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Electronic Supplementary Information

Hierarchical Porous Ionic Organic Polymer as a New Platform for Heterogeneous Phase Transfer Catalysis

Qi Sun,[ab] Shengqian Ma,*[b] Zhifeng Dai,[a] Xiangju Meng,[a] and Feng-Shou Xiao*[a]

[a] Key Lab of Applied Chemistry of Zhejiang Province and Department of Chemistry, Zhejiang University, Hangzhou 310028, China, E-mail: fsxiao@zju.edu.cn

[b] Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, Tampa, Florida 33620, United States, E-mail: sqma@usf.edu

Experimental Section

Sample Synthesis.

Synthesis of tris-(4-vinylphenyl)-phosphine. PCl_3 (4.11 g in 30 mL of THF) was added slowly to (4-vinylphenyl)magnesium bromide solution at 0 °C, which was synthesized from 4-bromostyrene (100 mmol) and magnesium powder (110 mmol), stirring at RT for 2 h. After quenching the reaction by the addition of 50 mL of saturated NH_4Cl aqueous solution, the organic phase was extracted with a large excess of diethyl ether. The combined organic phase was washed with 10 wt.% HCl aqueous solution and brine. The organic phase was dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by silica gel chromatography (5% EtOAc/ Petroleum ether) to afford a white solid.

Synthesis of (4-vinylbenzyl)-tris-(4-vinylphenyl)-phosphonium chloride (VP-IL). 4-vinylbenzyl chloride (0.76 g, 5 mmol) and tris-(4-vinylphenyl)-phosphine (1.31 g, 5 mmol) was dissolved in 10 mL of acetone, stirring at 60 °C under N_2 atmosphere for 48 h. After the reaction, the mixture was cooled to room temperature, followed by filtrating, washing with diethyl ether, and drying under vacuum overnight. The product was obtained as white solid (2.2 g, 91%). [^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ 7.52-7.68 (m, 12H), 7.05-7.11 (m, 4H), 6.65-6.72 (m, 3H), 6.51-6.58 (m, 1H), 5.75 (d, 3H, *J*=17.6Hz), 5.62 (d, 1H, *J*=17.6Hz), 5.43 (m, 3H, *J*=13.2Hz), 5.12 (d, 1H, *J*=11.2Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1, 30.6, 114.5, 115.9, 116.8, 118.9, 126.3, 126. 4, 126.8, 126.9 127.4, 127.5, 131.6, 131.7, 134.5, 134.6, 134.9, 135.9, 137.2, 143.6 ppm. ^{31}P NMR (162 MHz): δ 23.2 (s, 1P) ppm.]. Element analysis results indicate that the amount of C and H in the VP-IL is 78.9 wt.%, and 6.3 wt.%, respectively. The amount of P species in the compound was determined by ICP-OES technique, after combusting the sample in an oxygen bomb calorimeter and dissolving the yielded P_2O_5 in water, and the ICP-OES result reveals that the P content in the compound is 6.3 wt.%. Ion chromatograph analysis indicates that the compound contains 7.2 wt.% Cl ion. These results are consistent with C, H, P, and Cl calculated for $C_{33}H_{30}P^+Cl^-$ (C, 80.5; H, 6.1; P, 6.3; Cl, 7.2%).

Synthesis of $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ ($K_2W_2O_{11}$). Potassium tungstate (4 g) was dissolved in water (15 mL), followed by addition of 30% H_2O_2 (20 mL) at 0 °C. The formed yellow solution was treated with dilute HCl until it just turned colorless. White crystals appeared after standing the solution at 0 °C for 24 h, and the product was collected after filtrating, washing with ethanol, and drying under vacuum. IR: (KBr disk): ν/cm^{-1} 854 ν(O-O), 762 ν_{asym}(W-O-W), 567 ν_{asym}[W(O_2)].

Synthesis of benzyl-trisphenylphosphonium chloride (PPh_3BnCl). Benzyl chloride (0.63 g, 5 mmol) and PPh_3 (1.32 g, 5 mmol) was dissolved in 10 mL of acetone, stirring at 60 °C under N_2 atmosphere for 48 h. After the reaction, the mixture was cooled to room temperature, followed by filtrating, washing with diethyl ether, and drying under vacuum. Then product was obtained as white solid (1.85 g, 95%).

Synthesis of $(PPh_3Bn)_2W_2O_{11}$. Benzyl-trisphenylphosphonium chloride (1.0 g) was dissolved in 50 mL of water, followed by addition of 0.86 g of $K_2W_2O_{11}$. After stirring at room temperature for 24 h, the product was collected after filtrating, washing with water and drying.

Synthesis of porous ionic organic polymer of polymerized quaternary phosphonium salt (PQP salt). PQP salt was synthesized from polymerization of (4-vinyl-benzyl)-tris-(4-vinyl-phenyl)-phosphonium chloride (VP-IL) under solvothermal conditions. As a typical run, 1 g of VP-IL was dissolved in 10 mL of DMF, followed by the addition of 25 mg of azobisisobutyronitrile (AIBN). After stirring at room temperature for 3 h, the mixture was transferred into an autoclave at 100 °C for 24 h. After extraction of solvent with ethanol, a white solid product was obtained and designated as PQP salt. The content of the C, H, and P species in the PQP salt were studied by the same means as those of the VP-IL, giving C, H, and P weight percent at 78.1 %, 6.4 %, and 6.1%, respectively, which are in accordance with those of the monomer used.

Synthesis of W_2O_{11}/PQP. At first, chloride ions in PQP salt were exchanged into hexafluorophosphate ions by treating with excessive KPF_6 in acetonitrile solution. The obtained product (1.0 g) was stirred in 50 mL of water, followed by addition of 0.58 g of $K_2W_2O_{11}$. After stirring for 24 h, filtering, and washing at room temperature as well as drying under vacuum condition at 50 °C, the W_2O_{11}/PQP was obtained. ICP-OES results reveal a W loading of 7.4 wt.%.

