

Electronic Supplementary Information

Heteropolyanion-based polymeric hybrids: Highly efficient and recyclable catalysts for oxidation of alcohols with H₂O₂

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General remarks

All chemicals were of analytical grade and used as received. FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs). ¹H-NMR spectra were measured with a Bruker DPX 300 spectrometer at ambient temperature in D₂O using TMS as internal reference. TG analysis was carried out with a STA409 instrument in dry air at a heating rate of 10 °C/min. Elemental analyses (C, H, N) were performed on a CHN elemental analyzer (FlashEA 1112). Solid UV-vis spectra were measured with a PE Lambda 950 spectrometer, and BaSO₄ was used as an internal standard. The amount of leached tungsten species in the filtrate was measured using a Jarrell-Ash 1100 ICP-AES spectrometer.

Preparation of [AVIM]Br·HBr and [BVIM]Br

[3-aminoethyl-1-vinylimidazolium]Br·HBr ([AVIM]Br·HBr): The amino-containing ionic liquid (IL) monomer [AMIM]Br·HBr was prepared according to the literature (E. D. Bates, R. D. Mayton, I. Ntai, J. H. Davis, Jr, J. Am. Chem. Soc. 2002, 124, 926-927). N-vinylimidazole (9.42 g, 0.10 mol) and 2-bromoethylamine hydrobromide (20.49 g, 0.10 mol) were dissolved in acetonitrile (50 mL) at 80°C for 12 h under nitrogen atmosphere with stirring. On completion, the liquid was poured out and the solid was washed with anhydrous ethanol three times to remove the unreacted starting materials. After drying under vacuum, 3-aminoethyl-1-vinylimidazolium]Br·HBr was obtained. ¹H NMR (300 MHz, D₂O,

TMS) (**Fig S1**) δ (ppm) = 3.47 (m, 2H, -CH₂), 4.58 (m, 2H, -CH₂), 5.40 (d, 1H, -CH), 5.81 (d, 1H, -CH), 7.13 (m, 1H, -CH), 7.66 (s, 1H, -CH), 7.81 (s, 1H, -CH), 9.18 (s, 1H, -CH).

[3-butyl-1-vinylimidazolium]Br ([BVIM]Br): [BVIM]Br was prepared according to the previous report [T. Payagala, J. Huang, Z. S. Breitbach, P. S. Sharma, D. W. Armstrong, Chem. Mater. 2007, 19: 5848-5850]. N-vinylimidazole (9.42 g, 0.10 mol) and 1-bromobutane (0.10 mol) were dissolved in ethanol (50 mL) at 70°C for 24 h under nitrogen atmosphere. On completion, the yellow liquid of [BVIM]Br was obtained after the removing of solvent and washing with ether for three times. ¹H NMR (300 MHz, D₂O, TMS) (**Fig S2**) δ (ppm) = 0.89 (t, 2H, -CH₃), 1.29 (m, 2H, -CH₂), 1.82 (m, 2H, -CH₂), 4.24 (t, 2H, -CH₂), 5.41 (d, 1H, -CH), 6.01 (d, 1H, -CH), 7.35 (m, 1H, -CH), 8.00 (s, 1H, -CH), 8.28 (s, 1H, -CH), 9.76 (s, 1H, -CH).

