Electronic Supporting Information (ESI†)

Immobilization of Keggin-type polyoxometalates in cyclodextrin-based polymers for oxidation catalysis

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1. Materials and Methods

1.1. POM syntheses

All reagents were purchased from commercial sources and used without further purification. Solutions were prepared in distilled water.

The POMs $Na_3[PW_{12}O_{40}]\cdot 14H_2O$, $K_5[PV^{IV}W_{11}O_{40}]\cdot 16H_2O$, $K_4[PV^{V}W_{11}O_{40}]\cdot 9H_2O$, and $NaRb_5[H_2W_{12}O_{40}]\cdot 11\ H_2O$ were synthesized and purified according to published procedures.[1–3] The purity and chemical composition of the POMs were confirmed by TGA, NMR (^{31}P, ^{51}V, and ^{183}W) and FT-IR spectroscopies.

1.2. Polymer syntheses

The synthesis of γ-CD-EPI polymers was carried out according to the protocol described by Pellicer et al.,[4,5] with slight modifications. Copolymerization between the polyglycerol chains produced in situ and the CD is facilitated by the alkalinity of the medium. The presence of numerous hydroxyl groups on the CD molecule opens up a wide range of cross-linking possibilities.

Typically, 15 mg (0.4 mmol) of sodium borohydride (Sigma-Aldrich, 99%) as catalyst was mixed with 5.8 g (4.5 mmol) of γ-CD (TCI, 99.0%) and 6 mL of deionized (DI) water. The mixture was then magnetically stirred at 50 °C and 200 rpm during all subsequent steps. After 10 min, 6.3 mL of sodium hydroxide (40 wt%, VWR) were added to obtain a transparent and clear solution. After 5 min, 6.4, 8.5, or 10.4 g (67.5, 90, or 112.5 mmol) of EPI (Sigma-Aldrich, 99%) were added dropwise, then allowed to react under these conditions (stirring at 50 °C / 200 rpm) for a few hours until a creamy yellowish precipitate forms. The precipitate was washed with acetone, neutralized as much as possible with 6 M HCl (Fluka), washed again with DI water, and then with acetone, 5 times with ca. 10 mL for 10 min at each step. Finally, the polymers were freeze-dried for 2-3 days.

The solids collected exhibit different behaviors. Syntheses with a low EPI/CD molar ratio (6.4 and 8.5 g EPI, corresponding to 15 and 20 equivalents) resulted in ca. 7 g of powdered solids, fully soluble in water, while with high EPI/CD synthesis (10.6 g EPI, corresponding to 25 equivalents), the 14 g of polymer obtained were insoluble. These aqueous solutions (75 mg / 5 mL) of soluble polymers showed a high pH of ca. 12, and the supernatant of insoluble polymer also resulted in high alkaline pH of ca. 11. This means the neutralization step was not efficient enough, and further washing of the solid product is needed before utilization. The insoluble polymer was then neutralized and purified using a buffer acid solution (50 ml Na_2SO_4 0.1 M / H_2SO_4 0.1 M, pH 1.2): 75 mg / 5 mL under stirring 500 rpm / 1 h. The final CD-EPI polymer is recovered by filtration and air dried.

1.3. Adsorption studies

All experiments were performed at room temperature using POM stock solutions in Na_2SO_4 (0.5 M) / H_2SO_4 (0.5 M) buffer (pH 1) in the concentration range 0.1-6.4 mM. Vials containing 2.5 mL of POM solution were mixed with 75 mg of CD-EPI insoluble polymer and subjected to magnetic stirring at 500 rpm for contact times varying between 0 and 60 min. Immediately after each exposure time, the solid was separated from its solution by centrifugation for 1 min at a speed of 14000 rpm. The liquid part is quantitatively analyzed by UV-Vis spectroscopy, and the solid part by infrared spectroscopy, TGA, NMR, and elemental analysis (ICP and EDX). The adsorption of POM on the CD-EPI polymer can be represented schematically as follows:

	POM + CD-EPI →	POM@CD-EPI
At time $t = 0$:	c_0	$q_0 = 0$
At time t:	c_t	$q_t \propto (c_0 - c_t)$
At equilibrium:	c_e	$q_e \propto (c_0 - c_e)$

C_0, C_t, and C_e are the concentrations in liquid phase (μM) of initial POM, at contact time t and equilibrium, respectively, while q_t and q_e represent the quantities of POM adsorbed (μmol/g), respectively, at time t and equilibrium.

The amount of POM retained by the polymeric adsorbent was examined using equation (S1):[4]

$$q_e = \frac{V\,(C_0 - C_e)}{m} \qquad \text{(S1)}$$

where V is the volume of POM solution used (L) and m is the mass of polymer utilized (g). Typically, the volume V used was 5 mL and the amount m of the support was 75 mg. The equilibrium concentration C_e is determined either by direct measurement with UV-Vis spectroscopy of the adsorption solution, or deduced from the adsorbed material detected in the solid by TGA.

Adsorption kinetic parameters were determined by fitting the experimental data, and the best fits were obtained with the pseudo-second-order model (PSOM).[6] Equation (S2) represents the linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad \text{(S2)}$$

where k_2 (g.µmol^{-1}.min^{-1}) is the second-order adsorption rate constant.

The experimental data at the equilibrium were fitted using the Langmuir isotherm model. The Langmuir isotherm assumes saturated monolayer adsorption of adsorbed POM on homogeneous sites on the surface of the adsorbing polymer.[7] Equation (S3) provides the mathematical expression of this model:

$$q_e = \frac{\frac{K_L}{a_L} C_e}{\frac{1}{a_L} + C_e} \qquad \text{(S3)}$$

where q_e (µmol.g^{-1}) is the amount of adsorbed POM per gram of polymer, C_e (µmol.L^{-1}) is the POM equilibrium concentration in solution, K_L (L.g^{-1}) and a_L (L.µmol^{-1}) are Langmuir parameters. These parameters are used to calculate the maximum adsorption capacity q_{max} (µmol.g^{-1}), the dimensionless constant R_L, and the Gibbs free energy $\Delta G°$ (kJ.mol^{-1}) using equations (S4-6):[4,5]

$$q_{max} = \frac{K_L}{a_L} \qquad \text{(S4)}$$

$$R_L = \frac{1}{1 + a_L C_0} \qquad \text{(S5)}$$

$$\Delta G° = -RTln(Mw_{POM} C_{H_2O} K_L) \qquad \text{(S6)}$$

where R is the perfect gas constant (8.314 J.mol^{-1}.K^{-1}), T is the absolute temperature (K), Mw_{POM} is the POM molecular weight, and C_{H2O} is the molar concentration of water (55.5 mol.L^{-1}).