Syntehsis of insoluble hydrophobic porous polymer framework (polydivinybenzene, PDVB) containing $W_2O_{11}^{2-}$ species (W_2O_{11}/PDVB): W_2O_{11}/PDVB was synthesized from copolymerization of divinylbenzene (DVB) and (4-vinylbenzyl)-tris-(4-vinylphenyl)-phosphonium chloride (VP-IL) at the mole ratio of 3.0, followed by the anion-exchange of $W_2O_{11}^{2-}$.

As a typical run, 1.0 g of DVB and 1.23 g of VP-IL were dissolved in 20 mL of DMF, followed by the addition of 50 mg of azobisisobutyronitrile (AIBN). After stirring at room temperature for 3 h, the mixture was transferred into an autoclave at 100 °C for 24 h. After extraction of solvent with ethanol, a white solid product was obtained. The anion-exchange process was similar to the synthesis of W_2O_{11}/PQP. ICP-OES results reveal a W loading of 4.1 wt.%. N_2 sorption analysis gives the BET surface of W_2O_{11}/PDVB at 541 m^2/g.

Synthesis of insoluble amphiphilic nonporous ionic polymer anchoring $W_2O_{11}^{2-}$ species (W_2O_{11}/NP): W_2O_{11}/NP was synthesized from polymerization of triphenyl(4-vinylbenzyl)phosphonium chloride in ethanol at 80 °C in the presence of AIBN, followed by the anion-exchange of $W_2O_{11}^{2-}$. ICP-OES results reveal a W loading of 5.7 wt.%. N_2 sorption analysis gives the BET surface of W_2O_{11}/NP is less than 1 m^2/g.

The determination of the amount of W species loaded in the polymers. The sample for ICP analysis was prepared as follows: as a typical run, 50 mg of the dried W_2O_{11}/PQP was sealed in a quartz tube and heated at 450 °C for 10 h. The resultant black residue was stirred in the aqua fortis (2 mL) for 30 min and separated by centrifugation, which were repeated for 5 times and then washed by distilled water for 5 times. The combined solution was diluted with deionized water before ICP analysis. ICP results reveal a W loading of 7.4 wt.% in the W_2O_{11}/PQP.

Characterization.

Nitrogen sorption isotherms at the temperature of liquid nitrogen were measured using Micromeritics ASAP 2020M and Tristar system. The samples were outgassed for 10 h at 100 °C before the measurements. ICP-OES analysis was measured with a Perkin-Elmer plasma 40 emission spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts are expressed in ppm downfield from TMS at $\delta=0$ ppm, and J values are given in Hz. ^{13}C (100.5 MHz) cross-polarization magic-angle spinning (CP-MAS), and ^{31}P (161.8 MHz) MAS solid-state NMR experiments were recorded on a Varian infinity plus 400 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO_2 rotor. The ^{31}P NMR chemical shifts were referenced to the 85% H_3PO_4. FTIR spectra were performed on IFS 66 V (Bruker) IR spectrometer in the range 400-4000 cm^{-1}. Scanning electron microscopy (SEM) was performed using a Hitachi SU 1510. Transmission electron microscope (TEM) was performed using a Hitachi HT-7700. Photographs of water and organic compounds on the surface of the samples were measured with SL200KB (USA KNO Industry Co.), equipped with a CCD camera.

Catalytic tests.

Epoxidation of cyclooctene. As a typical run for epoxidation of cyclooctene, cyclooctene (110 mg, 1.0 mmol), H_2O_2 (30 % aq., 1.0 mmol, 113 mg), H_2O (4.0 mL), and in the presence of various catalysts with the same amount of W species were stirred at 50 °C. After the reaction, the mixture was extracted with ethyl acetate and catalyst was taken out from the system by centrifugation before analysis by gas chromatography (GC-1690 Kexiao Co. equipped with a flame ionization detector and a HP-INNOWax capillary column). Dodecane was added as an internal standard.

For recycling the catalyst, the catalyst was separated by centrifugation, washed with ethanol, and then another portion of cyclooctene (110 mg, 1.0 mmol), H_2O_2 (30 % aq., 1.0 mmol, 113 mg), and H_2O (4.0 mL) were added. The reactions were conducted at 50 °C for 24 h.

Oxidation of dibenzothiophene. As a typical run for oxidation of dibenzothiophene (DBT, 25 mg, 0.136 mmol), *n*-octane (10 g), H_2O_2 (30% aq., 0.68 mmol, 77 mg), and in the presence of various catalysts with the same amount of W species were stirred at 30 °C for 8 h. After the reaction, 10 g of acetone was added to dissolve the product and catalyst was taken out from the system by centrifugation and washed with acetone for three times. The combined organic solvents were evaporated under vacuum, and 1.0 g of acetone was added to dissolve the residuals before analysis by gas chromatography (GC-1690 Kexiao Co. equipped with a flame ionization detector and a HP-INNOWax capillary column). Dodecane was added as an internal standard.

For recycling the catalyst, the catalyst was separated by centrifugation, washed with acetone, dried, and then another portion of dibenzothiophene (25 mg, 0.136 mmol), H_2O_2 (30% aq., 0.68 mmol 77 mg), and *n*-octane (10 g) were added. The reactions were operated at 30 °C for 8 h.

Table S1. Textural parameters of various samples.

Sample	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)
PQP	758	0.59
PQP[a]	723	0.54
W_2O_{11}/PQP	520	0.41

[a] PQP treated in 10 M HCl aqueous solution for 12 h.

Table S2. Recycles of W_2O_{11}/PQP in epoxidation of cyclooctene.[a]

Recycles	Conv. (%)	Select. (%)
0	79.3	>99.0
1	76.4	>99.0
2	76.7	>99.0
3	77.1	>99.0
4	75.4	>99.0
5	75.9	>99.0

[a] Reaction conditions: cyclooctene (110 mg, 1.0 mmol), catalyst (50 mg), H_2O_2 (30% aq., 1.0 mmol, 113 mg), H_2O (4.0 mL), 50 °C, 24 h.

