Electronic Supplementary Information

Polyoxometalate as Inorganic Chiral Ligand for Synthesis of Chiral

Nanoparticles

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Experimental Section

Reagents and materials: The chiral POMs were synthesized according to published method.^[S1] The starting POM, $Na_{12}[A-\alpha-P_2W_{15}O_{56}]\cdot 18H_2O$, was prepared following another published procedure.^[S2] Other starting materials, $H_3PW_{12}O_{40}$, silver nitrate and L-tartaric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. D-tartaric acid and thioglycolic acid were obtained from Aladdin. Chloroauric acid was the product of Shanghai Chemical Reagent Factory. Sodium borohydride was the analytical grade product of Tianjin FuChen Chemical Reagent Factory. Water was used in high purity (18.2 M Ω resistivity) from a Millipore[®] Direct-Q water purification system.

Typical synthesis procedure of L-Zr-P₂W₁₅-stabilzed Ag(0) NPs. 11.4 mg L-Zr-P₂W₁₅ was dissolved in 2 mL water (0.625 mM). Then, 50 μ L of freshly prepared aqueous AgNO₃ solution (0.025 M) was added to the L-Zr-P₂W₁₅ aqueous solution. The molar ratio of L-Zr-P₂W₁₅ to Ag⁺ was 1:1. The clear mixed solution was stirred vigorously in an ice bath for 30 min. A fresh NaBH₄ aqueous solution (0.1 M) was prepared in an ice bath and 20 μ L of that was quickly added into the mixed solution of POM and AgNO₃ in one portion with vigorous stirring for another 30 min. The resultant brown solution was subsequently stirred for 10 min at room temperature, and then stored at 4 °C before characterization.

Typical synthesis procedure of D-Zr-P₂W₁₅-stabilzed Au(0) NPs. 11.4 mg D-Zr-P₂W₁₅ was dissolved in 2 mL water (0.625 mM). Then, 30 μ L of freshly prepared aqueous HAuCl₄ solution (0.2 M) was added to the D-Zr-P₂W₁₅ aqueous solution. The clear mixed solution was stirred vigorously in an ice bath for 30 min. A fresh NaBH₄ aqueous solution (0.1 M) was prepared in an ice bath and 50 μ L of that was quickly added into the mixed solution of POM and HAuCl₄ in one portion with vigorous stirring for another 30 min. The resultant red solution was subsequently stirred for 10 min at room temperature, and then stored at 4 °C before characterization.

Typical procedure of ligand treatment of the L-Zr-P₂W₁₅-stabilzed Ag(0) NPs. The L-Zr- P_2W_{15} stabilized Ag(0) NPs were prepared by the above typical synthesis procedure. 1 mL silver NP solution was separated and added excess NaOH or thioglycolic acid with vigorously stirring for about 1h. After that, the resultant solution was stored at 4 °C before characterization.

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. ³¹P NMR spectra were recorded on a Bruker Ultra-Shield TM 500 MHz spectrometer. UV-Vis and CD spectra were recorded on a Bio-Logic MOS-450 spectropolarimeter. Zeta potential measurement was performed on a Zetasizer NanoZS (Malvern Instruments). Cyclic voltammogram test was used with a working electrode of indium tin oxide ITO-coated glass slide for the measurement of cyclic voltammogram of POM aqueous solution, and a platinum wire as the counter electrode and Ag/AgCl (3 M KCl) as the reference. XPS data was acquired on an ESCALAB-250 spectrometer with a monochromic X-ray source (Al K α line, 1486.6 eV). The HR-TEM, and EDX measurements were carried on a JEM-2100F from JEOL Ltd with an accelerating voltage of 200 kV without staining. The Raman measurements were carried out on a Smart Raman spectrometer (LabRAM ARAMIS) at room temperature. The excitation source was a He-Ne laser (633 nm) with a power of 1.6 mW on the sample and the integration time was 10 s.