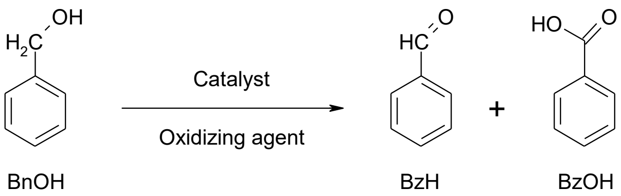
1.4. Characterization

The POMs and soluble CD-EPI polymers were characterized by UV-Vis and multinuclear NMR spectroscopies. The UV–Vis spectra of solutions were recorded on a Perkin-Elmer Lambda-750 using calibrated 1 cm Quartz-cell. The ^{1}H and ^{13}C{^{1}H} solution spectra were recorded in 5 mm o.d. tubes using a Bruker Avance 400 spectrometer equipped with a BBI probehead. Solid-state ^{13}C, ^{31}P, and ^{51}V under magic-angle spinning (MAS) NMR spectra were recorded on a Bruker Avance 500 spectrometer (B_0 = 11.7 T), using a 2.5 mm double-resonance probehead. Cross-polarization (CP) experiments were recorded for ^{13}C using contact time of 1 ms, recycle times of 3 s, and transient numbers of 4096. Quantitative direct-polarization ^{13}C experiments were also measured using echo pulse sequence with 90 s delay between scans. ^{1}H SPINAL-64 decoupling (75 kHz radio-frequency field) was applied during signal acquisition. The ^{51}V and ^{31}P spectra were recorded using one-pulse sequence under various MAS rates between 10 and 20 kHz. ^{31}P spectra of diamagnetic samples were measured with a repetition delay of 460 s accumulating ca. 100 scans, while a relaxation delay of 0.1 s and a number of scans of ca. 20000 were used for paramagnetic samples. The spectra were analyzed using DMFIT software,[8] and chemical shifts are referenced to external 1% Me_4Si in $CDCl_3$ (^{1}H and ^{13}C), aqueous 85% H_3PO_4 (^{31}P) and 90% $VOCl_3$ in C_6D_6 (^{51}V).

Solid samples were analyzed by infrared (IR) spectroscopy, and thermogravimetric (TGA) and elemental analyses. IR spectra were recorded on a Nicolet 30 ATR 6700 FT spectrometer. TGA was carried out under oxygen with a heating rate of 5 °C/min up to 700 °C on a Mettler Toledo TGA/DSC 3, Star System analyzer. Energy-dispersive X-ray (EDX) analysis was performed on a JEOL JSM7001F microscope using gold-coated samples equipped with a spectrometer and a X-Max SDD (Silicon Drift Detector) by Oxford. The C,H,N analyses were performed by Unité de Catalyse et Chimie du Solide at Lille university, 59652 Villeneuve d'Ascq, France. The accurate POM loading amounts in the CD-EPI polymer samples were analyzed by ICP coupled Atomic Emission Spectrometry (ICP-AES) (Thermo Scientific, iCAP PRO Duo ICP-OES). The polymer powders were digested in HNO_3 (70 wt%) by heating at 70 °C for ca. 1 h.

1.5. Catalytic tests

Benzyl alcohol oxidation was used as a benchmark catalytic test:



The reaction was carried out in a 10 mL round-bottom flask under reflux, after introducing successively the catalyst (POM or POM@CD-EPI), the substrate (BnOH), and an oxidizing agent (30 wt% aq. H_2O_2 or 70 wt% aq. t-Bu-OOH). Additional solvent (water or acetonitrile) was also considered in some specific experiments. Detailed reaction conditions are given in Table 5. Products were identified by comparison of their ^{1}H and ^{13}C NMR signals with standard samples. Reaction products were extracted with CD_3CN (used as NMR lock solvent) and the solid catalyst was separated by centrifugation, washed three times with acetonitrile, and air-dried overnight before recycling. Yield and selectivity when not specified are based on benzoic acid (BzOH) product, while conversion corresponds to transformed BnOH, calculated from quantitative ^{1}H NMR as follows:

$$Conversion\ (\%) = \left(1 - f_{BnOH}\right) \times 100 \qquad \text{(S7)}$$

$$Yield\ (\%) = \left(f_{BzOH}\right) \times 100 \qquad \text{(S8)}$$

$$Selectivity\ (\%) = \left(\frac{f_{BzOH}}{f_{BzOH} + f_{BzH}}\right) \times 100 \qquad \text{(S9)}$$

where f_{BnOH}, f_{BzH}, and f_{BzOH} are the fractions of benzyl alcohol, benzaldehyde (BzH), and benzoic acid respectively observed in the ^{1}H NMR spectrum ($f_{BnOH} + f_{BzH} + f_{BzOH} = 1$).

2. Characterization of CD-EPI polymers

2.1 Liquid-state NMR

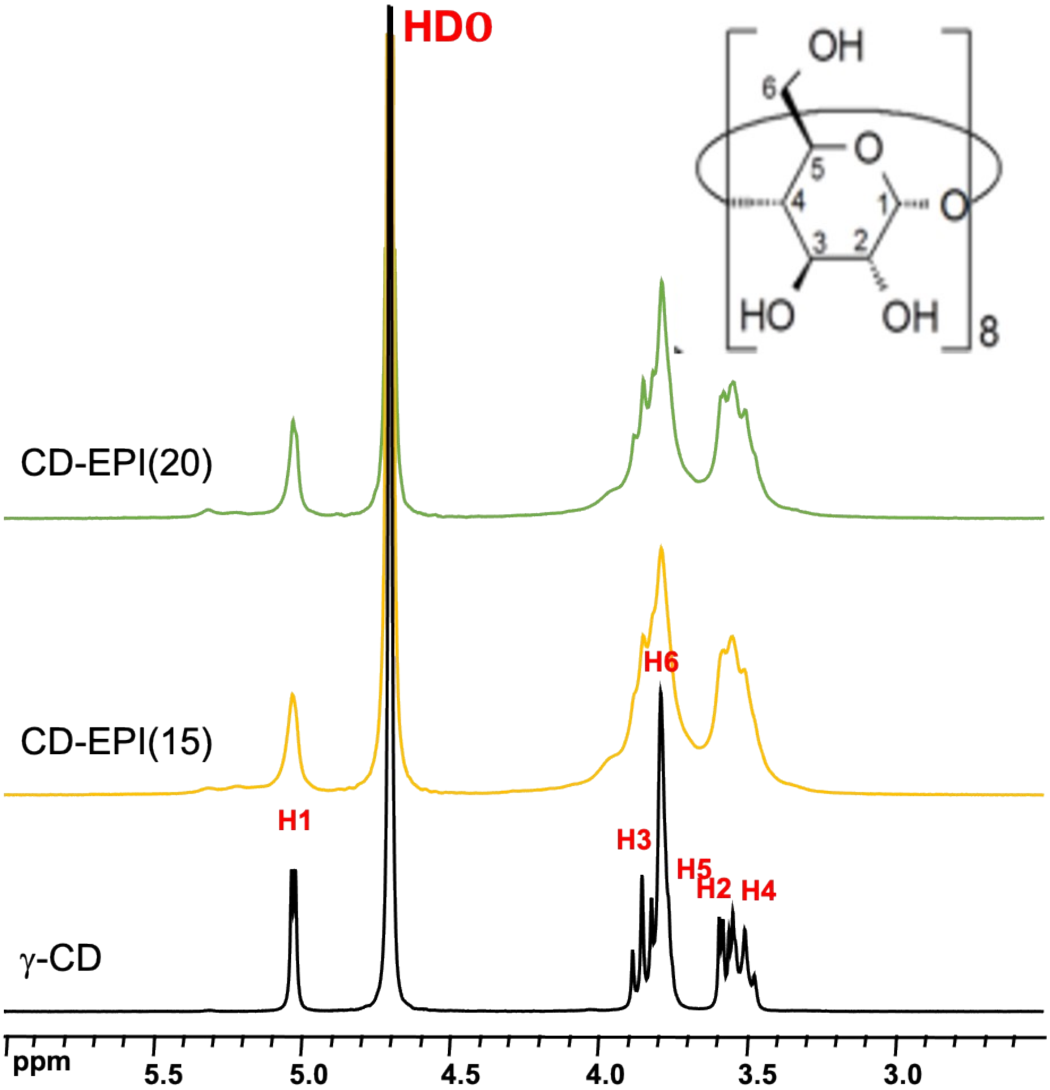


Figure S-1. ^{1}H NMR spectra in D_2O of native ϒ-Cyclodextrin and soluble polymers CD-EPI(15) and CD-EPI(20).