Table S3. Epoxidation of cyclooctene under various reaction conditions over W_2O_{11}/PQP catalyst.[a]

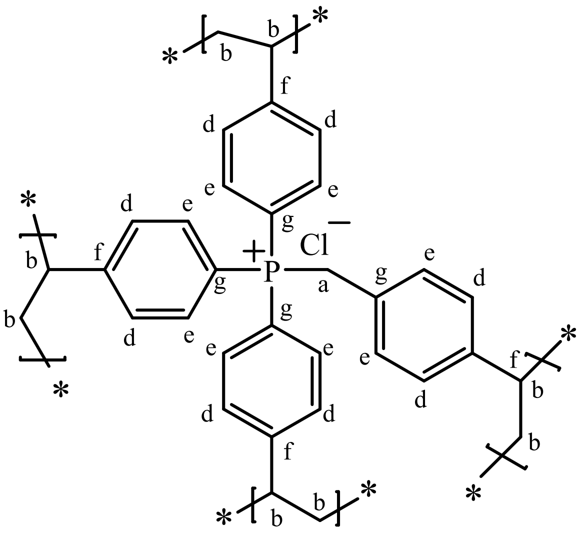
Entry	Temperature (°C)	Time (h)	Conv. (%)	Select. (%)	Efficiency of H_2O_2 (%)
1	30	8	46.0	>99.0	46.0
2	30	24	69.6	>99.0	69.6
3	30	36	82.1	>99.0	82.1
4	70	8	60.6	96.1	60.6
5	70	12	61.3	95.8	61.3
7[b]	50	12	97.6	94.3	45.6
8[c]	50	12	46.0	>99.0	91.9
9[d]	50	12	24.8	>99.0	>99.0

[a] Reaction conditions: cyclooctene (110 mg, 1.0 mmol), catalyst (50 mg), H_2O_2 (30% aq., 1.0 mmol, 113 mg), H_2O (4.0 mL); [b] H_2O_2 (30% aq., 2.0 mmol, 226 mg); [c] H_2O_2 (30% aq., 0.5 mmol, 56.5 mg); [d] H_2O_2 (30% aq., 0.25 mmol, 28.3 mg).

Table S4. Recycles of W_2O_{11}/PQP in oxidation of dibenzothiophene.[a]

Recycles	Conv. (%)	Select. (%)
0	>99.8	>99.0
1	>99.8	>99.0
2	>99.8	>99.0
3	>99.8	>99.0
4	>99.8	>99.0
5	>99.8	>99.0

[a] Reaction condition: dibenzothiophene (25 mg, 0.136 mmol), *n*-octane (10 g), catalyst (3.4 mg), H_2O_2 (30% aq., 0.68 mmol, 77 mg), 30 °C, 8 h.



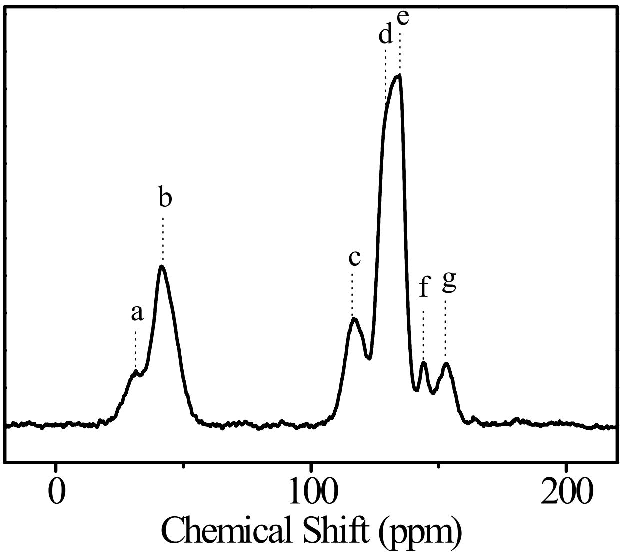


Fig. S1. ^{13}C MAS NMR spectrum of PQP salt. The peak at *c* is assigned to a small amount of the unpolymerized vinyl groups.

