

Supporting Information

Efficient and recyclable multi-cationic polyoxometalate-based hybrid catalyst for heterogeneous cyclohexane oxidation with H₂O₂

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Preparation of ionic liquid precursors

N-butyronitrile pyridine chloride ([PyCN]Cl): The nitrile-tethered pyridinium ionic liquid (IL) precursor [PyCN]Cl was prepared according to the literature ¹. A mixture of pyridine (7.90 g, 0.100 mol) and Cl(CH₂)₃CN (12.43 g, 0.120 mol) was stirred at 80 °C for 24 h under nitrogen atmosphere. Two phases were formed at the end of the reaction. After cooling to room temperature, the upper phase was decanted. Successively, acetonitrile (100 mL) and activated carbon (3.0 g) were added to the lower phase with stirring for 30 min. The solution was then reheated to 80 °C and filtered. The resulting product was crystallized upon cooling to 0 °C, washed with diethyl ether (3 × 30 mL), and dried under vacuum at 60 °C for 24 h to afford [PyCN]Cl. The analogue IL precursor, 1-butyronitrile-3-methylimidazolium chloride ([MimCN]Cl) was prepared accordingly.

1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium) dibromide ([Dmim]Br₂): The dicationic IL precursor [Dmim]Br₂ was prepared according to the literature ². Methylimidazole (0.20 mol) and 1,4 dibromobutane (0.10 mol) were dissolved in isopropanol (50 mL) at 80 °C for 48 h under nitrogen atmosphere with stirring. On completion, the solvent was removed by distillation, and the residue was washed with THF for three times to afford the [Dmim]Br₂ as a white solid.

N,N'-bis(carboxymethyl) 4,4'-bipyridinium dibromide ([DPyCOOH]Br₂): 4,4'-dipyridinium(10 mmol) and bromoacetic acid (30 mmol) were dissolved in acetonitrile (50 mL), and the mixture was heated to 80 °C for 24 h under nitrogen atmosphere with stirring. On completion, the white solid of [DPyCOOH]Br₂ was obtained after the removing of solvent and washing with acetonitrile for three times. Two analogue IL precursors, N,N'-bis(3-cyanopropyl) 4,4'-bipyridinium dichloride ([DPyCN]Cl₂) and N,N'-dibutyl 4,4'-bipyridinium dibromide ([DPyC₄]Br₂), were prepared similarly.

N-aminoethyl-pyridinium bromide hydrobromide [PyAM]Br·HBr was prepared according to the steps similar to [DPyAM]Br₂·2HBr, and 1-butyl-3-methylimidazolium bromide ([MimC₄]Br) was used as received.

Preparation of control catalysts

The obtained IL precursors were added to an aqueous solution of H₅PMo₁₀V₂O₄₀ with the stoichiometric molar ratios of 5 (monocationic ionic liquid precursors) or 2.5 (dicationic ionic liquid precursors), and then the mixture was stirred at room temperature for 24 h. The formed precipitate was filtered and washed with water for three times, followed by drying in a vacuum to give the catalysts.

¹H-NMR DMSO 303K AV-300

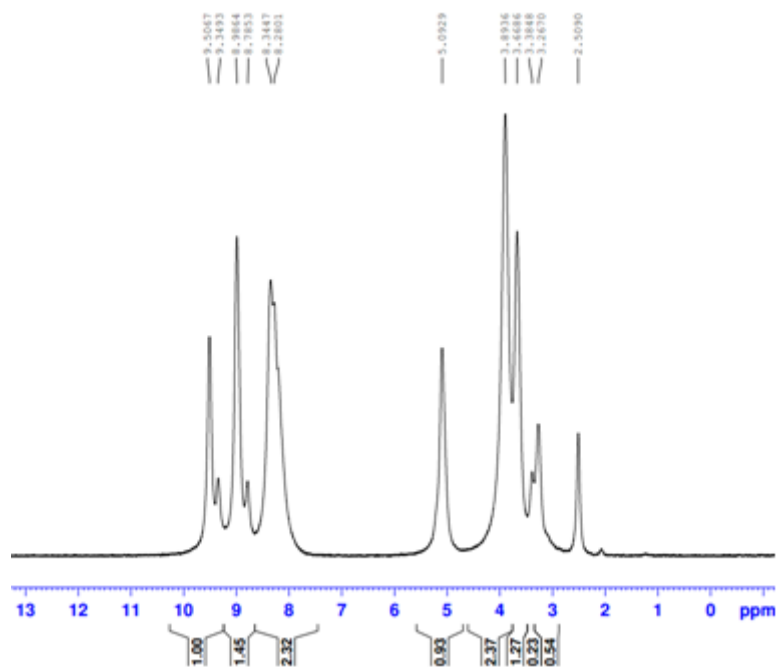


Fig. S1 ¹H NMR spectrum of [DPyAM]Br₂·2HBr.