The mass fraction of CD in the polymer (W/W) is calculated using equation (S10):

$$CD\ (\%) = \frac{H1_S \times m_{ref}}{H1_{ref} \times m_S} \times 100 \tag{S10}$$

Where $H1_S$ and $H1_{ref}$ are the NMR integration of the H1 signal of the sample (CD-EPI polymer) and the reference (γ-CD). m_S and m_{ref} are the mass weights of the sample (CD-EPI polymer) and the reference (γ-CD).

The molar fraction EPI/CD in the polymer is calculated using equation (S11):

$$\frac{EPI}{CD} = \left(\frac{H1_{ref} \times m_S}{H1_S \times m_{ref}} - 1\right) \times \frac{MW_{CD}}{MW_{EPI}} \tag{S11}$$

Where MW_{CD} and MW_{EPI} are the molecular weights of CD (1297 g/mol) and EPI (57 g/mol), respectively.

2.2 Solid-state NMR

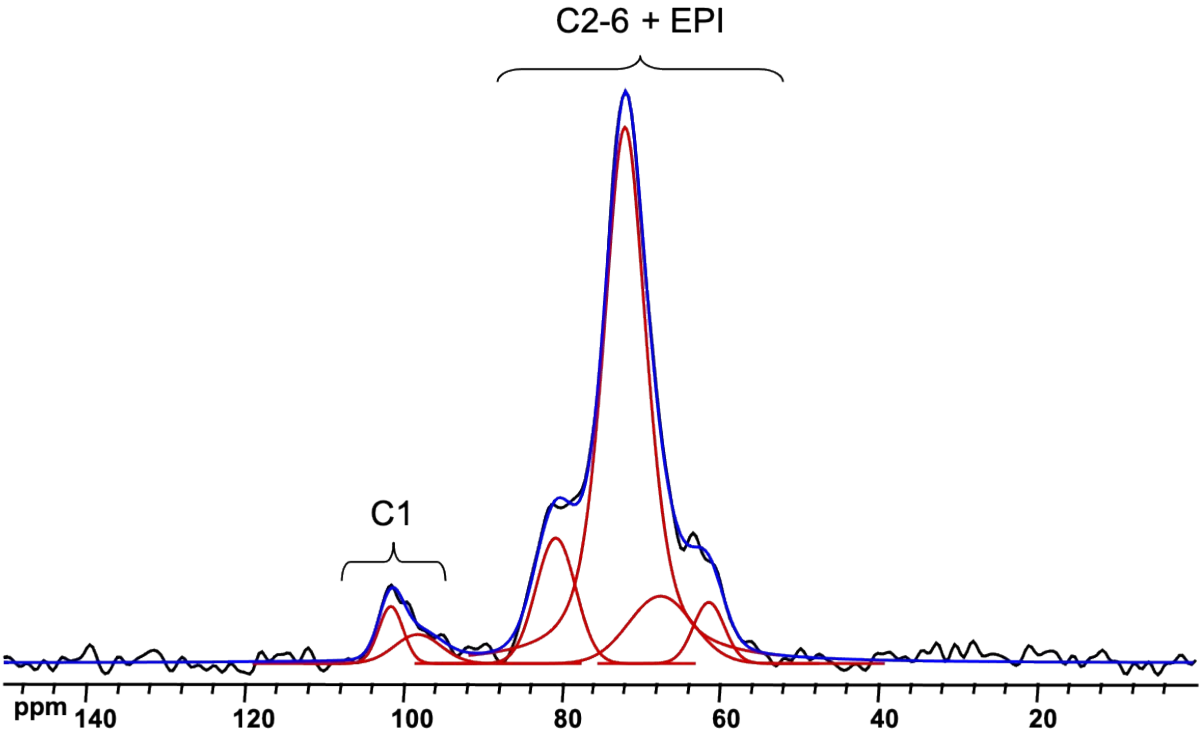


Figure S-2. Spectral decomposition of quantitative $^{13}C\{^1H\}$ MAS NMR of insoluble polymer CD-EPI(25).

The molar fraction EPI/CD in the insoluble polymer is calculated from ^{13}C MAS NMR after determining the fraction $C1$ of signal C1 with respect to total signal. This quantity is determined with the following equation (S12):

$$\frac{EPI}{CD} = \left(\frac{(1 - C1) - (C1 \times 5)}{C1 \times 6}\right) \times \frac{MW_{CD}}{MW_{EPI}} \tag{S12}$$

Where MW_{CD} and MW_{EPI} are the molecular weights of CD (1297 g/mol) and EPI (57 g/mol), respectively. $C1$ is the fraction of the signal C1, a value between 0 and 1.

To determine the mass fraction of CD in the insoluble polymer (W/W) from ^{13}C MAS NMR, we use the previous molar fraction EPI/CD in following equation (S13):

$$CD\ (\%) = \frac{MW_{CD}}{MW_{CD} + (\frac{EPI}{CD} \times MW_{EPI})} \times 100 \tag{S13}$$

2.3 Infrared spectroscopy

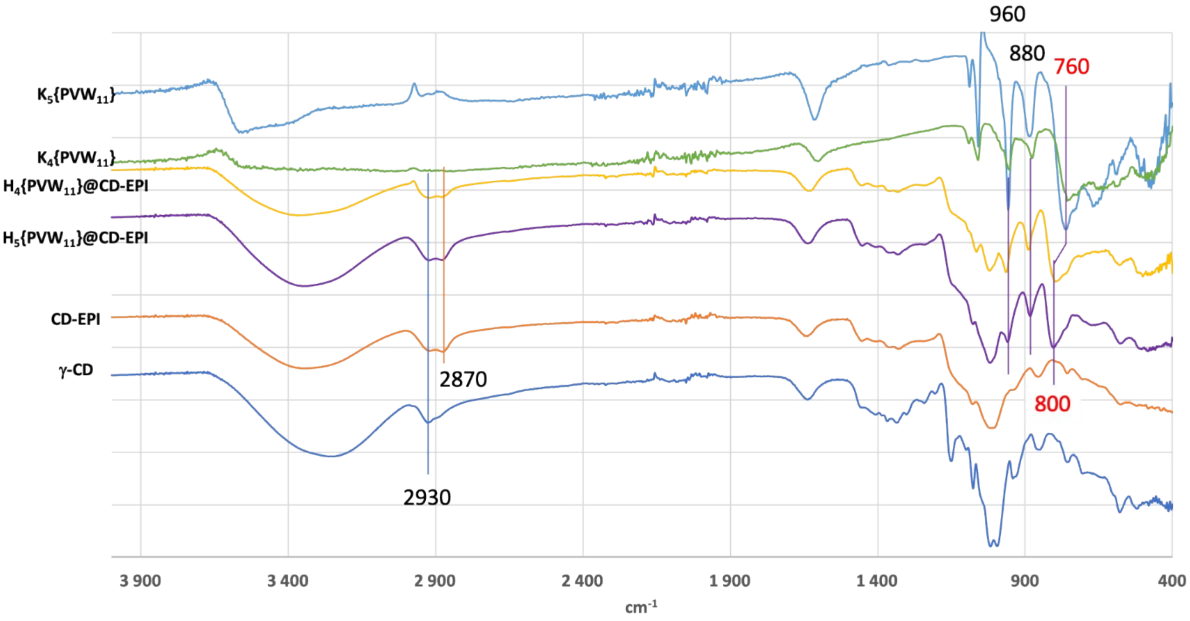


Figure S-3: Infrared spectra of POM@CD-EPI composites compared to the spectra of parent polymer CD-EPI(25), native γ-CD, and the studied POMs $K_5[PVW_{11}O_{40}].16H_2O$, and $K_4[PVW_{11}O_{40}].9H_2O$.