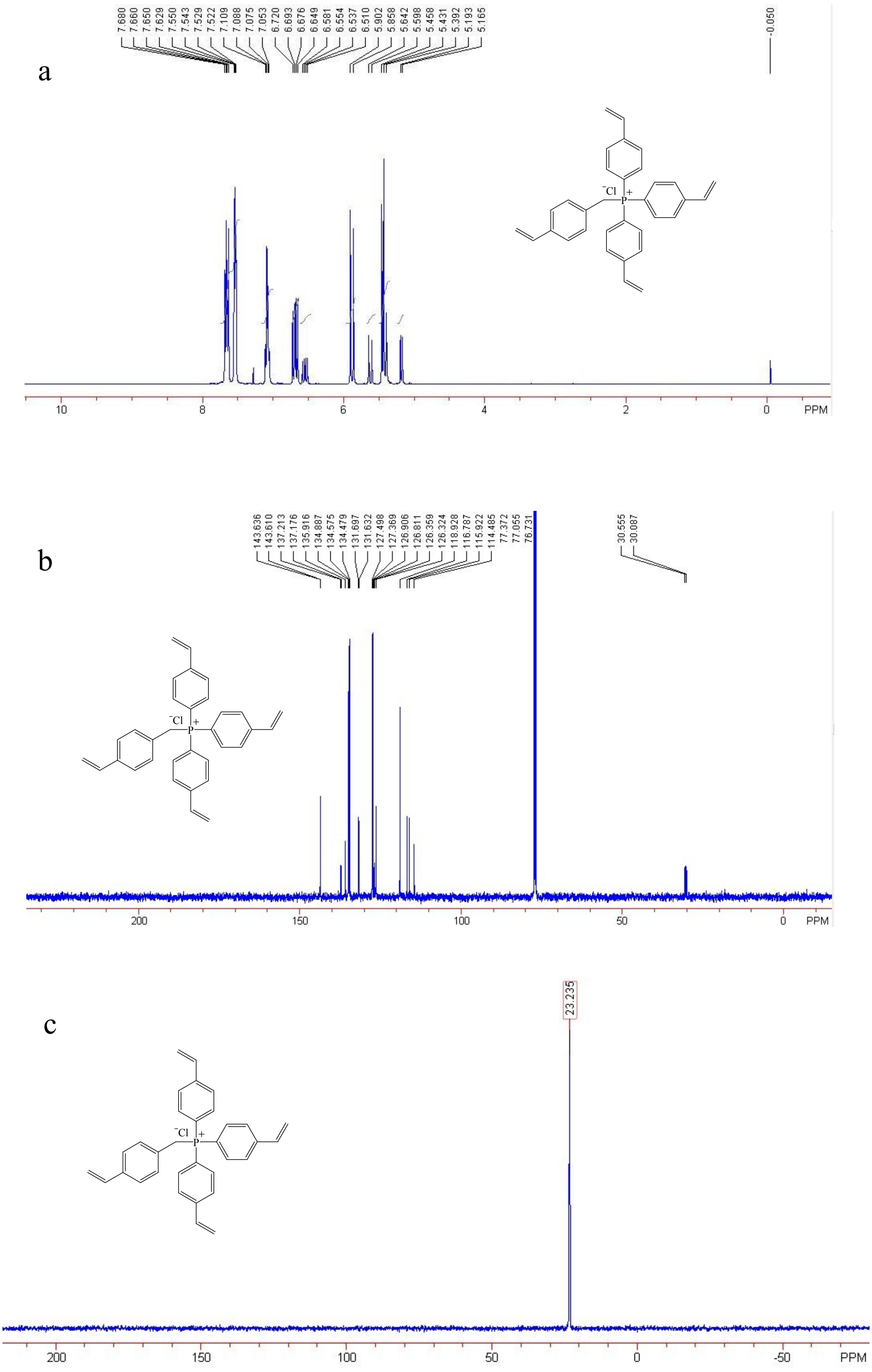


Fig. S2. (a) ^{1}H, (b) ^{13}C, and (c) ^{31}P liquid NMR spectra of vinyl-functionalized quaternary phosphonium ionic liquid monomer (VP-IL).

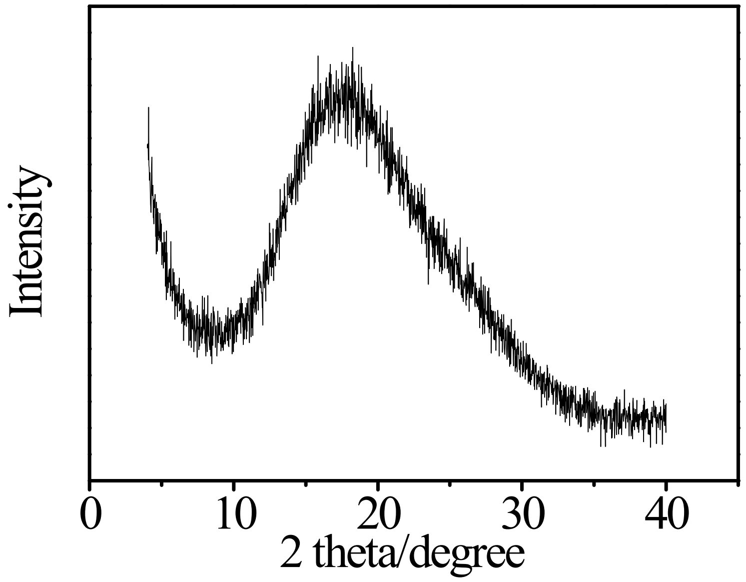


Fig. S3. XRD pattern of PQP salt.

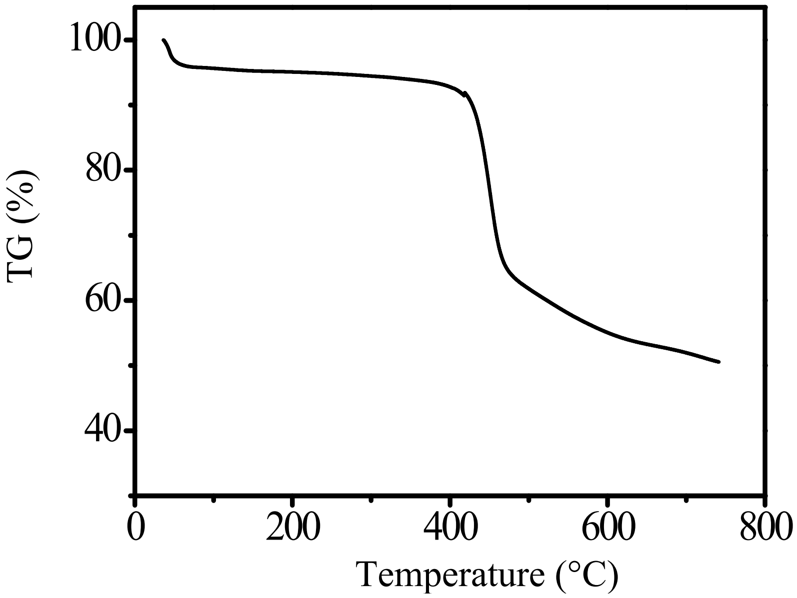


Fig. S4. TG curve of PQP salt.

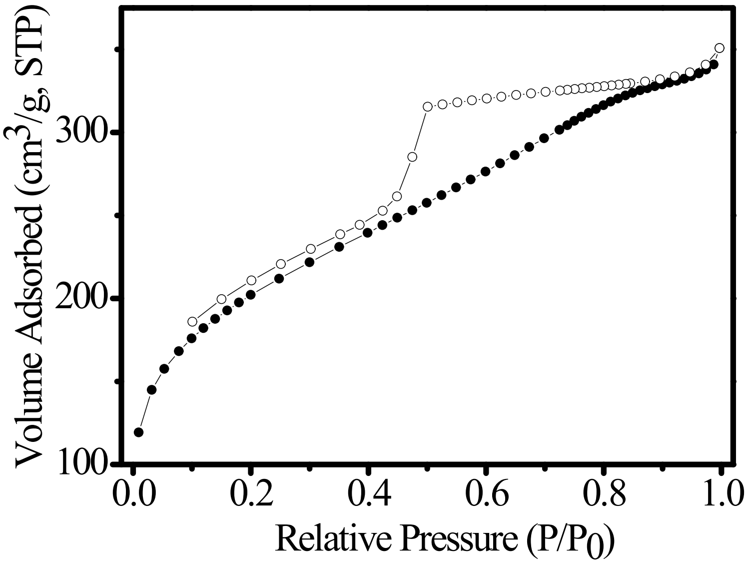


Fig. S5. Nitrogen sorption isotherms of PQP salt after treatment in 10 M HCl aqueous solution for 12 h. The BET surface area and pore volume were estimated at 723 m^2/g, and 0.54 cm^3/g, respectively.