¹H-NMR DMSO 303K AV-300

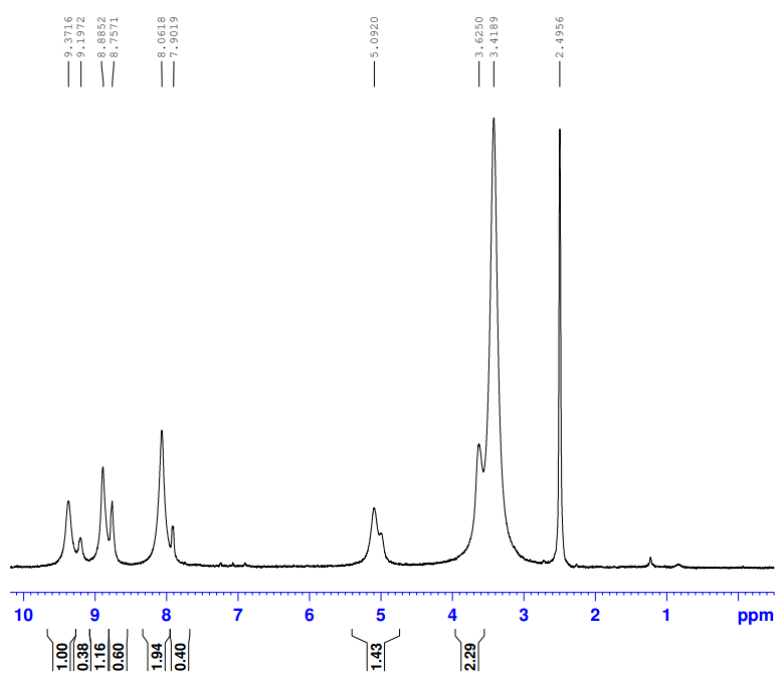
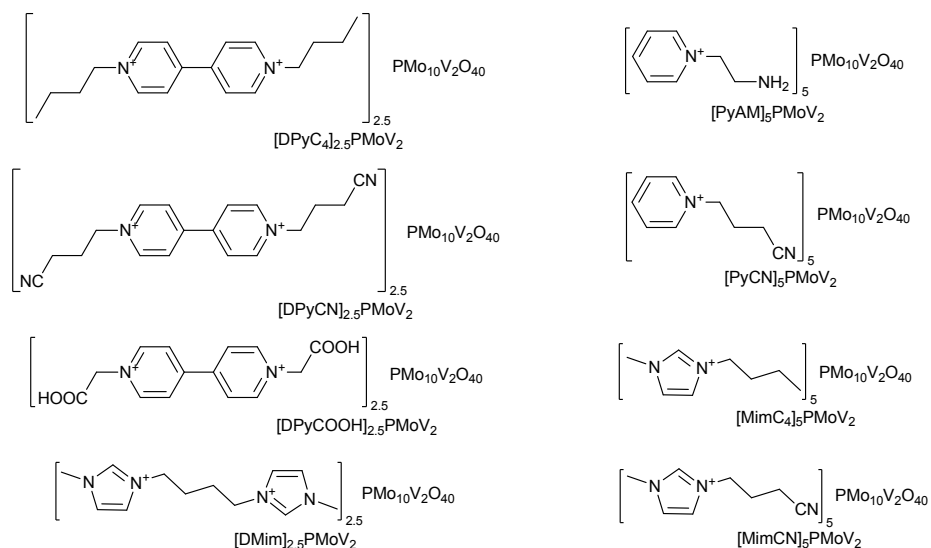


Fig. S2. ¹H NMR spectrum of the hybrid [DPyAM(H₂)]_{1.25}PMoV₂.



Scheme S1 The chemical structures of the control catalysts.

References

- 1 P. Zhao, J. Wang, G. Chen, Y. Zhou and J. Huang, *Catal. Sci. Technol.*, 2013, **3**, 1394-1404.
- 2 Y. Leng, J. Wang, D. Zhu, L. Shen, P. Zhao and M. Zhang, *Chem. Eng. J.*, 2011, **173**, 620-626.