2.4 Thermogravimetry analysis

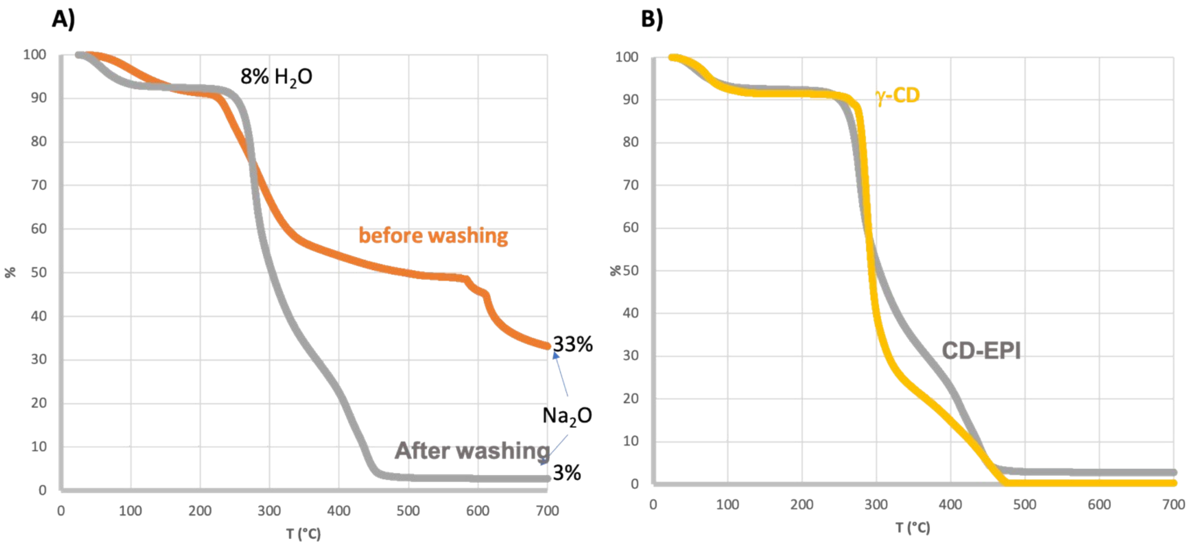


Figure S-4. TGA curves of A) insoluble polymer CD-EPI(25) before and after washing with an acidic buffer solution, and of B) washed insoluble polymer CD-EPI(25) compared to native γ-CD.

3. Adsorption study

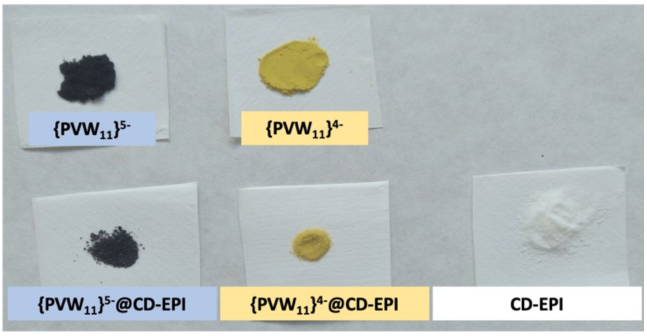


Figure S-5. Photographs of pure POM powders, the synthesized insoluble polymer CD-EPI(25), and POM@CD-EPI composites recovered after 1 h contact between 5 mL 3.2 mM POM and 75 mg CD-EPI polymer, showing the polymer's color change from white to yellow or dark blue with POM $[PVW_{11}O_{40}]^{4-}$ or $[PVW_{11}O_{40}]^{5-}$, respectively.

3.1 UV-Vis study

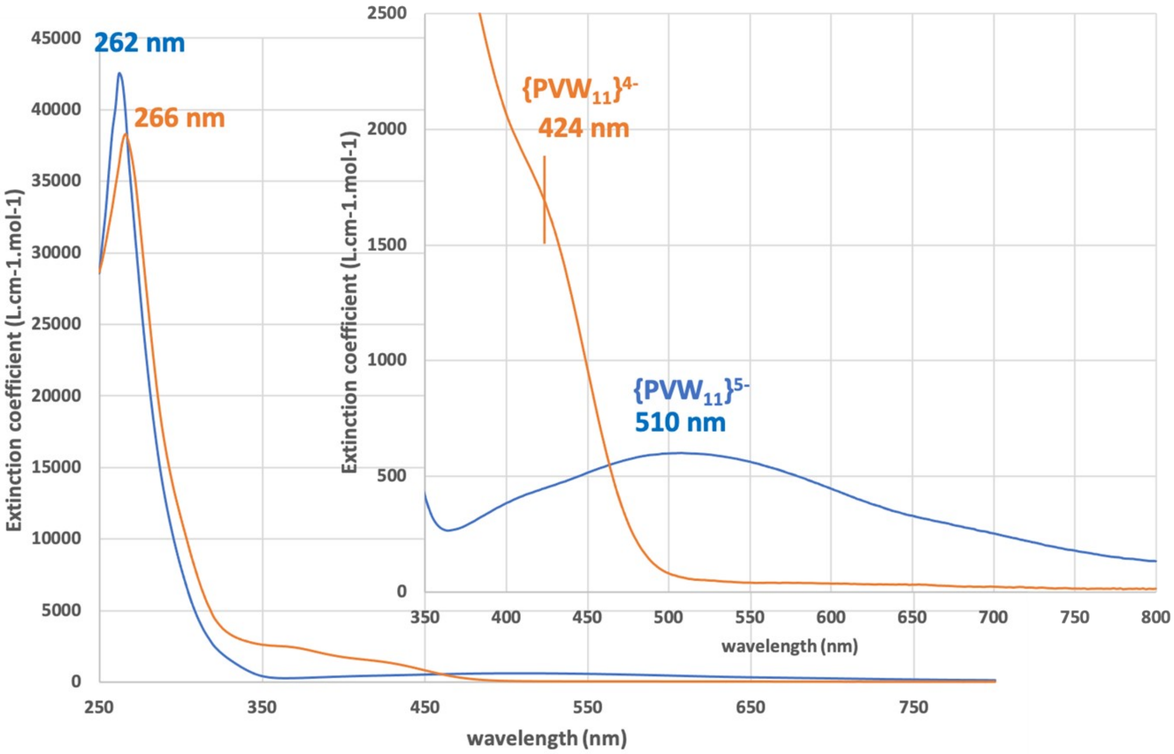
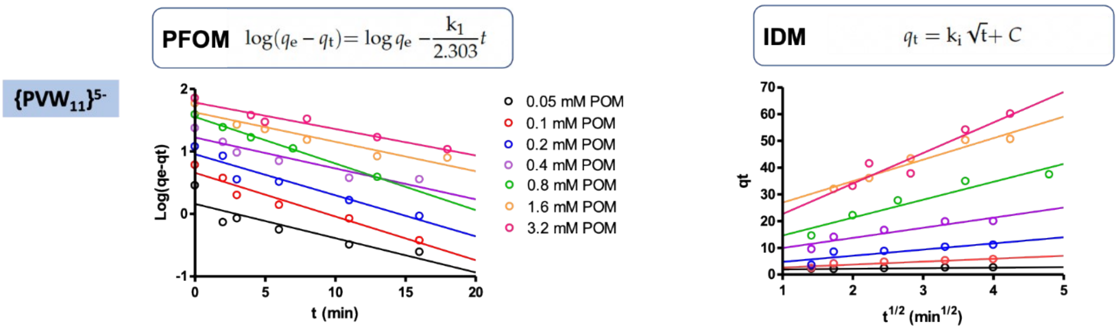