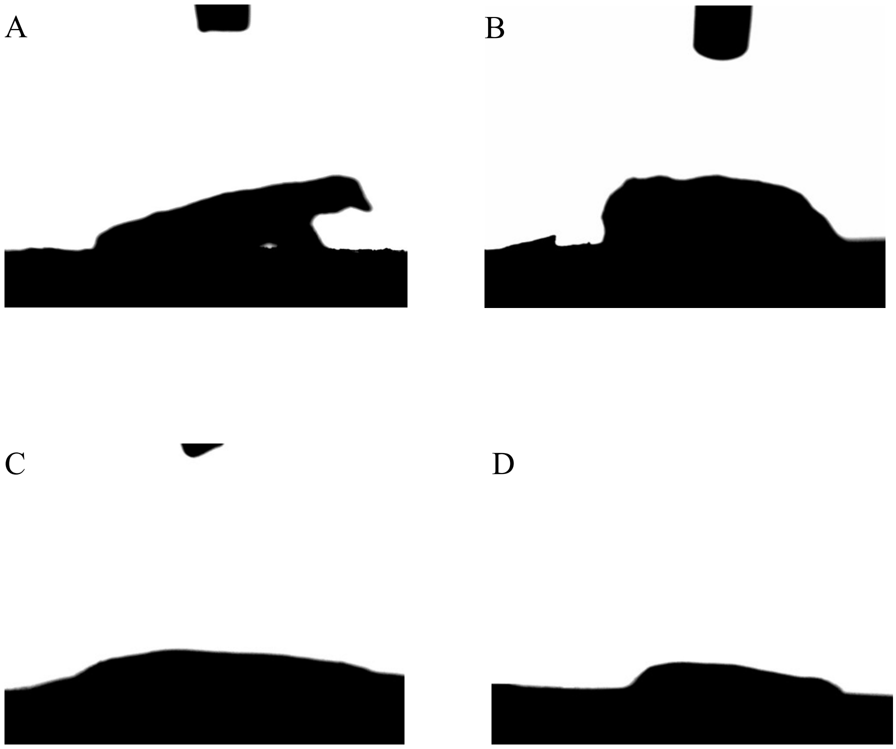


Fig. S6. Photographs of (A) water, (B) ethanol, (C) hexane, and (D) DMF droplets on the surface of PQP salt. When solvent droplets were contacted with the surface of PQP salt, they were momentarily adsorbed into the sample, giving swollen surfaces.

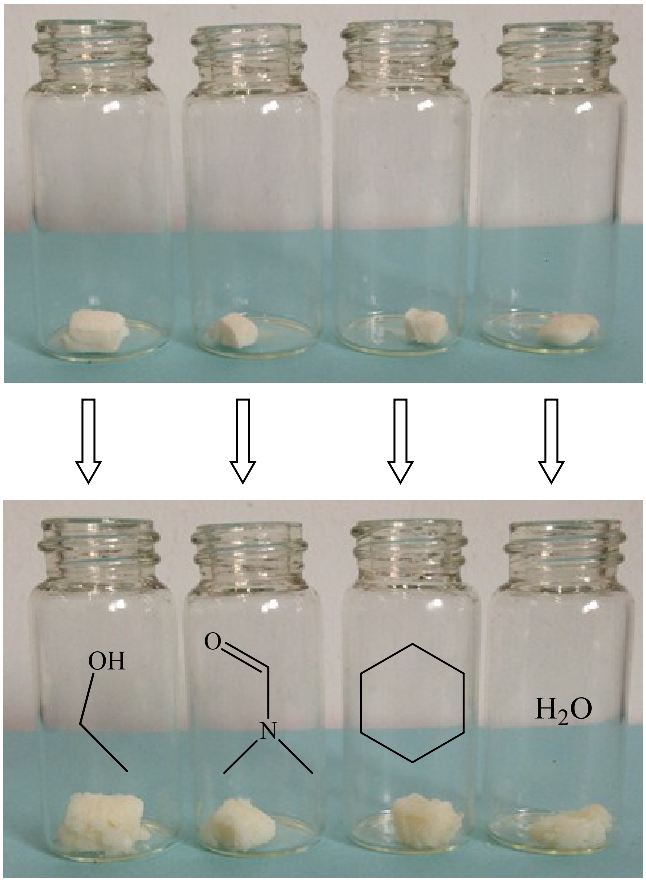


Fig. S7. Photographs of PQP salt (A) before, and (B) after adsorption of various solvents.

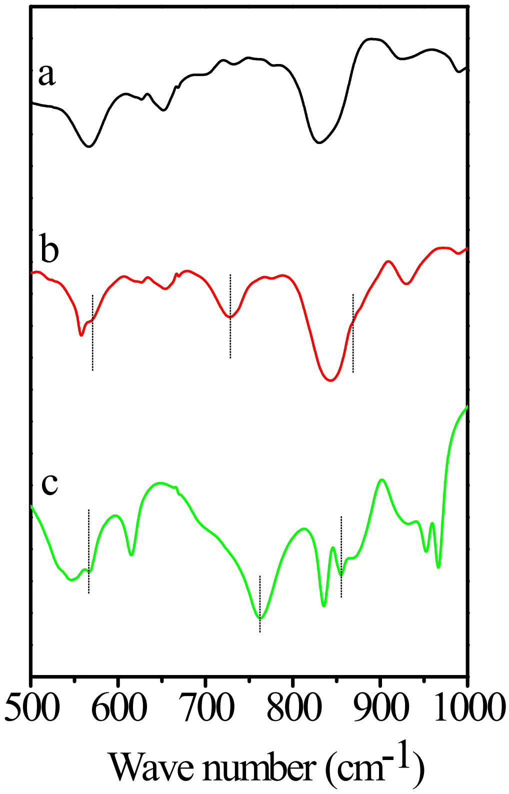


Fig. S8. IR spectra of (a) PQP salt, (b) W_2O_{11}/PQP, and (c) $K_2W_2O_{11}$.

