

Electronic Supplementary Information

Ionic self-assembly affords mesoporous ionic networks by crosslinking linear polyviologens with polyoxometalate clusters

Guojian Chen,^{a,b} Wei Hou,^a Jing Li,^a Xiaochen Wang,^a Yu Zhou^{*a} and Jun Wang^{*a}

^a State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing, 210009, China.

E-mail: njutzhouyu@njtech.edu.cn (Y. Zhou), junwang@njtech.edu.cn (J. Wang).

Tel: +86 25-83172264, Fax: +86-25-83172261.

^b School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou, 221116, China.

Experimental Details

Materials and Methods

4,4'-bipyridine, dibromomethane, 1,2-dibromoethane, 1,4-dibromobutane, bromoethane, 1-bromobutane, polyoxometalates $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and solvents were commercially available and used as received. The double V-containing POM $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ was prepared according to the procedure described in our previous report.^{S1} Liquid-state ^1H and ^{13}C NMR spectra were measured with a Bruker DPX 500 spectrometer at ambient temperature in the solvents of D_2O and $\text{D}^6\text{-DMSO}$ using TMS as internal reference. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on an Agilent Cary 660 FT-IR instrument (KBr discs) in the region $4000\text{--}400\text{ cm}^{-1}$. Solid UV-visible adsorption spectra were measured with a SHIMADZU UV-2600 spectrometer and BaSO_4 was used as an internal standard. Electron spin resonance (ESR) spectra were recorded on a Bruker EMX-10/12 spectrometer at the X-band at ambient temperature. X-ray photoelectron spectra (XPS) were conducted on a PHI 5000 Versa Probe X-ray photoelectron spectrometer equipped with $\text{Al K}\alpha$ radiation (1486.6 eV). The CHN elemental analysis was performed on an elemental analyzer Vario EL cube. Thermogravimetric analysis (TGA) was carried out with a STA409 instrument in air atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. X-ray diffraction (XRD) measurements were made with a SmartLab diffractometer (Rigaku Corporation) equipped with a 9 kW rotating-anode Cu source at 40 kV and 200 mA, from 5 to 80° with a scan rate of 0.2° s^{-1} . Field emission scanning electron microscope (FESEM; Hitachi S-4800, accelerated voltage: 5 kV) accompanied by Energy dispersive X-ray spectrometry (EDS; accelerated voltage: 20 kV) was used to study the morphology and the element mapping distribution. Transmission Electron Microscopy (TEM) images were obtained by using a JEOL JEM-2100F 200 kV field-emission transmission electron microscope. N_2 adsorption isotherms were measured at 77 K with the BELSORP-MINI analyzer. Before measurement, porous carbon samples were degassed for 3 h at $150\text{ }^\circ\text{C}$ in a high vacuum.

Synthesis of polyoxometalate-based mesoporous ionic networks (PMINs)

Firstly, three cationic polyviologens were prepared by one-step quaternization reactions of 4,4'-bipyridine with dibromoalkane including dibromomethane (DBM), 1,2-dibromoethane (DBE) and 1,4-dibromobutane (DBB). In a typical run, 4,4'-bipyridine (1.56 g, 10 mmol) was dissolved in 5 mL DBM to form a homogeneous solution at room temperature. Then, the solution was heated at $100\text{ }^\circ\text{C}$ for 48 h in a 25 mL Teflon-lined autoclave. After reaction, the yellow solid was dispersed into ethanol with vigorous stirring for 4 h, and finally the yellow solid

product [PMV]Br₂ was obtained by the successive filtration, washing with ethanol and drying processes. In similar processes, the other two polyviologens [PEV]Br₂ and [PBV]Br₂ were synthesized by using DBE or DBB respectively.

[PMV]Br₂: a yellow solid yield of 60%, ¹H NMR (300 MHz, D₂O, TMS) (Fig. S1A): δ 9.62~9.68 (4H), 9.02 (4H), 8.77~8.85 (4H), 8.49~8.55 (4H) and 7.64 ppm (2H). ¹³C NMR (75.5 MHz, D₂O, TMS) (Fig. S1B): 152.54, 149.35, 145.91, 131.55 and 80.30 ppm. Elemental analysis: Found C, 38.95; H, 3.60; N, 8.35. Calc. for [PMV]Br₂ C₁₁H₁₀N₂Br₂(0.5H₂O): C, 38.97; H, 3.27; N, 8.26 wt%.

[PEV]Br₂: a brown solid yield of 76%, ¹H NMR (300 MHz, D₂O, TMS) (Fig. S2A): δ 9.50 (4H), 9.32(4H), 8.93 (4H) and 4.74 ppm (4H). ¹³C NMR (75.5 MHz, D₂O, TMS) (Fig. S2B): 149.06, 145.56, 129.39~131.17 and 63.15 ppm. Elemental analysis: Found C 39.61, H 4.19, N 7.28. Calc. for [PEV]Br₂ C₁₂H₁₂N₂Br₂(H₂O): C, 39.81; H, 3.90; N, 7.74 wt%.

[PBV]Br₂: a yellow solid yield of 63%, ¹H NMR (300 MHz, D₂O, TMS) (Fig. 3A): δ 9.17 (4H), 8.57(4H), 4.84 (4H) and 2.28 ppm (4H). ¹³C NMR (75.5 MHz, D₂O, TMS) (Fig. 3B): 152.88, 148.19, 129.82, 63.71 and 30.03 ppm. Elemental analysis: Found C, 42.20; H, 5.05; N, 6.67. Calc. for [PBV]Br₂ C₁₄H₁₆N₂Br₂(1.5H₂O): C, 42.13; H, 4.80; N, 7.02 wt%.

Secondly, polyoxometalate-based mesoporous ionic networks (PMINs) were prepared through the ionic self-assembly of the above water-soluble cationic polyviologens with heteropolyacids such as H₅PMo₁₀V₂O₄₀, H₅PMo₁₂O₄₀ and H₃PW₁₂O₄₀. In a typical synthesis by using [PMV]Br₂ and H₅PMo₁₀V₂O₄₀, [PMV]Br₂ (0.100 g, 5 mg mL⁻¹) with 0.5960 mmol N⁺ cationic center was dissolved in deionized water (20 mL), and the equivalent H₅PMo₁₀V₂O₄₀ (0.207 g, 0.119 mmol) aqueous solution (10 mg mL⁻¹) was slowly added into the above homogeneous solution with steady stirring for 24 h at room temperature. Finally, after the consecutive basic operations including filtration, washing and drying, the yellow product named PMIN-1(V) was obtained with a yield of 78%. Ionic self-assembly of [PEV]Br₂ and [PBV]Br₂ with H₅PMo₁₀V₂O₄₀ can produce the samples PMIN-2(V) and PMIN-3(V), respectively. Besides, H₃PMo₁₂O₄₀ and H₃PW₁₂O₄₀ were also employed as anionic POM units for preparing a series of mesoporous ionic networks. The corresponding elemental analysis results and specific molecular formulas were listed in Table S1.

Synthesis of the control viologen-polyoxometalate ionic hybrids

Two viologen-based dicationic salts were also synthesized by the reaction of 4,4'-bipyridine with bromoalkanes including bromoethane and 1-bromobutane. In a typical run, 4,4'-bipyridine (0.78 g, 5 mmol) and bromoethane

(1.64 g, 15 mmol) was dissolved in solvent acetonitrile (20 mL), and then the solution was moved into a Teflon-lined autoclave, which was taken place at 100 °C in a constant temperature oven for 24 h. After reaction, the yellow solid product [C₂Bpy]Br₂ was obtained from the solution by the successive filtration, washing with ethanol and drying processes. [C₄Bpy]Br₂ was similarly prepared by the reaction of 4,4'-bipyridine and 1-bromobutane.

[C₂Bpy]Br₂: a yellow solid yield of 80%, ¹H NMR (300 MHz, D₂O, TMS) (Fig. S4A): δ 9.14~9.16 (4H), 8.56~8.58 (4H), 4.80~4.82 (4H) and 1.69~1.74 ppm (6H). ¹³C NMR (75.5 MHz, D₂O, TMS) (Fig. S4B): 152.64, 147.90, 129.79, 60.39 and 18.44 ppm.