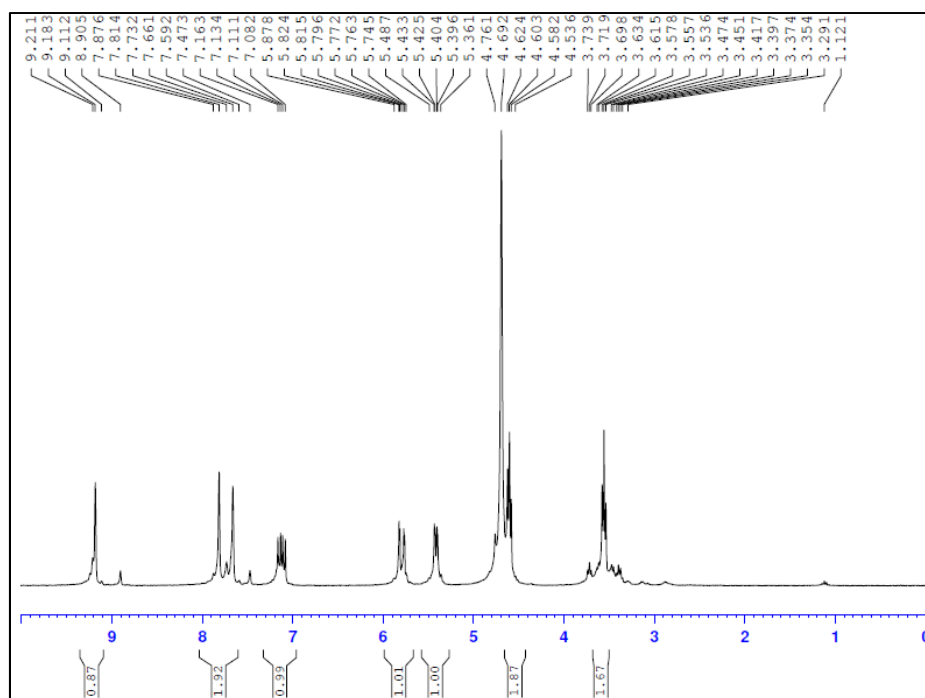


Fig. S1A ¹H NMR of [AVIM]Br·HBr.

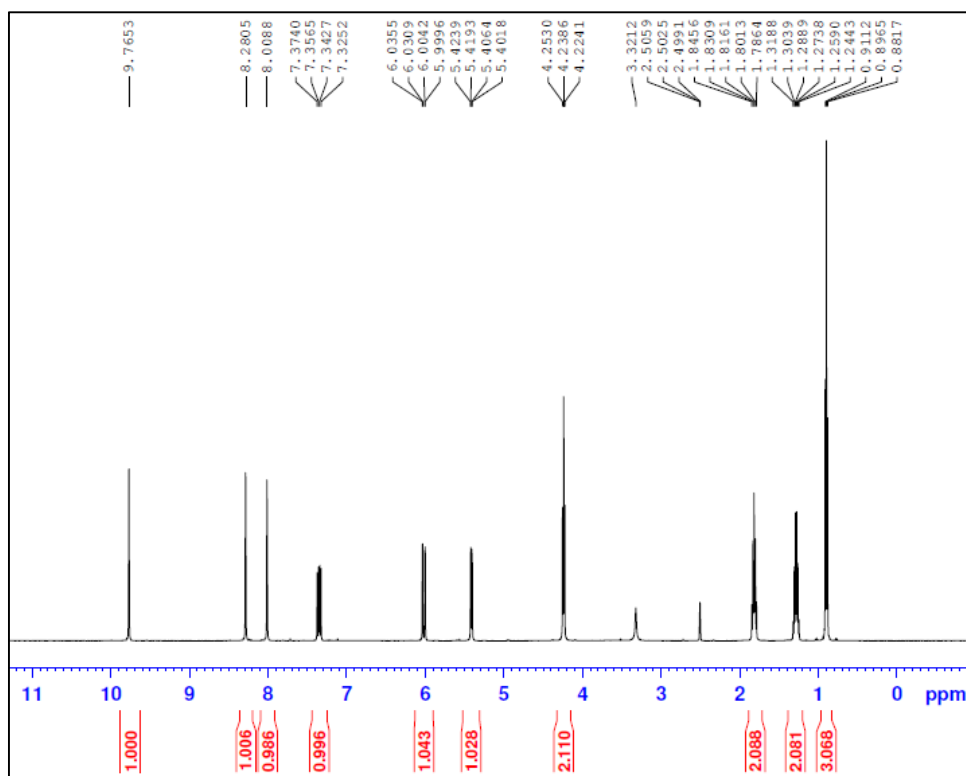


Fig. S1B ^1H NMR of [BVIM]Br.