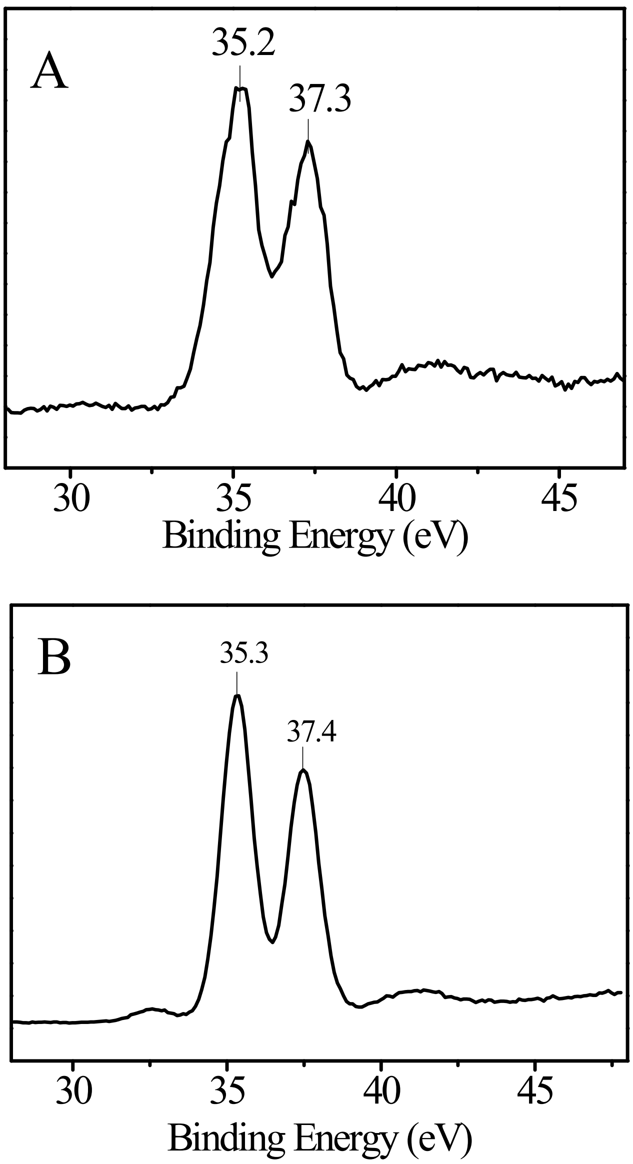


Fig. S9. W4f spectra of (A) W_2O_{11}/PQP, and (B) $K_2W_2O_{11}$.

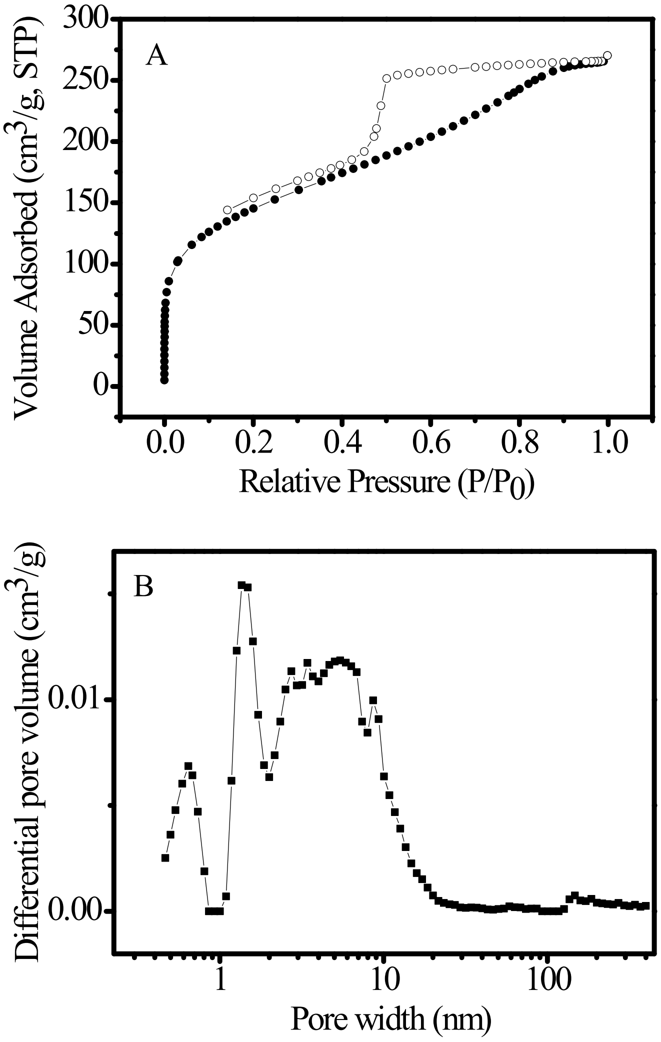


Fig. S10. (A) Nitrogen sorption isotherms and (B) pore size distribution of W_2O_{11}/PQP. Pore size distribution is calculated from non-local density functional theory (NLDFT).