[C₄Bpy]Br₂: a yellow solid yield of 84%, ¹H NMR (300 MHz, D₂O, TMS) (Fig. S5A): δ 9.10~9.12 (4H), 8.54~8.56 (4H), 4.72~4.74 (4H), 2.00~2.08 (4H), 1.35~1.42 (4H) and 0.91~0.96 ppm (6H). ¹³C NMR (75.5 MHz, D₂O, TMS) (Fig. S5B): 152.60, 148.12, 129.72, 64.70, 35.28, 21.49 and 15.46 ppm.

POM-viologen ionic hybrids [C₂Bpy]_{2.5}PMoV₂, [C₄Bpy]_{2.5}PMoV₂ and [Bpy]_{2.5}PMoV₂ were prepared by the reaction of H₅PMo₁₀V₂O₄₀ with [C₂Bpy]Br₂, [C₄Bpy]Br₂ and 4,4'-bipyridine in aqueous solution, respectively. Elemental analyses for **[C₂Bpy]_{2.5}PMoV₂:** Found C, 18.50; H, 2.05; N, 3.06. Calc. for (C₁₄H₁₈N₂)_{2.5}PMo₁₀V₂O₄₀, C, 18.53; H, 2.00; N, 3.09 wt%. **[C₄Bpy]_{2.5}PMoV₂:** Found C, 22.32; H, 2.70; N, 2.90. Calc. for (C₁₈H₂₆N₂)_{2.5}PMo₁₀V₂O₄₀, C, 22.44; H, 2.72; N, 2.91 wt%. **[Bpy]_{2.5}PMoV₂:** Found C, 14.05; H, 1.16; N, 3.28. Calc. for (C₁₀H₁₀N₂)_{2.5}PMo₁₀V₂O₄₀, C, 14.11; H, 1.18; N, 3.29 wt%.

Catalysis assessment

Catalytic performances were assessed in the selective aerobic oxidation of 5-hydroxymethylfurfural (HMF) into 2,5-diformylfuran (DFF) using O₂ as oxidant. In a typical run, HMF (100.8 mg, 0.80 mmol), catalyst PMIN-2(V) (0.01 g), solvent DMSO (4 mL) were successively added into a 25 mL Schlenck tube, and then the tube was vacuumized by the water pump. The mixture was stirred at 120°C for 3 h in an oil bath with an oxygen balloon (1.0 bar). After the reaction, 2-methyl-1-pentanol was added into the mixture as the internal standard, and then the homogeneous mixture was analyzed by gas chromatography (Agilent 7890B) equipped with a flame ionization detector and a capillary column (HP-5, 30 m × 0.25 mm × 0.25 μm). The solid catalyst could be also recovered by filtration or centrifugation, and used for the next run.

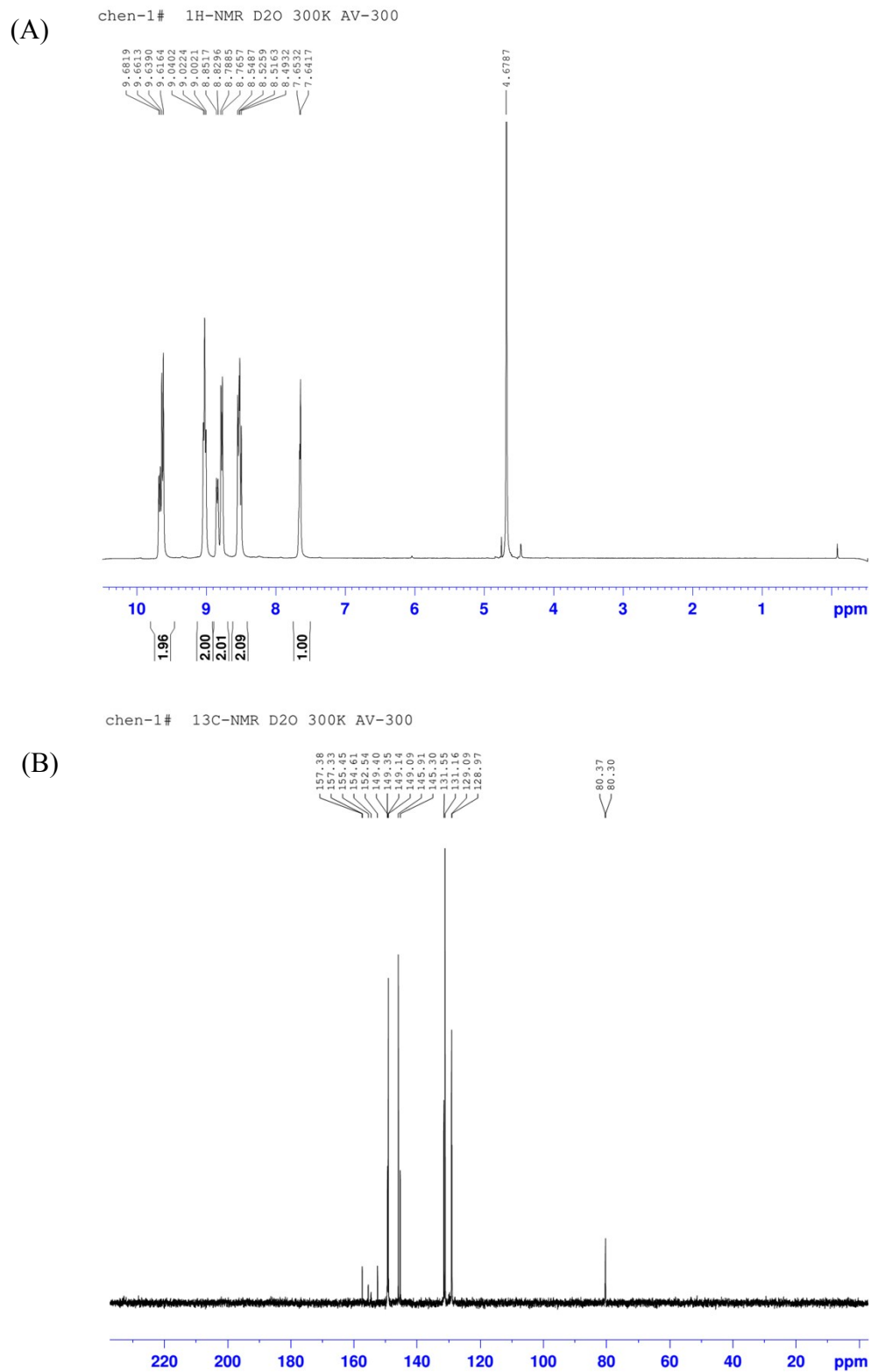


Fig. S1 (A) ^1H NMR and (B) ^{13}C NMR spectra of $[\text{PMV}]\text{Br}_2$.