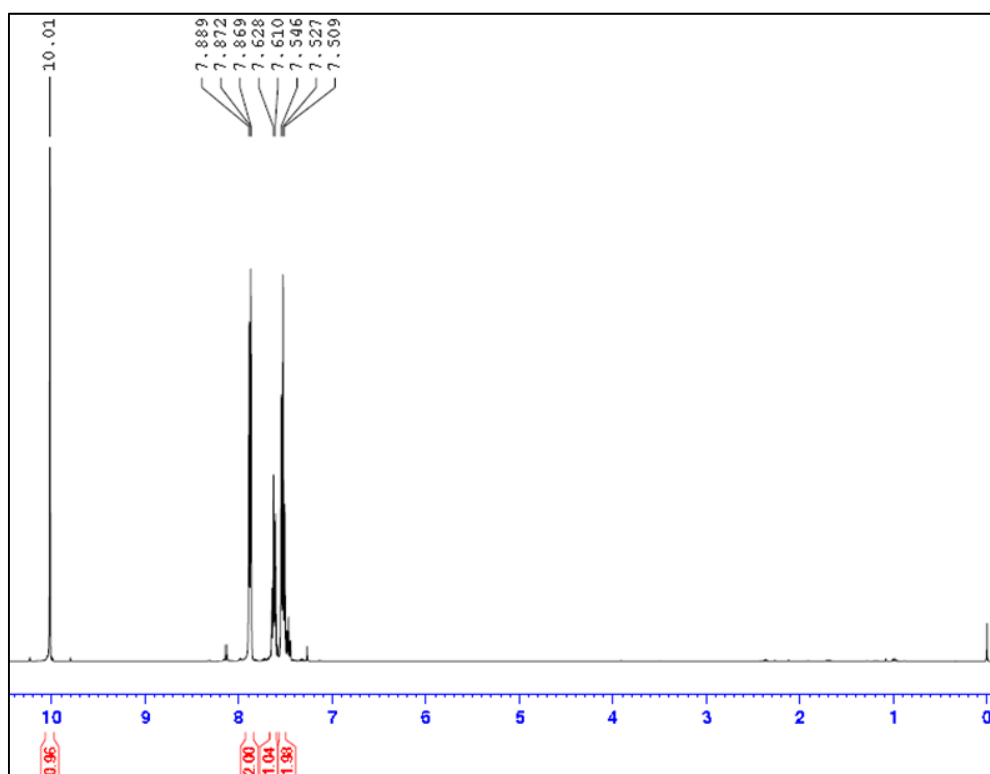


Fig. S1C ^1H NMR of isolated product benzaldehyde.

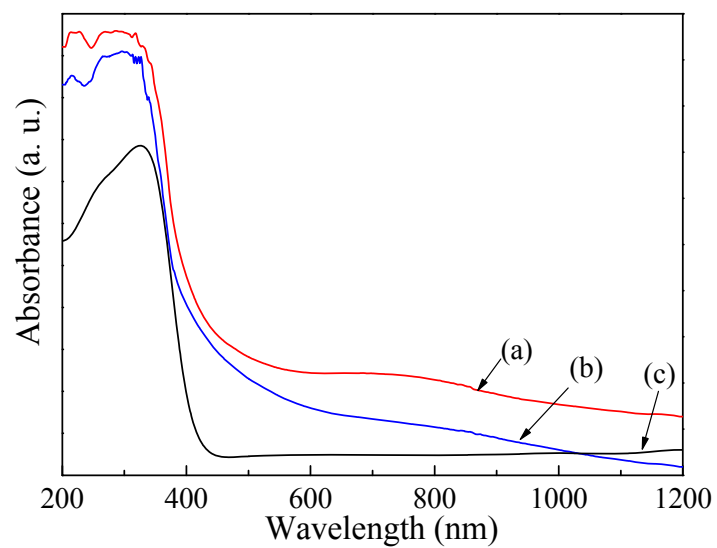


Fig. S2 UV-vis spectra of (a) NDMAM-AVIM-PW, (b) NDMAM-BVIM-PW, and (c) $\text{H}_3\text{PW}_{12}\text{O}_{40}$

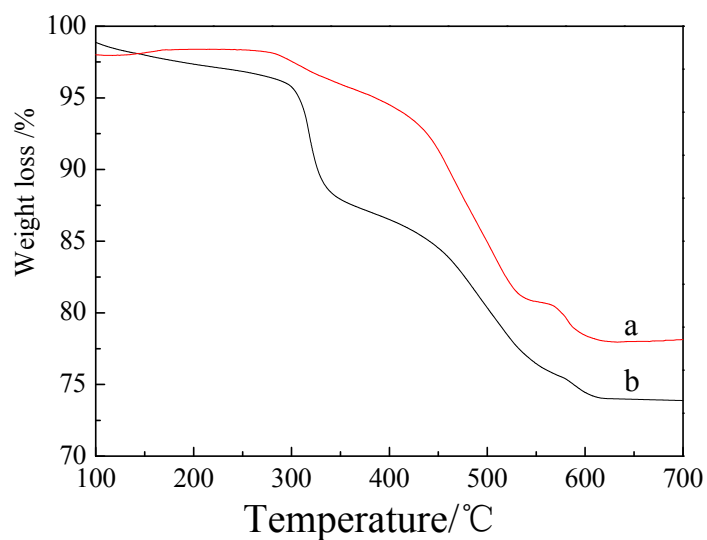


Fig. S3A TG pattern of (a) NVPL-BVIM-PW and (b) NVPL-AVIM-PW.