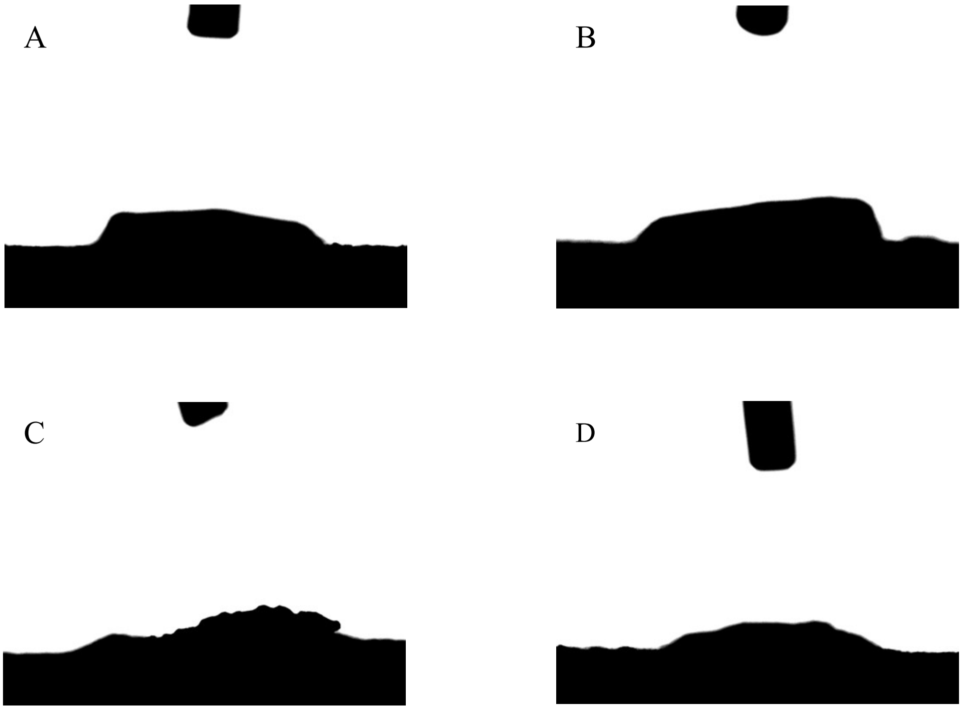


Fig. S11. Photographs of (A) water, (B) ethanol, (C) hexane, and (D) DMF droplets on the surface of W_2O_{11}/PQP. When solvent droplets were contacted with the surface of W_2O_{11}/PQP, they were momentarily adsorbed into the sample, giving swollen surfaces.

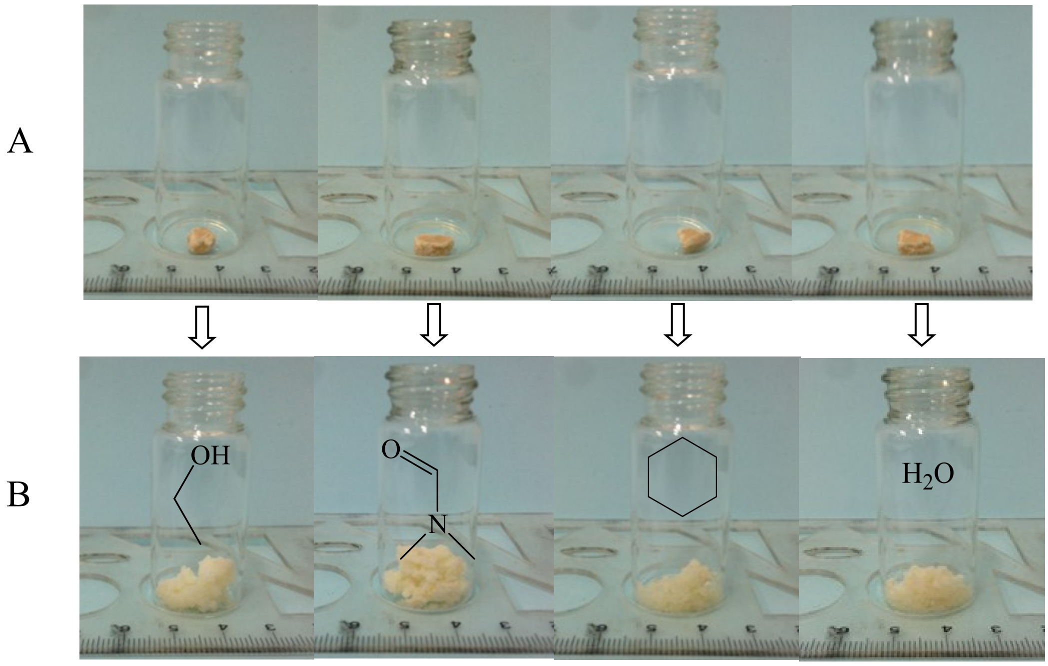


Fig. S12. Photographs of W_2O_{11}/PQP (A) before, and (B) after adsorption of various solvents.