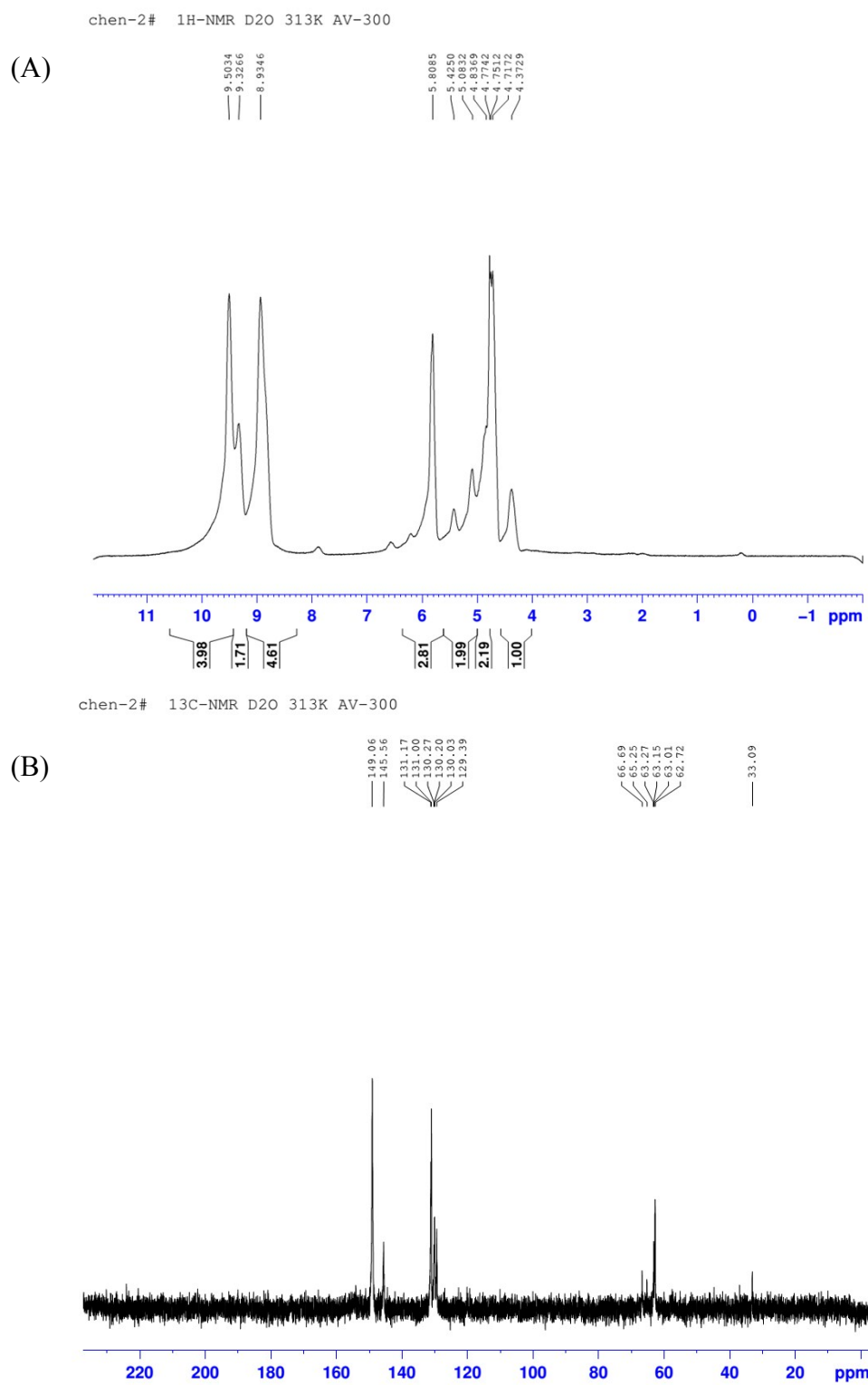


Fig. S2 (A) ^1H NMR and (B) ^{13}C NMR spectra of $[\text{PEV}]\text{Br}_2$.

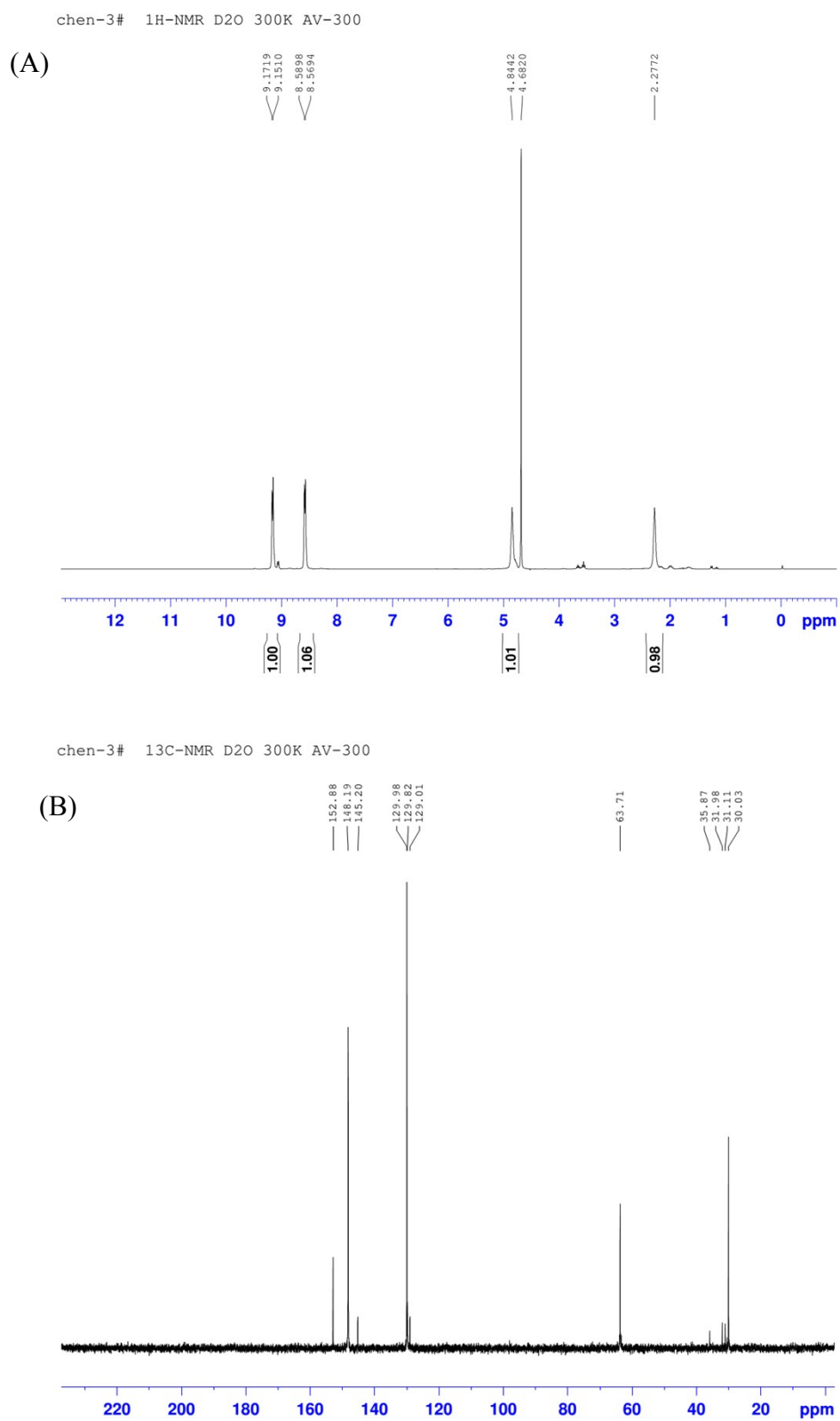


Fig. S3 (A) ^1H NMR and (B) ^{13}C NMR spectra of $[\text{PBV}]\text{Br}_2$.