Characterization of Inherent Chiral POMs:



Figure S1. UV-Vis spectra of L-Zr-P₂W₁₅ and D-Zr-P₂W₁₅ in aqueous solution at concentration of 2.0×10^{-6} mol L⁻¹.



Figure S2. FT-IR spectra of L-Zr- P_2W_{15} and D-Zr- P_2W_{15} in KBr pellet.



Figure S3. CD spectra of L- and D- Zr-P₂W₁₅ in aqueous solution at 2.2×10^{-4} mol L⁻¹.



Figure S4. UV-Vis spectra of D-Zr- P_2W_{15} aqueous solution at initial state and after standing one day.



Figure S5. CD spectra of D-Zr- P_2W_{15} aqueous solution at initial state (red line) and after one day aging (blue line).

Characterization of Chiral POM Stabilized Silver and Gold NPs:



Figure S6. UV-Vis spectrum of L-Zr- P_2W_{15} stabilized silver NPs in aqueous solution.



Figure S7. XPS spectrum of L-Zr- P_2W_{15} solid, in which characteristic peaks of W, Zr, C and O elements are observed.



Figure S8. XPS spectrum of L-Zr- P_2W_{15} stabilized silver NPs, in which the W, Zr, C, O, P and Ag elments are observed, suggesting the existence of both POMs and silver NPs.



Figure S9. XPS spectrum of L-Zr- P_2W_{15} stabilized silver NPs, in which Ag3d energy level appears in given binding energy region.



Figure S10. Representative HR-TEM image of L-Zr- P_2W_{15} stabilized silver NPs. The inset indicates the size distribution, where spheroids are found in average size ca. 12 nm.



Figure S11. (a) HR-TEM image of a single silver NP stabilized by L-Zr-P₂W₁₅ (the cycle marks the area focused by EDX test), and (b) corresponding EDX spectrum.



Figure S12. (a) HR-TEM image of a single silver NP stabilized by L-Zr-P₂W₁₅ (the cycle marks the area performing EDX test), and (b) corresponding EDX spectrum.



Figure S13. ³¹P NMR spectra of isolated L-Zr- P_2W_{15} (black line), after the addition of NaBH₄ (red line) and then AgNO₃ (blue line) in D₂O.



Figure S14. UV-Vis spectrum of D-Zr- P_2W_{15} stabilized gold NPs in aqueous solution.



Figure S15. Representative HR-TEM image of D-Zr-P₂W₁₅ stabilized gold NPs.



Figure S16. XPS spectra of O1s energy level of pure L-Zr- P_2W_{15} and L-Zr- P_2W_{15} stabilized silver NP.



Figure S17. XPS spectra of Zr3d energy level of pure L-Zr- P_2W_{15} and L-Zr- P_2W_{15} stabilized silver NP.



Figure S18. XPS spectra of P2p level of pure L-Zr- P_2W_{15} and L-Zr- P_2W_{15} stabilized silver NP.

Table S1. The summary of XPS data of pure L-Zr- P_2W_{15} and L-Zr- P_2W_{15} stabilized silver NP, and the cooresponding peak shifts.

	C (eV)	O (eV)	Zr (eV)	P (eV)	W (eV)	Ag (eV)
L - Zr - P_2W_{15}	284.7	530.5	182.8	133.6	36.1	
	286.3		185.2		38.2	
L-Zr-P ₂ W ₁₅ -Ag	284.7	530.4	182.6	133.3	35.6	367.5
	286.3		185.0		37.7	373.6
Peak shift	0	-0.1	-0.2	-0.3	-0.5	
	0		-0.2		-0.5	



Figure S19. XPS spectra of (a) W4f and (b) C1s levels of L-Zr-P₂W₁₅ and L-Zr-P₂W₁₅ stabilized Ag NPs.



Figure S20. UV-Vis spectra of D-Zr- P_2W_{15} aqueous solution before and after addition of reductant NaBH₄.



Figure S21. UV-Vis spectra of pure water (black) and D-Zr- P_2W_{15} aqueous solution after addition of NaBH₄ (red).