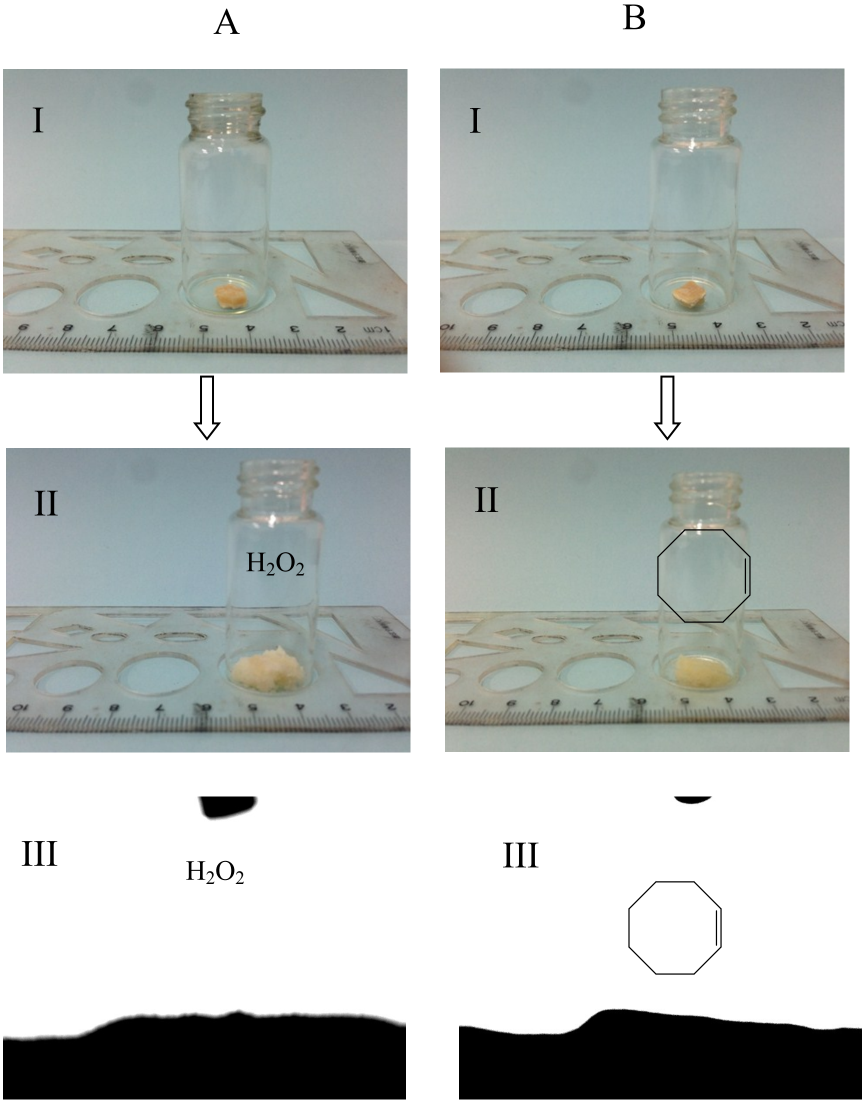


Fig. S13. Photographs of (A) H_2O_2 and (B) cyclooctene (I) before adsorption and (II) after adsorption on bulk sample, and (III) adsorption on the surface of W_2O_{11}/PQP.

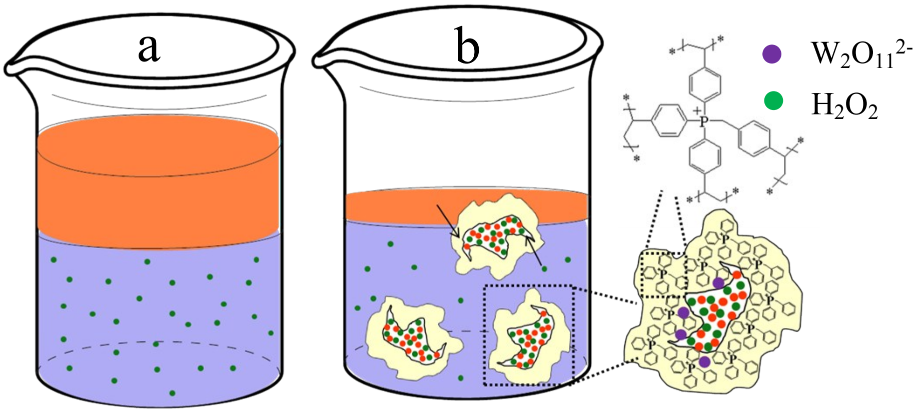


Fig. S14. Proposed scheme for the reactants enriched in the heterogeneous W_2O_{11}/PQP catalyst.

Two phase system (cyclooctene-water, 1mmol of cyclooctene, 1 mmol of H_2O_2 and 4 mL of H_2O) (a) before and (b) after addition of W_2O_{11}/PQP catalyst (50 mg). After addition of the catalyst in the system, the concentration of H_2O_2 in the pores of the catalyst is 10 times of that in the system, and about 90% of cyclooctene in the system has been adsorbed by the catalyst.

The enrichment of H_2O_2 concentration in W_2O_{11}/PQP catalysts was calculated by the pore volume of W_2O_{11}/PQP catalysts and the change of H_2O_2 concentration (ΔC) in the mixture before and after adding the solid samples by the $KMnO_4$ titration method. Enrichment of cyclooctene concentration in W_2O_{11}/PQP was determined by the change of cyclooctene in the liquid phase before and after the addition of the W_2O_{11}/PQP catalyst. The adsorption amount was calculated based on GC analysis. Notably, both of the adsorption equilibriums were achieved in less than 5 minutes.

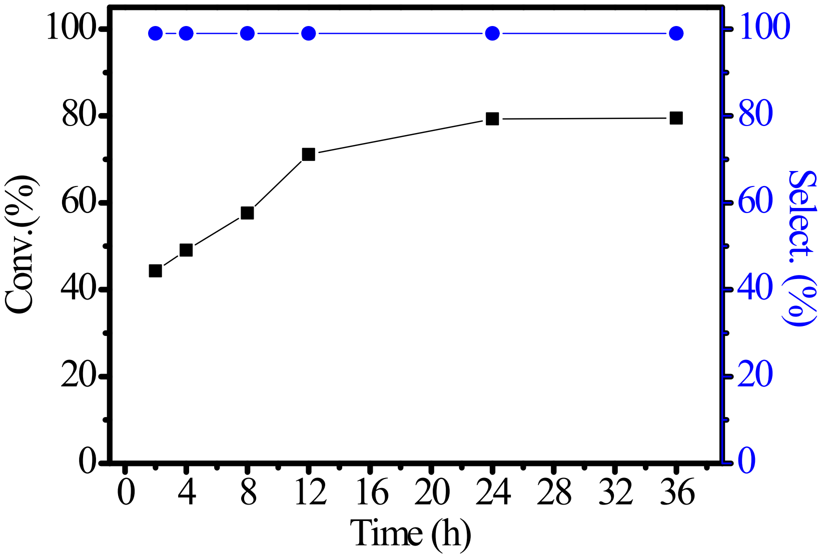


Fig. S15. Catalytic kinetics over W_2O_{11}/PQP in epoxidation of cyclooctene. Reaction conditions: cyclooctene (110 mg, 1.0 mmol), catalyst (50 mg), H_2O_2 (30% aq., 1.0 mmol, 113 mg), H_2O (4.0 mL), 50 °C.