

Supporting Information

Preparation of Polyoxometalate Precursors

H₆PV₃Mo₉O₄₀ : K₂HPO₄, 7.1 g, was dissolved in 50 ml of water and mixed with 36.6 g of sodium metavanadate that had been dissolved by heating in 200 ml of water. After 5 ml of concentrated sulfuric acid was added to the cooled mixture, it attained a cherry red color. This solution was mixed with 54.5 g of Na₂MoO₄·2H₂O dissolved in 150 ml of water, and then, while it was being vigorously stirred, 85 ml of concentrated sulfuric acid was slowly added. The hot solution was allowed to cool to room temperature. The free acid was extracted with 400 ml of ethyl ether. The etherate was freed of ether when a stream of air was passed through the solution. The red solid remaining was dissolved in 40 ml of water and concentrated to crystal formation in a vacuum desiccator over concentrated sulfuric acid. The red crystals were filtered and washed with water. The yield was 7.2 g.

Na₆PV₃Mo₉O₄₀ : 20.0 g of H₆PV₃Mo₉O₄₀ was dissolved in 50 ml of water, and the resultant solution was slowly passed through an ion-exchange column containing 20-50 mesh Dower 50-X8 ion-exchange resin in the sodium form. The resin bed was 1.25 in. in diameter and 20 in. in height, The orange effluent containing the desired sodium salt was then placed in a vacuum desiccator over concentrated sulfuric acid for removal of water. Evaporation was continued to dryness since this sodium salt is very soluble in water.

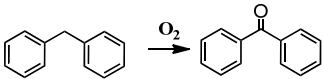
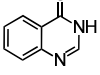
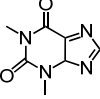
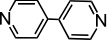
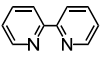
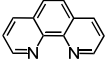
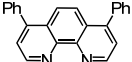
Table S1 Comparison of the reported results.

Oxidant	Catalyst	Reaction	Reaction conditions	Ref.
O ₂	Ag ₅ [PV ₂ Mo ₁₀ O ₄₀]		RT, 2,2,2-Trifluoroethanol 1.0 atm air, 8.4 h.	[1]
O ₂	Ag ₅ [PV ₂ Mo ₁₀ O ₄₀]		140 °C, 60 bar air, CH ₃ COOH, 3h.	[2]
PMSO	Q ₃ [PMo ₁₂ O ₄₀]	 	170 °C, 1ml DCB, 15 h.	[3]
N ₂ O	Q ₅ [PV ₂ Mo ₁₀ O ₄₀]	 	150 °C, 1ml PhCN, 1.0 atm N ₂ O, 8 h.	[4]
NO ₃ ⁻	H ₅ PV ₂ Mo ₁₀ O ₄₀	 	80 °C, 1ml AcOH, Ar, 14 h.	[5]

Reference

- [1] J. T. Rhule, W. A. Neiwert, K. I. Hardcastle, B. T. Do, C. L. Hill *J. Am. Chem. Soc.* **2001**, 123, 12101-12102.
- [2] F. Liu, C. Marchal-Roch, P. Bouchard, J. Marrot, J. P. Simonato, G. Herve, F. Secheresse *Inorg. Chem.* **2004**, 43, 2240-2242.
- [3] A. M. Khenkon, R. Neumann *J. Am. Chem. Soc.* **2002**, 124, 4198-4199.
- [4] R. Ben-Daniel, R. Neumann *Angew. Chem. Int. Ed.* **2003**, 42, 92-95.
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Table S2 Catalytic activity of self-assembled nanostructures from different N-donor ligands for oxidation of diphenylmethane.

		
N-donor Ligands		Conversion (%)
Monodentate N-donor ligands		98.2
		90.4
		85.5
		78.6
		73.8
		68.7
Linear didentate bridging ligands		>99.9
		92.3
		77.2
Nonplanar didentate chelating ligands		97.8
Planar didentate chelating ligands		>99.9
		95.4

Reaction conditions: 2.0 mmol diphenylmethane, 1.0 ml PhCN, 100°C, oxygen balloon, 50 mg catalyst, reaction time 10h.

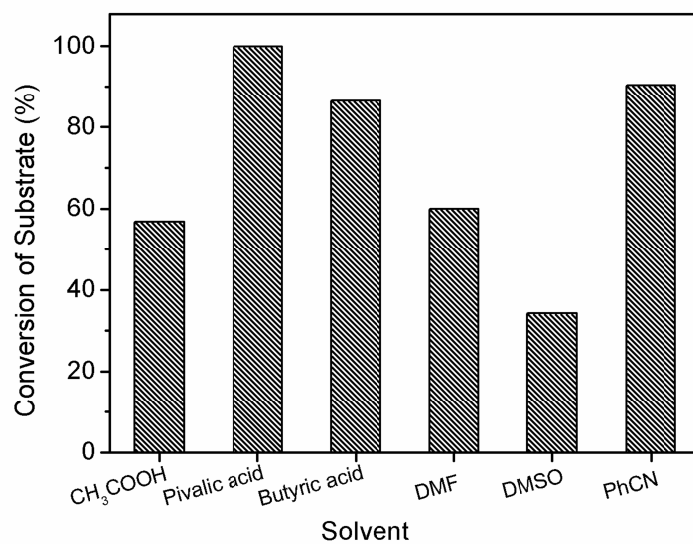


Fig. S1 Screening experimental results of reaction media. Reaction conditions: 2.0 mmol diphenylmethane, 1.0 ml solvent, 100°C, oxygen balloon, 50 mg catalyst (1b), reaction time 10h.