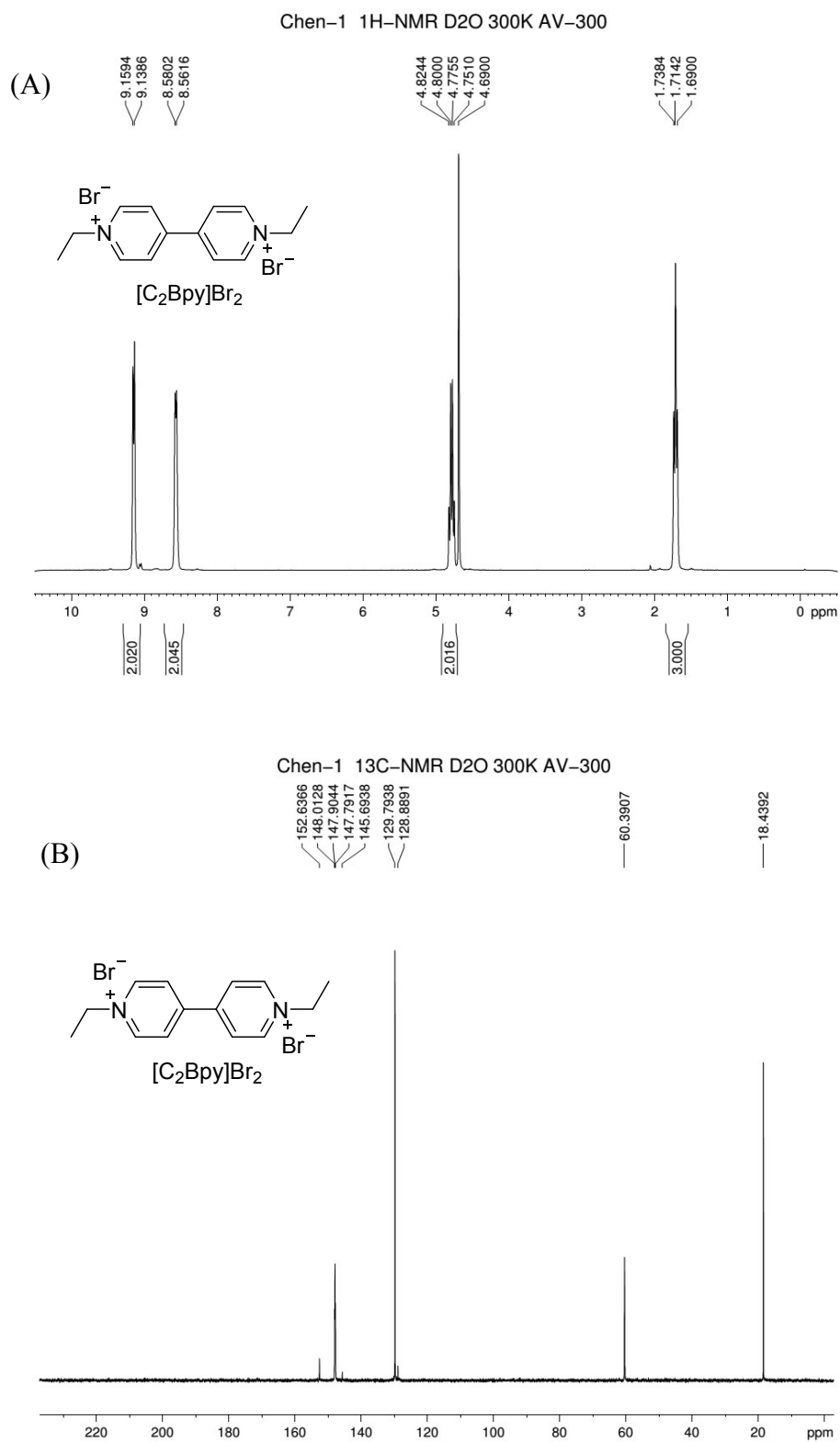


Fig. S4 (A) ¹H NMR and (B) ¹³C NMR spectra of [C₂Bpy]Br₂.

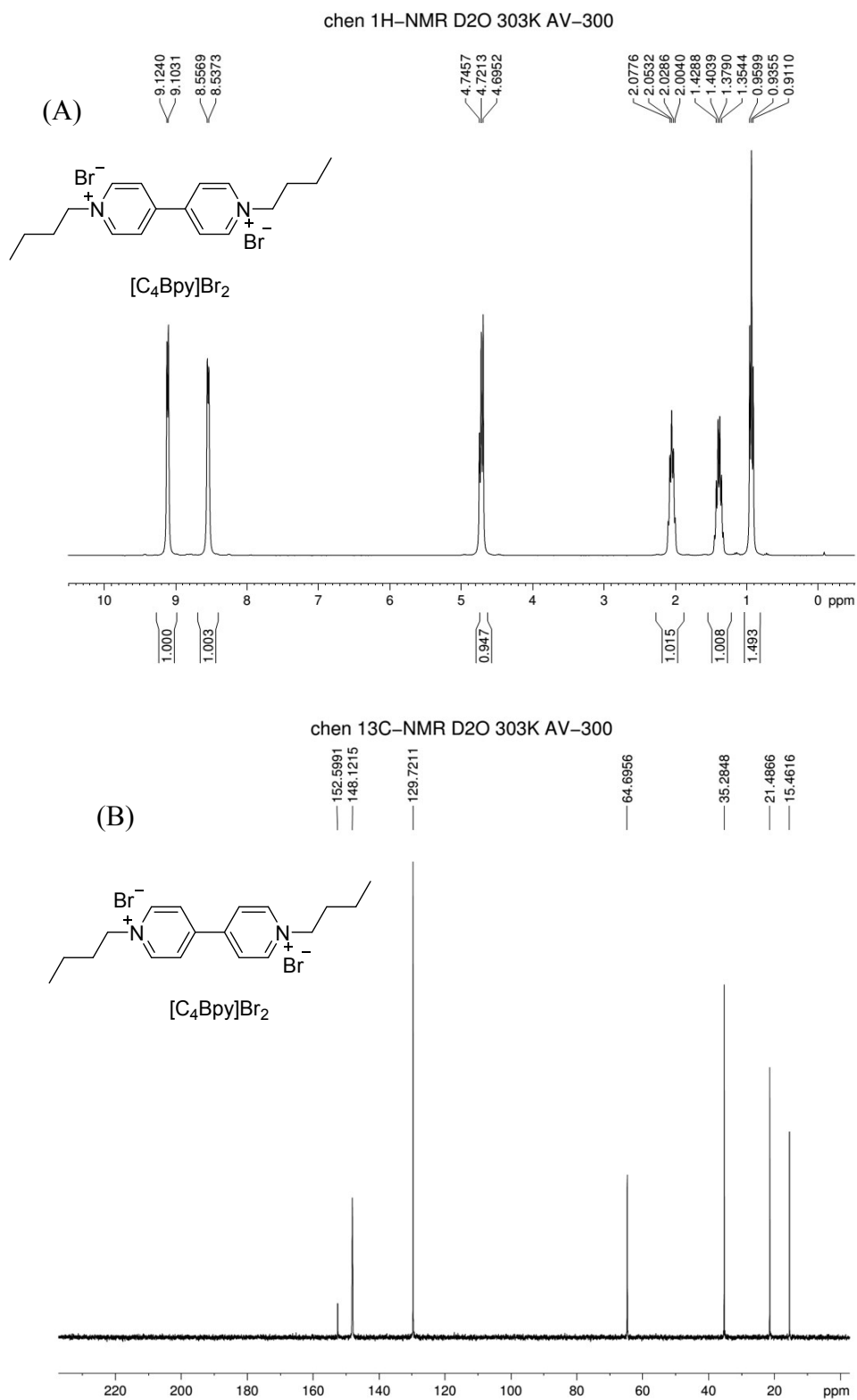


Fig. S5 (A) 1H NMR and (B) ^{13}C NMR spectra of $[C_4Bpy]Br_2$.

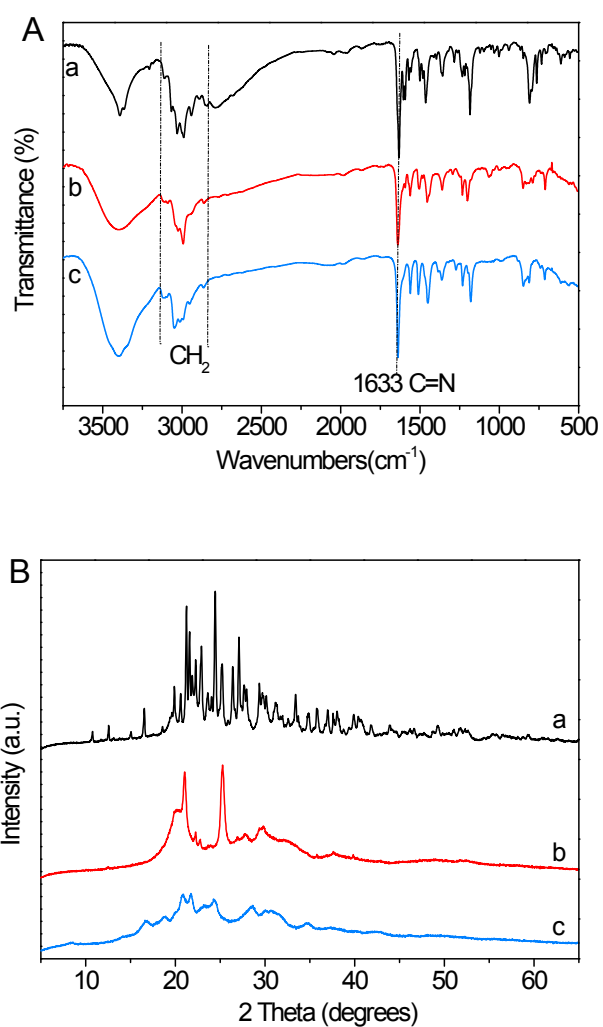


Fig. S6 (A) FT-IR spectra and (B) XRD patterns of (a) [PMV]Br₂, (b) [PEV]Br₂, and (c) [PBV]Br₂.