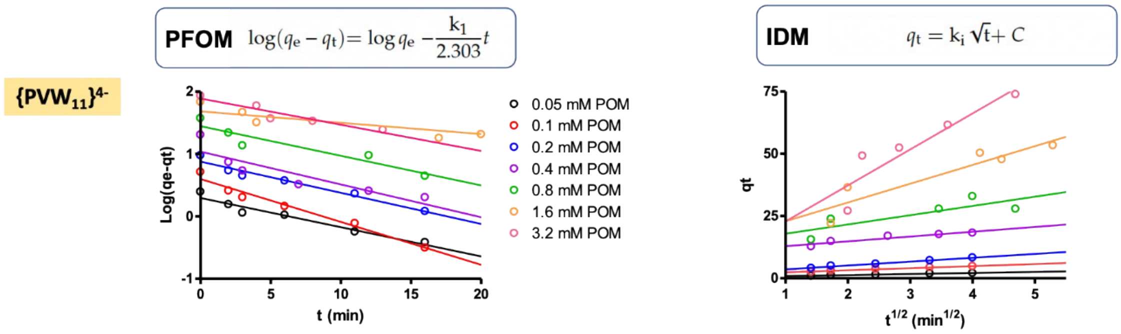
Figure S-6. Adsorption spectra of $[PVW_{11}O_{40}]^{5-}$ and $[PVW_{11}O_{40}]^{4-}$ in aqueous solution at pH 1 showing the characteristic transitions at 424 nm (ε = 1680 L cm^{-1} mol^{-1}) and 510 nm (ε = 600 L cm^{-1} mol^{-1}), respectively.



C_0 (mM)	K_1 (min^{-1})	qe_{calc} (µmol/g)	qe_{exp} (µmol/g)	R^2
0.0500	0.12 ± 0.02	1.6 ± 0.2	2.8	0.7914
0.104	0.16 ± 0.02	4.6 ± 0.3	6.1	0.9453
0.205	0.16 ± 0.02	9.1 ± 0.8	12	0.9139
0.435	0.12 ± 0.02	17 ± 1	23	0.8767
0.819	0.17 ± 0.01	35.5 ± 0.7	38.7	0.9949
1.69	0.11 ± 0.02	43 ± 2	58	0.9039
3.19	0.10 ± 0.01	60 ± 3	71	0.9448

C_0 (mM)	K_i (µmol/g min$^{-1/2}$)	C (µmol/g)	R^2
0.0500	0.23 ± 0.04	1.7 ± 0.1	0.9195
0.104	1.1 ± 0.3	1.6 ± 0.8	0.8189
0.205	2.3 ± 0.8	2 ± 2	0.7241
0.435	3.8 ± 0.8	6 ± 2	0.8694
0.819	7 ± 1	8 ± 4	0.9199
1.69	8 ± 1	19 ± 3	0.9446
3.19	11 ± 2	11 ± 7	0.8843

Figure S-7. a) Kinetics analyses of $[PVW_{11}O_{40}]^{5-}$ adsorption on insoluble polymer CD-EPI(25) using pseudo-first order model (PFOM) and interparticle diffusion model (IDM). Experimental conditions: CD polymer amount = 75 mg, POM volume = 5 mL, POM concentration = 0.05-3.2 mM, contact time = 0-60 min, stirring speed = 500 rpm, pH = 1, temperature = 25 °C.



C_0 (mM)	K_1 (min^{-1})	qe_{calc} (µmol/g)	qe_{exp} (µmol/g)	R^2
0.0457	0.11 ± 0.01	2.0 ± 0.1	2.5	0.9488
0.0984	0.16 ± 0.01	4.0 ± 0.2	5.1	0.9717
0.176	0.12 ± 0.01	7.6 ± 0.3	9.5	0.9607
0.356	0.12 ± 0.02	10 ± 1	20	0.8003
0.713	0.12 ± 0.02	28 ± 3	37	0.8853
1.43	0.04 ± 0.01	48 ± 3	68	0.9323
2.84	0.10 ± 0.02	78 ± 5	86	0.8928

C_0 (mM)	K_i (µmol/g min$^{-1/2}$)	C (µmol/g)	R^2
0.0457	0.42 ± 0.06	0.5 ± 0.2	0.9429
0.0984	0.84 ± 0.07	1.5 ± 0.2	0.9818
0.176	1.56 ± 0.09	2.0 ± 0.3	0.9899
0.356	1.9 ± 0.4	11 ± 01	0.8956
0.713	4 ± 1	14 ± 5	0.6743
1.43	8 ± 2	15 ± 7	0.8531
2.84	14 ± 4	8 ± 12	0.8391

Figure S-8. a) Kinetics analyses of $[PVW_{11}O_{40}]^{4-}$ adsorption on insoluble polymer CD-EPI(25) using pseudo-first order model (PFOM) and interparticle diffusion model (IDM). Experimental conditions: CD polymer amount = 75 mg, POM volume = 5 mL, POM concentration = 0.05-3.2 mM, contact time = 0-60 min, stirring speed = 500 rpm, pH = 1, temperature = 25 °C.

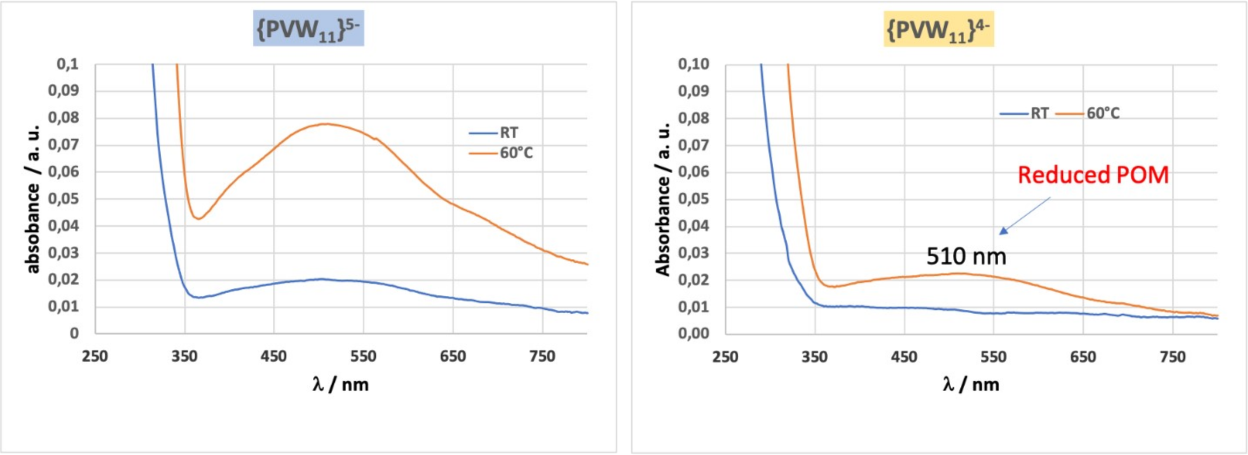


Figure S-9: UV-Vis spectra of solutions after treating POM@CD-EPI composites in water at room temperature (25 °C) and 60 °C for 1 h. Experimental conditions: Initial POM loading = 68 µmol/g ($PW_{11}VO_{40}^{4-}$) and 58 µmol/g ($PW_{11}VO_{40}^{4-}$), POM@CD polymer amount = 60 mg, volume = 5 mL, contact time = 60 min, stirring speed = 500 rpm, pH = 1, temperature = 25 and 60 °C.