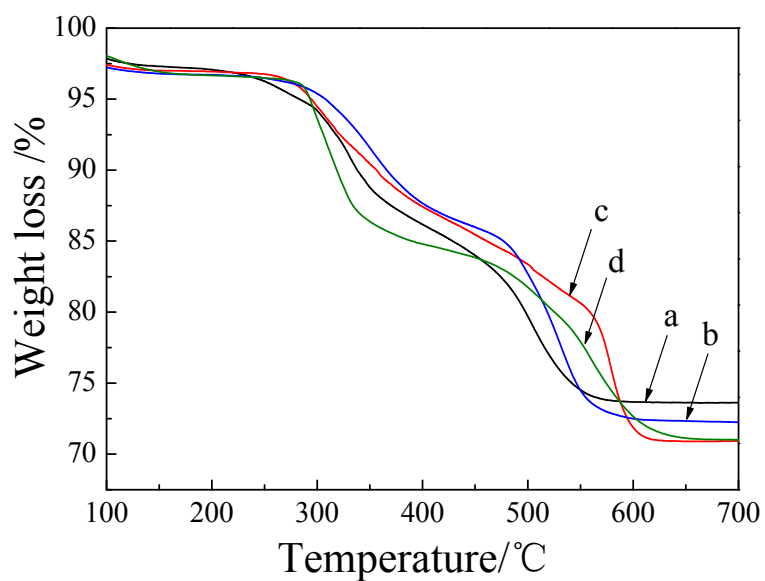


Fig. S3B TG pattern of (a) NDMAM-AVIM-PW, (b) recovered NDMAM-AVIM-PW, (c) NDMAM-BVIM-PW, (d) recovered NDMAM-BVIM-PW.

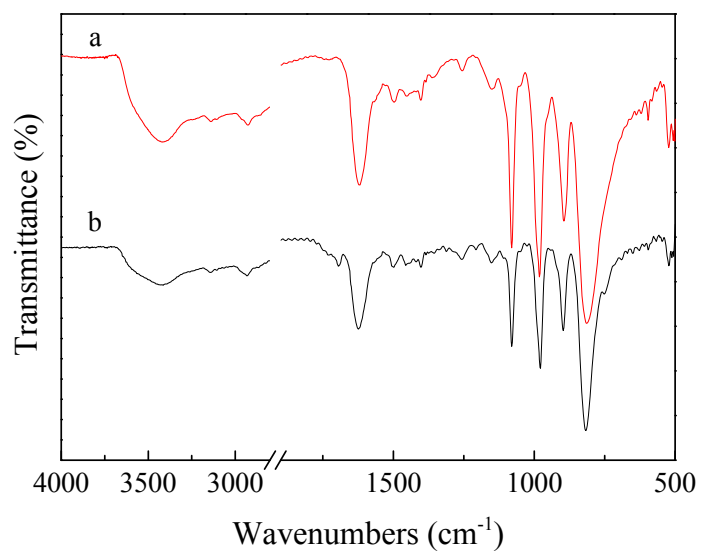


Fig. S4A FT-IR spectra of (a) fresh NDMAM-AVIM-PW and (b) recycled NDMAM-AVIM-PW.

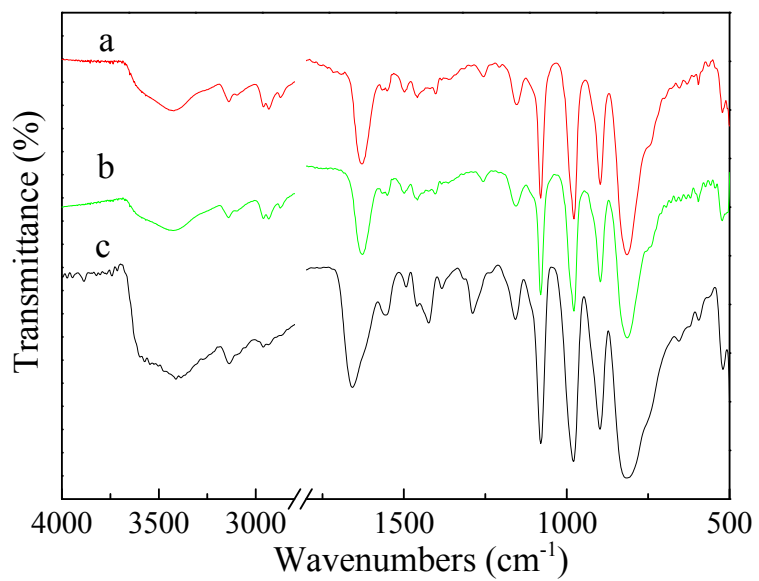


Fig. S4B FT-IR spectra of (a) fresh NDMAM-BVIM-PW, (b) recycled NDMAM-BVIM-PW, and (c) NVPL-BVIM-PW.