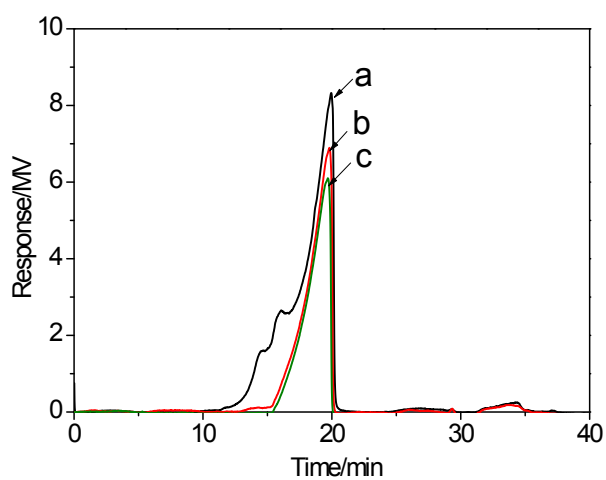


Fig. S7 Differential refractive index GPC trace of polymers (a) [PMV]Br₂ ($M_w=19948\text{Da}$), (b) [PEV]Br₂ ($M_w=19810\text{Da}$), and (c) [PBV]Br₂ ($M_w=19694\text{Da}$) in water.

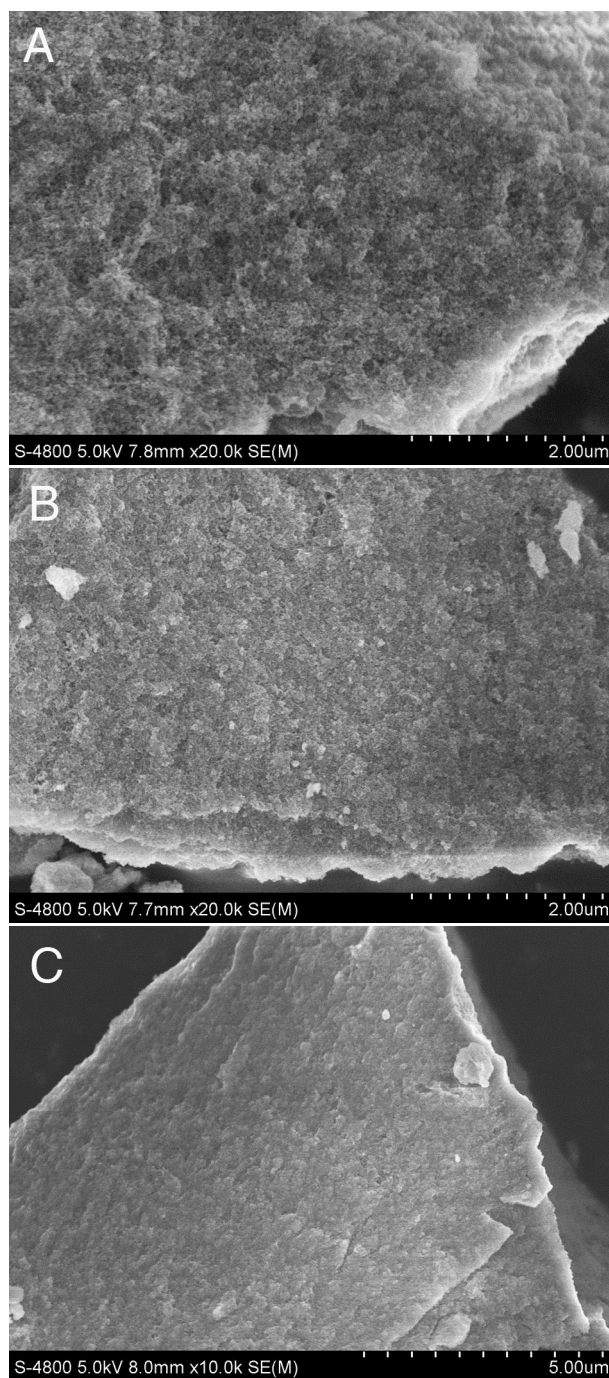


Fig. S8 Low-resolution SEM images of (A) PMIN-1(V), (B) PMIN-2(V) and (C) PMIN-3(V).

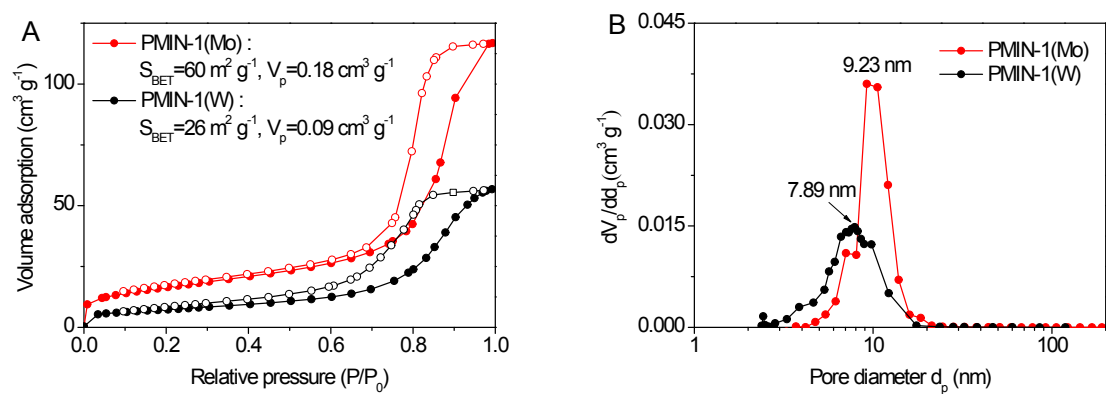


Fig. S9 (A) N₂ adsorption-desorption isotherms and (B) BJH pore size distributions of PMIN-1(Mo), PMIN-1(W).