3.2 Thermogravimetry analysis

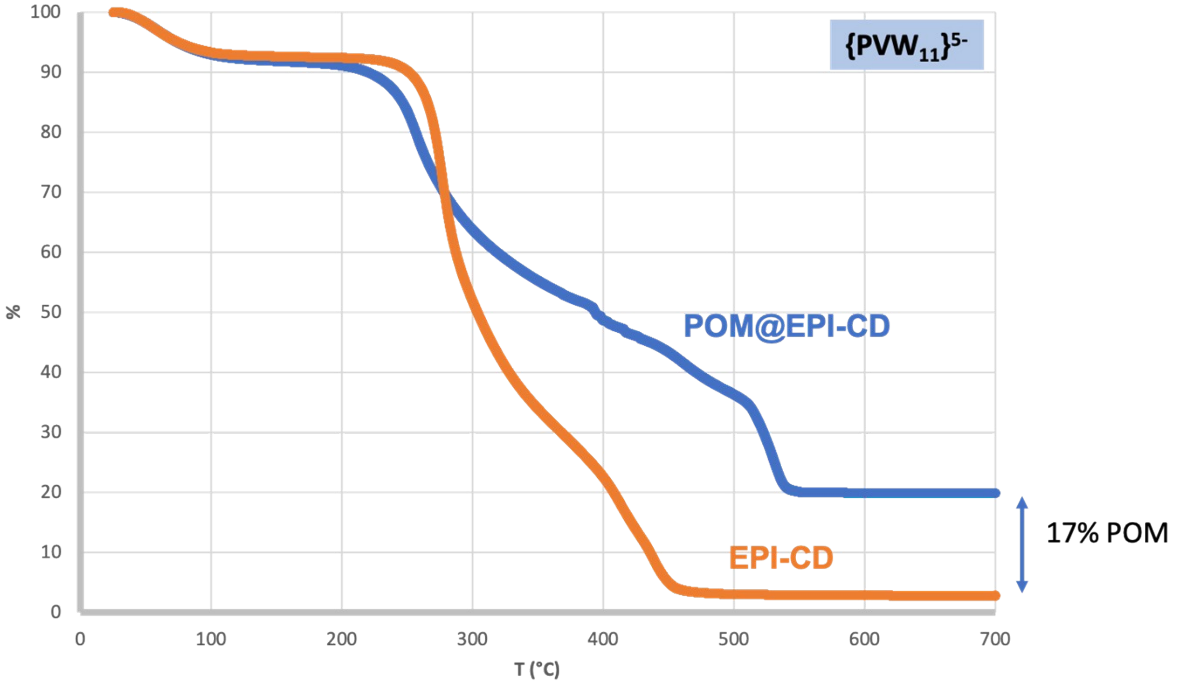


Figure S-10: TGA curves of $\{PVW_{11}\}^{-5}$@CD-EPI composite compared to parent polymer CD-EPI(25). The composite is obtained under the following conditions: CD polymer amount = 75 mg, POM volume = 5 mL, POM concentration = 3.2 mM, contact time = 60 min, stirring speed = 500 rpm, pH = 1, temperature = 25 °C.

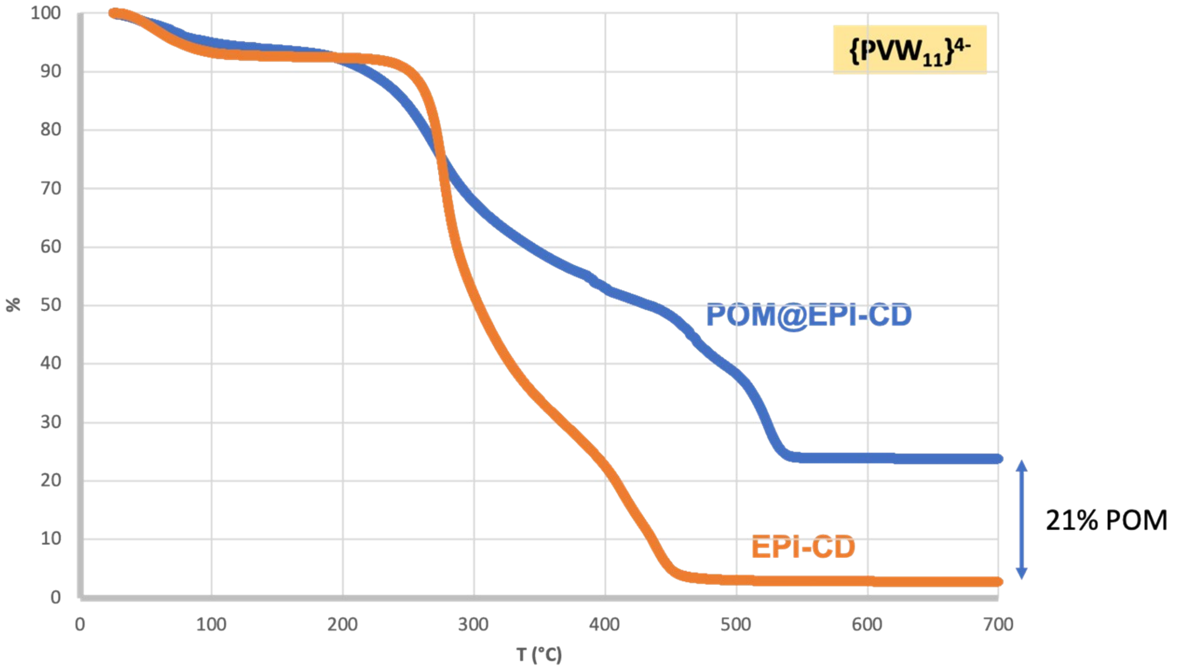


Figure S-11: TGA curves of $\{PVW_{11}\}^{-4}$@CD-EPI composite compared to parent polymer CD-EPI(25). The composite is obtained under the following conditions: CD polymer amount = 75 mg, POM volume = 5 mL, POM concentration = 3.2 mM, contact time = 60 min, stirring speed = 500 rpm, pH = 1, temperature = 25 °C.

3.3. ICP-AES analyses

Analyses by ICP-AES were conducted on digested solids in 70 wt% HNO_3 (> 99.999%, Sigma Aldrich), heated 1 h at 70 °C. Calibrations were performed on standard solutions in the same medium (matrix) for vanadium (200 mg/L V, Sigma-Aldrich), phosphorus (200 mg/L P, Sigma-Aldrich), and tungsten (1002 g/L W, Sigma-Aldrich). For sodium, a stock mother solution (100 mg/L Na) was prepared from NaCl (> 99.5%, Alpha-Aesar). Ultra-pure water (milliQ) was used to prepare the solutions and dilutions. The concentration ranges for the calibration solutions were: 50-800 µg/L P, 80-1280 µg/L V, 3000-50000 µg/L W, and 50-800 µg/L Na. For each element, signals at two wavelengths were recorded and an average value was considered. The calibration curves are shown in Figure S-12. The amounts found in the analyzed samples were in the range: 0-70 µg/L P, 0-90 µg/L V, 0-19000 µg/L W, and 6-150 µg/L Na.