Figure S22. Cyclic voltammetry of L-Zr- P_2W_{15} by using ITO electrode as a working electrode with scan rate of 100 mV s⁻¹ in distilled water.



Figure S23. CD spectra of racemic mixture of D- and L-Zr- P_2W_{15} in aqueous solution (black line) and silver NP solution prepared by the racemic mixture (red line).



Figure S24. CD spectrum of gold NP aqueous solution stabilized by D-Zr-P₂W₁₅.





Figure S25. UV-Vis spectrum of silver NP solution prepared under existence of L-tartaric acid.



Figure S26. EDX spectrum of silver NPs prepared under existence of L-tartaric acid.



Figure S27. Representative HR-TEM image of L-tartaric acid stabilized silver NPs.



Figure S28. CD spectra of pure L-tartaric acid and L-tartaric acid stabilized silver NP in aqueous solution.



Figure S29. UV-Vis spectrum of silver NP solution prepared by stabilization of achiral PW_{12} in aqueous solution.



Figure S30. UV-V is spectrum of silver NP solution prepared by stabilization of A- α -P₂W₁₅.



Figure S31. CD spectrum of silver NP solution prepared by stabilization of achiral PW_{12} .



Figure S32. CD spectrum of the silver NP solution prepared by the addition A- α -P₂W₁₅.



Figure S33. Possible orientations and widths of L-Zr-P2W15 adsorbed on surface of silver NP with angle of (a) 0, (b) 90, and (c) 30°.



Figure S34. Normal Raman spectrum of L-Zr- P_2W_{15} (black line) and SRES spectrum of L-Zr- P_2W_{15} stabilized silver NPs (red line) between 850 and 1020 cm⁻¹.



Figure S35. Two possible binding models of chiral POM stabilizing on silver NP.



Figure S36. Possible bond stretching analysis of L-Zr-P₂W₁₅ by referring its crystal strucutre, in which (a) v_s (W–O_a) are marked as green, (b) v_s (W=O_d) modes are marked as light blue, (c) v_{as} (W–O_b–W) marked as pink, and (d) v_s (–C–H) marked as red color. The blue, orange, pink, light green, dark green and red balls show W, Zr, P, C, H and O atoms, respectively.

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Vibration mode	Number	0~30° (%)	30~60° (%)	60~90° (%)
v_{s} (W–O _a)	31	11 (35)	13 (42)	7 (23)
<i>v</i> _{as} (W–O _b –W)	22	8 (36)	11 (50)	3 (14)
$v_{\rm s}$ (W=O _d)	33	15 (45)	15 (45)	3 (10)
v _a (–C–H)	2	0	2 (100)	0

Table S2. The summary of total numbers and corresponding orientation of vibration modes in the inherent chiral POM framework based on proposed binding mode on NPs.



Figure S37. HR-TEM image of L-Zr- P_2W_{15} stabilized silver NP. The domain in the marked box shows distinguishable L-Zr- P_2W_{15} clusters covering on NPs.



Figure 38. (a) HRTEM image of single silver nanoparticle with distorted arrangement pattern; and (b) another representation of (a), in which the white boxes mark the areas of distorted arrangement pattern and the red lines exhibit the corresonding orentation of lattice finges.



Figure S39. (a) HR-TEM image of a L-Zr- P_2W_{15} stabilized silver NP after the reaction with NaOH, and (b) its corresponding EDX spectrum.



Figure S40. (a) HR-TEM image of a L-Zr- P_2W_{15} stabilized silver NP treated with thioglycolic acid, and (b) its corresponding EDX spectrum.



Figure S41. CD spectra of L-Zr- P_2W_{15} stabilized silver NPs at initial state (black line), treated with thioglycolic acid (red line), and reacted with NaOH (blue line).

References:

[S1] X. K. Fang, T. M. Anderson, C. L. Hill, *Angew. Chem. Int. Ed.* 2005, 44, 3540–3544.
[S2] R. G. Finke, M. W. Droege, P. J. Domaille, *Inorg. Chem.* 1987, 26, 3886–3896.