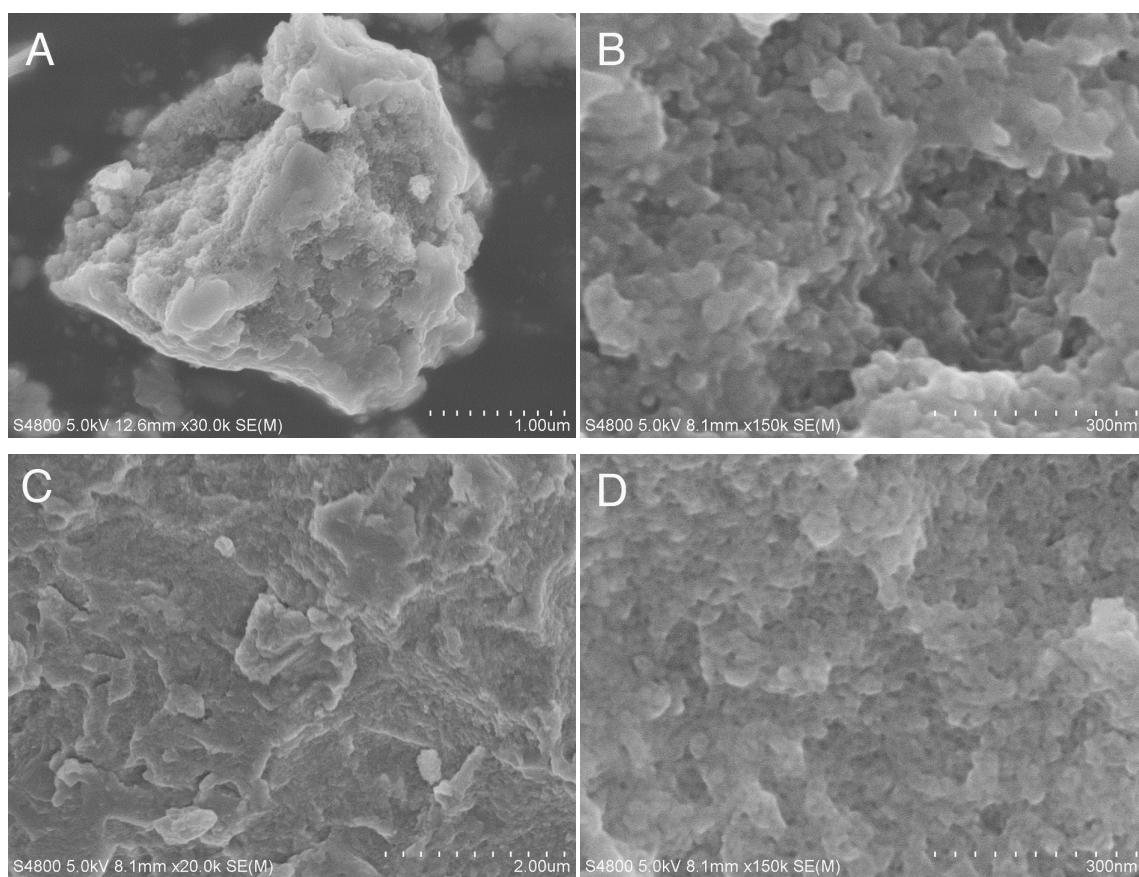


Fig. S10 SEM images of (A, B) PMIN-1(Mo) and (C,D) PMIN-1(W).

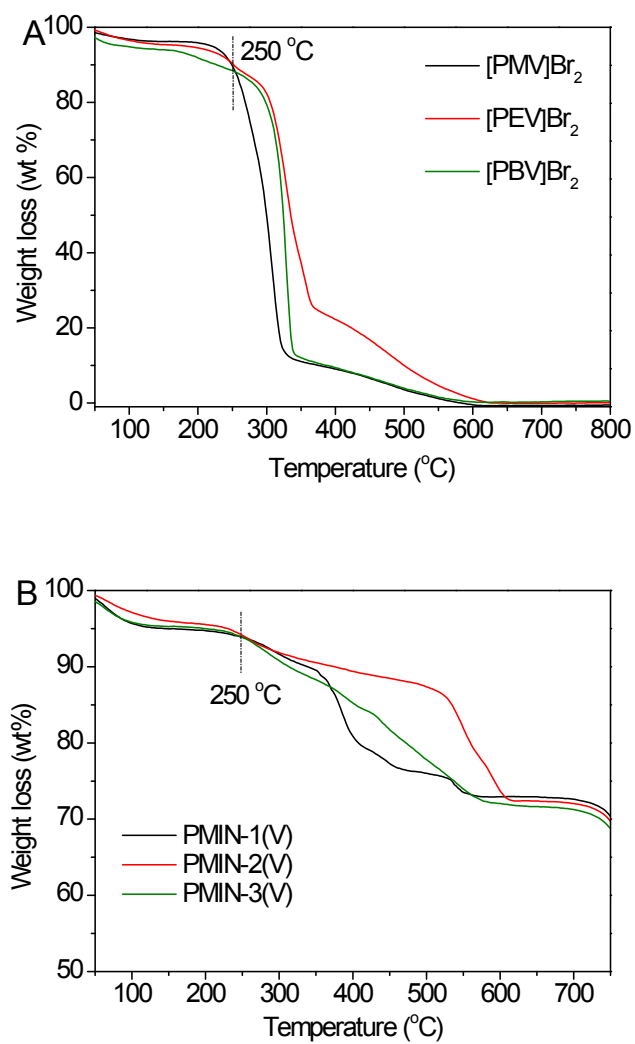


Fig. S11 Thermogravimetric analysis (TGA) of (A) three polyviologens: $[PMV]Br_2$, $[PEV]Br_2$ and $[PBV]Br_2$. (B) POM-based mesoporous ionic networks: PMIN-1(V), PMIN-2(V), and PMIN-3(V).

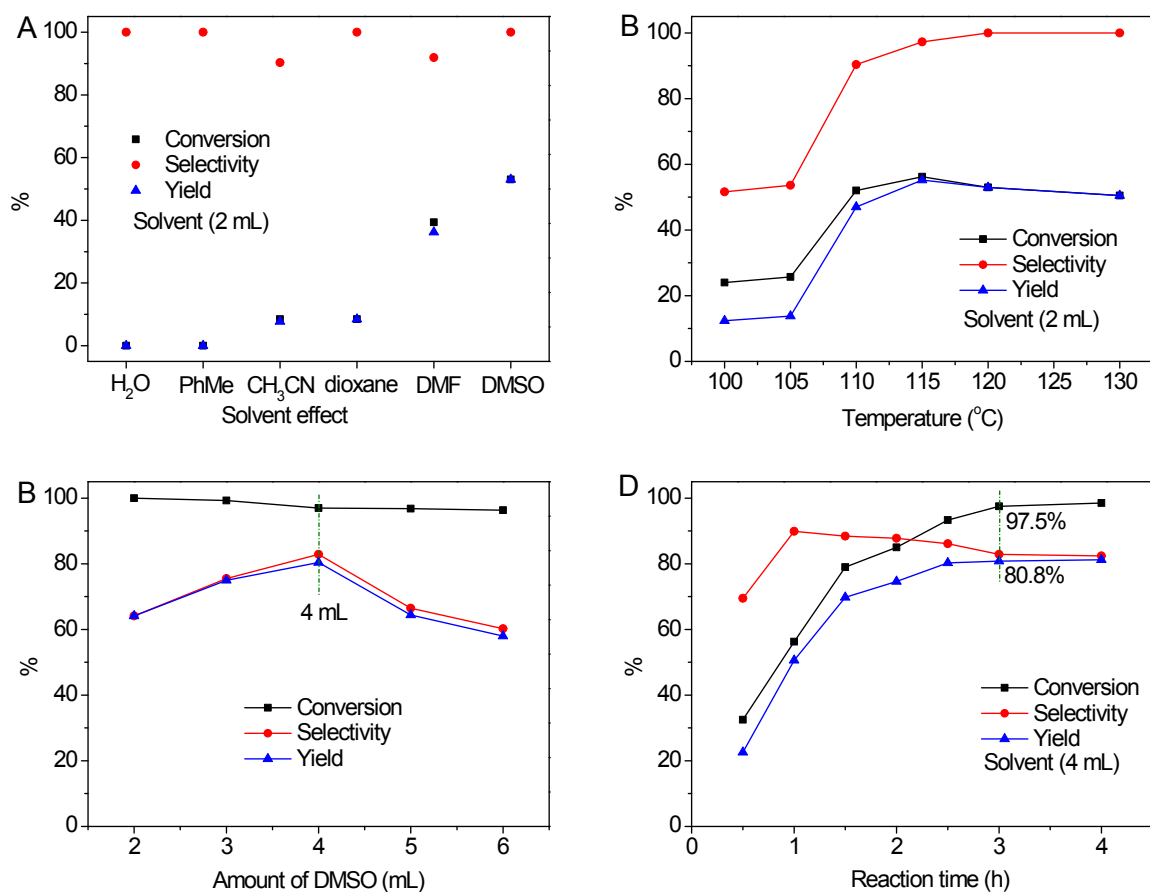


Fig. S12 Influences of reaction conditions on the catalytic activity in oxidation of HMF to DFF by H₅PMo₁₀V₂O₄₀. (A) Solvent effect; (B) Temperature; (C) Amount of DMSO; (D) Reaction time. The optimized reaction conditions: HMF (100.8 mg, 0.80 mmol), catalyst (0.01 g, H₅PMo₁₀V₂O₄₀), oxygen balloon 1.0 bar, DMSO 4 mL, 120 °C, 3h.