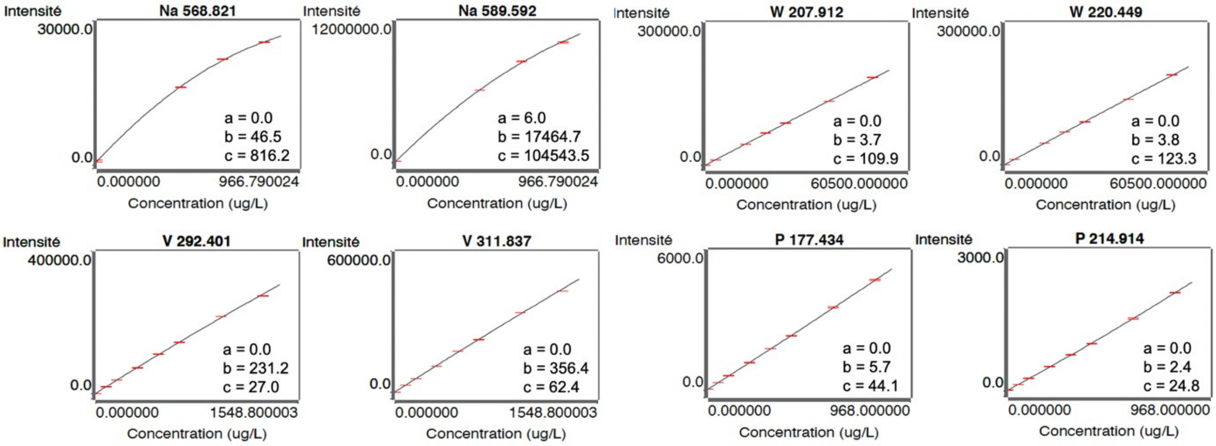


Figure S-12: Calibration curves of ICP analyses for Na, W, V, and P at two wavelengths using quadratic relationship of the form Int(conc.) = $ax^2 + bx + c$.

Table S-1: Elemental analysis of insoluble CD-EPI polymer and POM@CD-EPI composites[a]

	wt%					
Sample	**C**[c]	**H**[c]	**Na**[d]	**P**[d]	**V**[d]	**W**[d]
CD-EPI(25)	42.5 (52)	6.9 (9)	0.07 (0.02)	0.000	0.000	0.0
$\{PVW_{11}\}^{5-}$@CD-EPI[b]	32.4 (43)	5.1 (7)	0.09 (0.02)	0.047 (0.18)	0.065 (0.3)	13.6 (12)
$\{PVW_{11}\}^{4-}$@CD-EPI[b]	36.6 (41)	5.6 (7)	0.06 (0.02)	0.047 (0.24)	0.060 (0.4)	12.8 (16)

a) Calculated values shown in brackets are based on the combined results of solid-state ^{31}C NMR, ATG, and UV-Vis spectroscopy. b) Composites obtained by adsorption of a POM solution with a concentration of 3.2 mM on CD-EPI. c) by C,H,N analysis. d) by ICP-AES method.

3.4. EDS analyses

Table S-2: Elemental analysis by EDS of POM@CD-EPI composites[a]

Sample	**P**	**V**	**W**	**Na**	**K**
$\{PVW_{11}\}^{5-}$@CD-EPI	2.1 (1)	1.0 (1)	11 (11)	1.1	0.3 (5)
$\{PVW_{11}\}^{4-}$@CD-EPI	1.9 (1)	1.0 (1)	11 (11)	1.1	0.0 (4)

a) Values shown in parentheses correspond to expected values based on the POM stoichiometry and charge.

3.5 Solid-state NMR

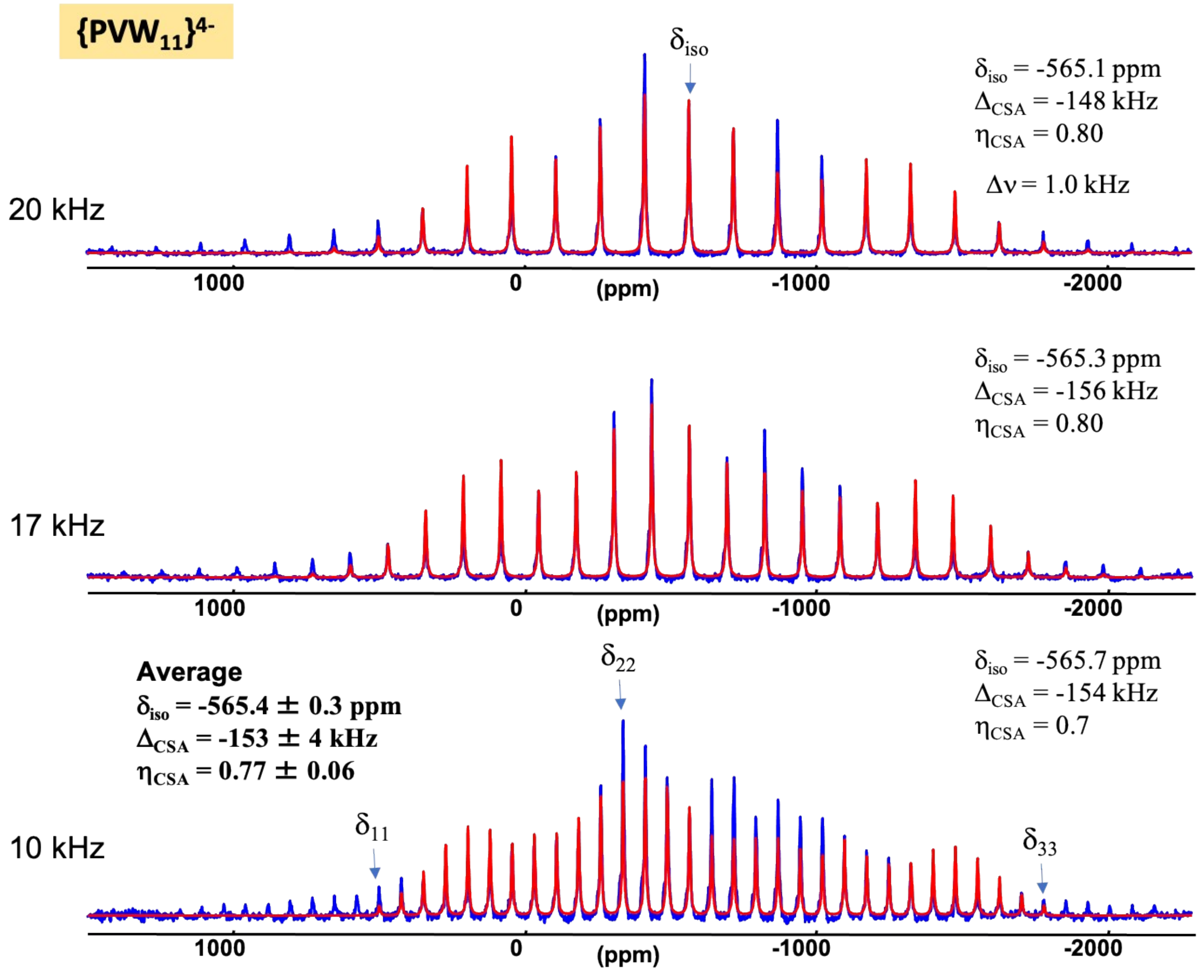


Figure S-13: Experimental (blue line) and calculated (red line) ^{51}V NMR spectra of $K_4[PVW_{11}O_{40}].9\ H_2O$ at different MAS rates.

