.0 \times 10^{-3}$ mol L^{-1}) respectively.

References:

[S1] X. Fang, T. M. Anderson, C. L. Hill, *Angew. Chem. Int. Ed.* **2005**, *44*, 3540–3544; *Angew. Chem.* **2005**, *117*, 3606–3610.

[S2] K. Nomiya, S. Matsuoka, T. Hasegawa, Y. Nemoto, *J. Mol. Catal. A: Chem.* **2000**, *156*, 143–152.

[S3] C. Marchal-Roch, N. Laronze, N. Guillou, A. Tézé, G. Hervé, *Appl. Catal., A* **2000**, *199*, 33–44.

[S4] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem*. **1983**, *22*, 207–216.

[S5] P. J. Domaille, *J. Am. Chem. Soc* **1984**, *106*, 7677–7687.