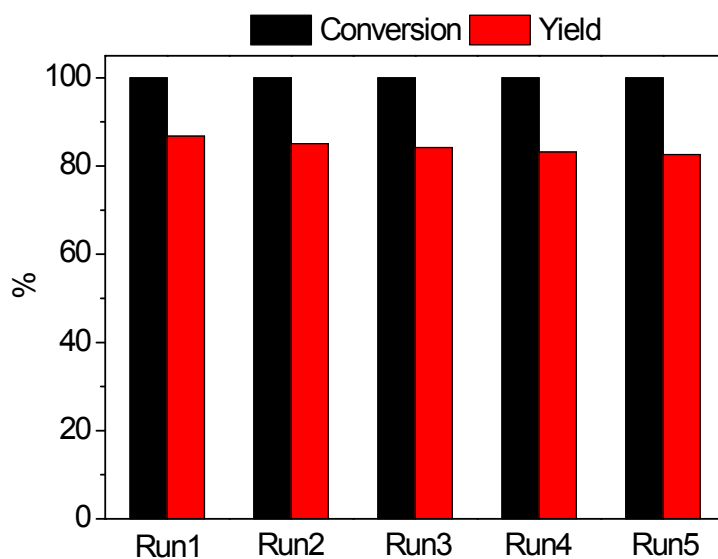


Fig. S13 Catalytic reusability of PMIN-2(V) for the aerobic oxidation of 5-hydroxymethylfurfural (HMF) into 2,5-diformylfuran (DFF). Reaction conditions: HMF (100.8 mg, 0.80 mmol), catalyst PMIN-2(V) (0.01 g), oxygen balloon (1.0 bar), DMSO (4 mL), 120 °C, 3 h.

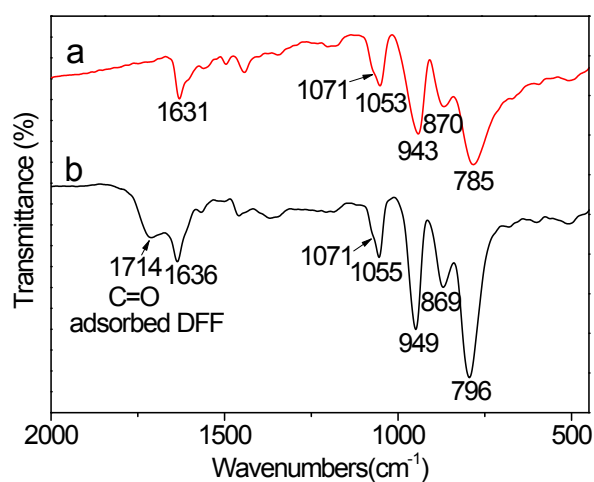


Fig. S14 FT-IR spectra of (a) fresh PMIN-2(V) (b) reused PMIN-2(V) from the fifth recycling run.

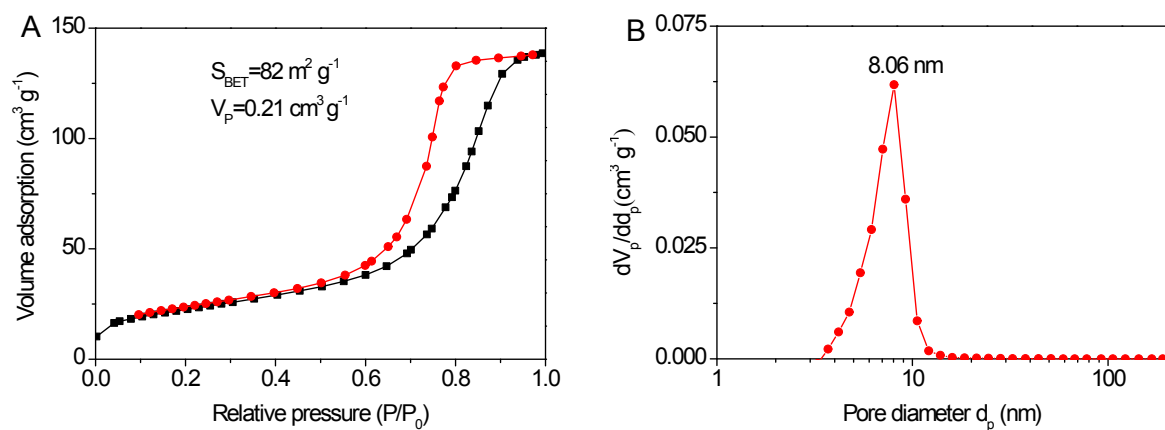


Fig. 15 (A) N₂ adsorption-desorption isotherms and (B) BJH mesopore size distribution of the reused PMIN-2(V) catalyst.

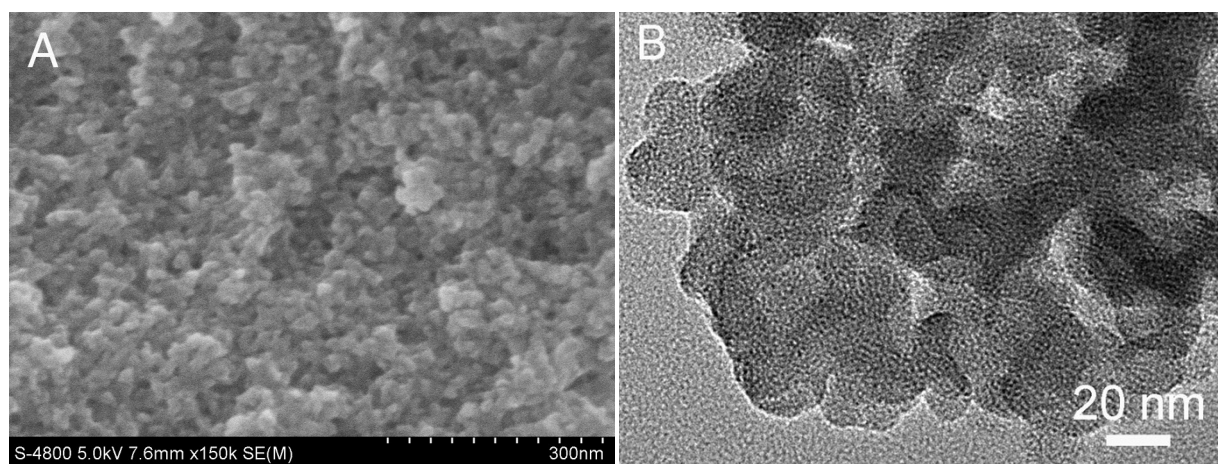


Fig. S16 (A) SEM image and (B) TEM image of the reused PMIN-2(V) catalyst from the fifth recycling run.

Table S1 Elemental analysis results (CHN) of POM-based mesoporous ionic networks (PMINs).

Samples	Molecular formula	C (wt %)	H (wt %)	N (wt %)
		Found /Calcd.	Found/Calcd.	Found/Calcd.
PMIN-1(V)	$(C_{11}H_{10}N_2)_{2.5}PMo_{10}V_2O_{40}(5H_2O)$	14.75/14.69	1.89/1.57	2.98/3.12
PMIN-2(V)	$(C_{12}H_{12}N_2)_{2.5}PMo_{10}V_2O_{40}(10H_2O)$	15.27/15.18	1.92/2.12	2.74/2.95
PMIN-3(V)	$(C_{14}H_{16}N_2)_{2.5}PMo_{10}V_2O_{40}(10H_2O)$	17.14/17.21	2.27/2.48	2.64/2.87
PMIN-1(Mo)	$(C_{11}H_{10}N_2)_{1.5}PMo_{12}O_{40}$	10.54/9.54	1.46/0.78	2.27/2.02
PMIN-1(W)	$(C_{11}H_{10}N_2)_{1.5}PW_{12}O_{40}$	6.56/6.33	1.18/0.48	1.16/1.34

The quantitative analysis of the composition of the PMINs has been measured by elemental analyses plus TG analyses, providing the accurate molecular formulas for each PMIN. Taking PMIN-1(V) as an example, the elemental analysis found (wt %) C 14.75, H 1.89, and N 2.98, well corresponding to the calculated values (wt %) of C 14.69, H 1.57, and N 3.12 based on the molecular formula of $(C_{11}H_{10}N_2)_{2.5}PMo_{10}V_2O_{40}(5H_2O)$. The above result implies that the hybrid PMIN-1(V) is composed of two point five unit of viologen cations with one $PMo_{10}V_2O_{40}^{5-}$ anion, and five water molecules. Each PMIN sample possesses specific molecular formulas and chemical compositions in accordance with the related polyviologen cations and POM anions.