The isotropic chemical shift (δ_{iso}), the axial chemical shift anisotropy (Δ_{CSA}), and the asymmetry parameter (η_{CSA}), are defined as followed using with equations (S14), (S15), and (S16):

$$\delta iso = \frac{\delta 11 + \delta 22 + \delta 33}{3} \qquad \text{(S14)}$$

$$\Delta_{CSA} = \delta 33 - \delta iso \qquad \text{(S15)}$$

$$\eta CSA = \frac{\delta 22 - \delta 11}{\delta 33 - \delta iso} \qquad \text{(S16)}$$

$$\text{with } |\delta 33 - \delta iso| > |\delta 11 - \delta iso| > |\delta 22 - \delta iso| \qquad \text{(S17)}$$

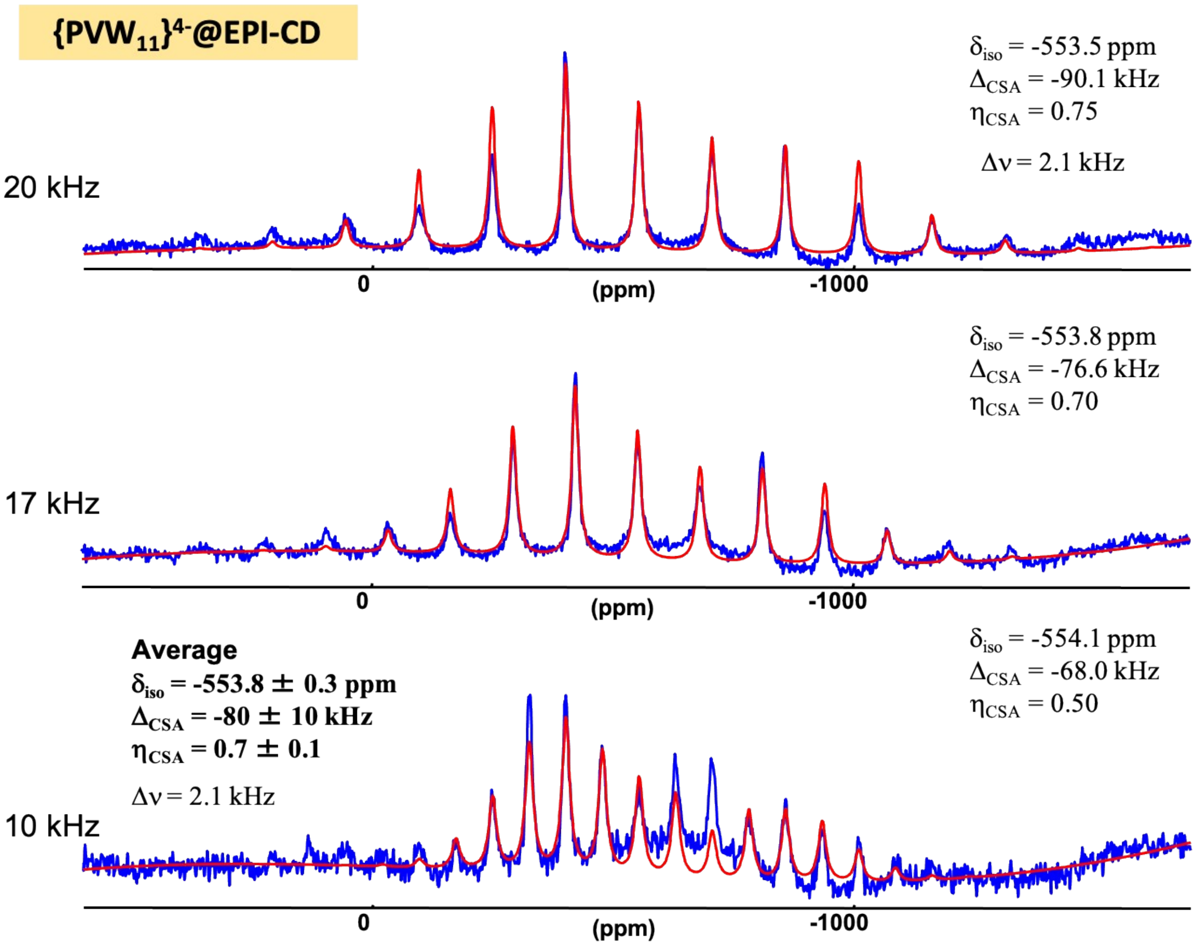


Figure S-14: Experimental (blue line) and calculated (red line) ^{51}V NMR spectra of $[PVW_{11}O_{40}]^{4-}$@CD-EPI composite at different MAS rates.

4. Catalysis study

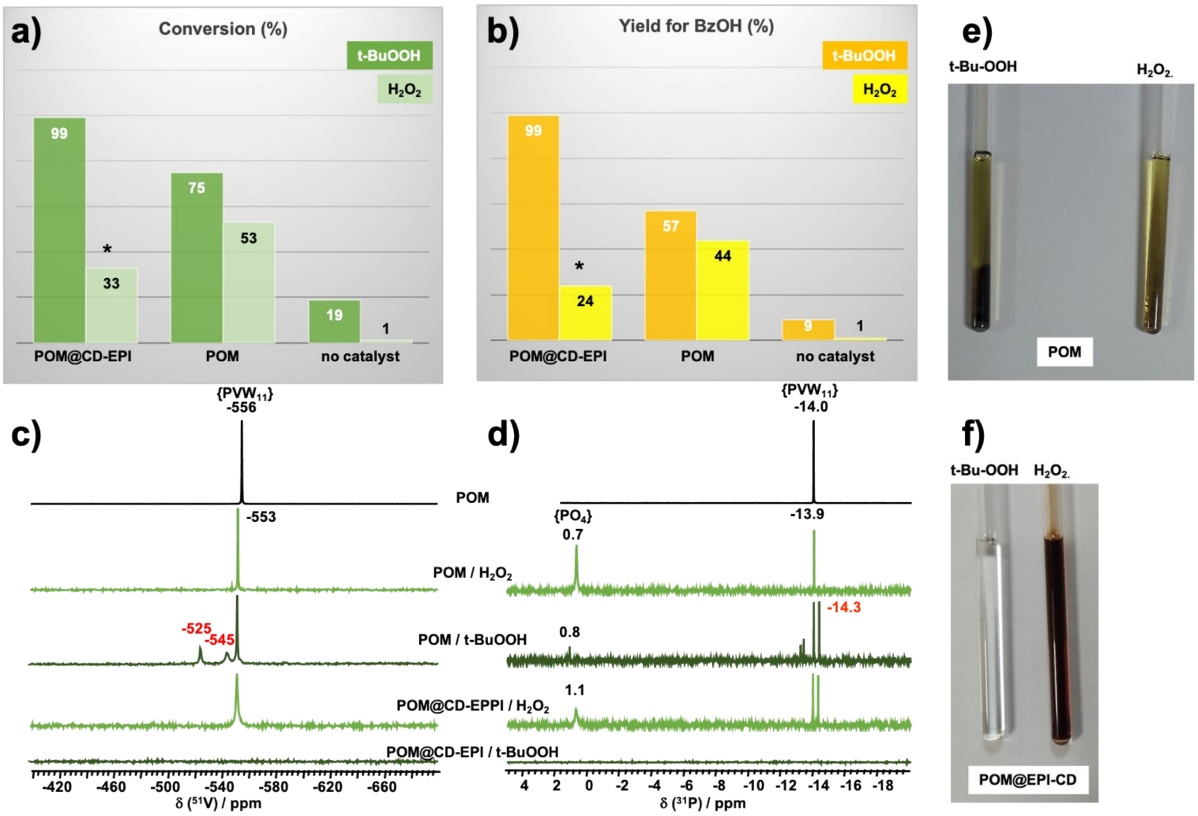


Figure S-15: Oxidation of benzyl alcohol to benzoic acid with POM@CD-EPI and POM (POM = $\{PVW_{11}\}^{5-}$) using H_2O_2 or t-BuOOH: a) Conversion and b) yield. NMR analyses of liquid part of reaction mixture: c) ^{51}V and d) ^{31}P. Photographs of NMR tubes: e) POM catalyst and f) POM@CD-EPI catalyst. The system POM@CD-EPI/t-BuOOH exhibits i) high catalytic performance (full conversion and selectivity), ii) no ^{51}V or ^{31}P signals, and iii) colorless liquid.

Table S-3: Quantities of leached POM by ICP elemental analysis in the liquid product after successive catalytic cycles

Sample	P (%)	V (%)	W (%)
Cycle 1	0	0	0
Cycle 2	0	0	0.5
Cycle 3	0	0.2	0.6
Cycle 4	2.2	1.1	10
Cycle 5	4.0	1.5	16

5. References

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