Table S2 Comparisons of BET surface areas and pore volumes of various POM-based porous materials.

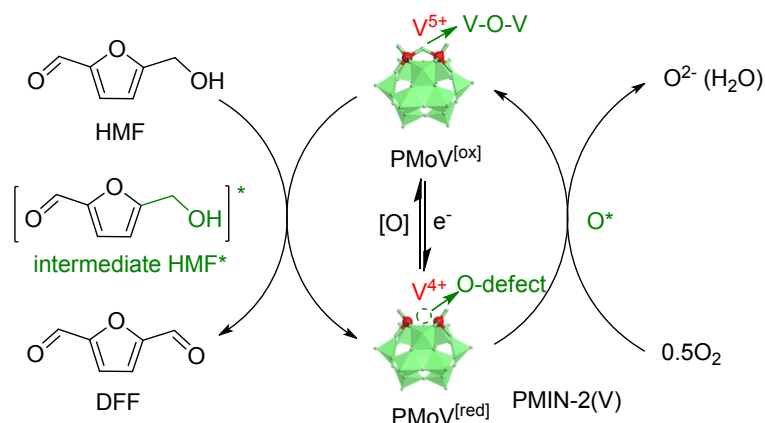
Sample	S_{BET} (m ² g ⁻¹) ^a	V_{P} (cm ³ g ⁻¹) ^b	Reference
1-POM ^c	51	Not available	S2
2-POM ^c	27	Not available	S2
[TMGDH] _{2.3} H _{0.7} PW	28.0	0.06	S3
[TMGHA] _{2.4} H _{0.6} PW	25.0	0.11	S4
[MimHA] ₃ PW	31.9	0.35	S4
[TAHpy] ₃ PW-2	26.0	0.09	S5
[D-3-CNPY] ₂ HPMoV ₂	41.4	0.46	S6
[D-3-NH ₂ Py] ₂ HPMoV ₂	46.6	0.36	S6
[Co(tacn) ₂][α -PW ₁₂ O ₄₀]·2H ₂ O	41	Not available	S7
[Co(tacn) ₂] ₂ [α -SiV ₂ W ₁₀ O ₄₀]·6H ₂ O	25	Not available	S7
[Ni(tacn) ₂] ₂ [α -SiW ₁₂ O ₄₀]·4H ₂ O	31	Not available	S7
[Ni(tacn) ₂] ₂ [α -SiV ₂ W ₁₀ O ₃₈ (OH) ₂]·3H ₂ O	18	Not available	S7
[Zn(dipp)(L)] ₄ [PMo ₁₁ VO ₄₀]	49.6	Not available	S8
PIILP-PW ₄ ^d	42	0.15	S9
P-[DVB-VBIM] ₅ PMoV ₂	104	0.17	S10
PW@HMP(1)	54	0.21	S11
PW@HMP(3)	65	0.23	S11
POSS-BM ₁₁ -PW	42.0	0.16	S12
Cesium salt of [PW ₁₂ O ₄₀] ³⁻	156	0.052	S13
(NH ₄) ₃ PW ₁₂ O ₄₀	116	0.043	S14
PMIN-1(V)	72	0.24	This work
PMIN-2(V)	120	0.28	This work
PMIN-3(V)	115	0.17	This work

^a BET surface area. ^b Pore volume. ^c POM: [ZnWZn₂(H₂O)₂(ZnW₉O₃₄)₂]¹²⁻; 1: tris[2-(trimethylammonium)-ethyl]-1,3,5-benzenetricarboxylate; 2: 1,3,5-tris[4-(N,N,N-trimethylammoniummethylcarboxyl)-phenyl]benzene trications. ^d PIILP: polymer-immobilised ionic liquid phase. ^e POSS: polyhedral oligomeric silsesquioxane.

Table S3 The catalytic performances in the aerobic oxidation of HMF to DFF under atmospheric pressure over various heterogeneous catalysts.

Catalyst	Reaction condition		HMF Conv. (%)	DFF Sel. (%)	TON ^a	Reference
	T, t & P	HMF/Catalyst (mg/mg)				
Ru/HT	393 K, 12 h, O ₂ (1 bar)	126/100	94.8	97	22	S15
SBA-NH ₂ -Cu ²⁺ and SBA-NH ₂ - VO ²⁺	110 °C, 6 h O ₂ (20 mL/min)	100/130	98.8	63.5	33	S16
polyaniline-VO (acac) ₂	110 °C, 12 h O ₂ (30mL/min)	100/80	99.2	86.8	38	S17
Ru-6C-1N	105 °C, 6 h O ₂ (1 bar)	126/45	94	89	158	S18
Fe ₃ O ₄ @SiO ₂ - NH ₂ -Ru(III)	110 °C, 4 h O ₂ (20 mL/min)	100/150	99.7	87.1	154	S19
Fe ₂ O ₃ @HAP-Ru	90 °C, 12 h O ₂ (20 mL/min)	100/150	100	89.1	26	S20
V-g-C ₃ N ₄	130 °C, 12 h O ₂ (1 bar)	126/100	>99	82	5.8	S21
Fe ₃ O ₄ /Mn ₃ O ₄	120 °C, 12 h O ₂ (20 mL/min)	126/160	100	82.1	0.397	S22
V ₂ O ₅ /H-beta	100 °C, 5.5 h O ₂ flow (1 bar)	100/100	84	>99	34	S23
K-OMS-2	110 °C, 6 h O ₂ (10 mL/min)	126/100	100	99	0.792	S24
PMIN-2(V)	120 °C, 3 h O₂ balloon 1.0 bar	100.8/10	100	86.8	121	This work

^a Turnover number (TON): mole of product DFF per mol of catalyst.



Scheme S1 Proposed possible catalytic mechanism for the aerobic oxidation of HMF to DFF with O₂ over the catalyst PMIN-2(V).

According to previous studies, the V species in V-POMs are well accepted as the catalytically active sites for versatile organic oxidations.^{S25,S26} In the aerobic oxidation of HMF to DFF, the catalytic activity center is V-O-V structure in PMoV anion of PMIN-2(V) catalyst, while polyviologen actions affect the charge state of PMoV anions. PMoV anion takes a catalytic effect through follow Mars-van Krevelen-type mechanism, where the lattice oxygen of PMoV selectively oxygenates organic substrates via a valence variation between V⁵⁺ and V⁴⁺.^{S27,S28}

Based on the previous reports, we provide a proposed possible catalytic mechanism for the aerobic oxidation of HMF to DFF with O₂ over the catalyst PMIN-2(V). As depicted in Scheme R1, the whole aerobic oxidation process follows Mars-van Krevelen mechanism, i.e. an electron-oxygen transfer (ET-OT) mechanism.^{S29-S31} First, the reaction substrates HMF and O₂ adsorb dissociatively on the PMIN-2(V) catalyst surface to form the adsorbed alcoholate intermediate HMF* and the atomic oxygen (O*) species, respectively.^{S32} Immediately, the original oxidation state of PMoV with V⁵⁺ species (denoted as PMoV^[ox]), attacks the intermediate HMF* to produce the adsorbed DFF and water, wherein the lattice oxygen atom of a V-O-V structure in PMoV^[ox] moves into the intermediate with the PMoV^[ox], forming reduction of V⁵⁺ to V⁴⁺-containing PMoV^[red].^{S26,S29} Finally, the catalytic cycle is closed with the timely expelling of product DFF and water from the catalyst surfaces and the resuming of PMoV^[ox] after O₂ re-oxidizes V⁴⁺ of PMoV^[red] into V⁵⁺ species. The formation of the reduced V⁴⁺ centers was detected by XPS and ESR as mentioned before. It is worthy to note that the O-defect reduced V⁴⁺-containing PMoV^[red] in PMIN-2(V) can promote the indirect dissociation of O₂ molecule by the oxidation of HMF to DFF,^{S33} thus providing the enhanced heterogeneous catalytic activity compared with the homogeneous counterpart. According to a very recently report by the theoretical study, the oxidation of each HMF catalyzed by POMs involves two main reaction steps: the cleavage of the O-H bond in the hydroxyl group and that of the C-H bond in

the methylene group of HMF.^{S33}

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