

## Heterogeneous Epoxidation of Alkenes with H<sub>2</sub>O<sub>2</sub> Catalyzed by a Recyclable Organic–Inorganic Polyoxometalate-based Frameworks Catalyst

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### Supporting Information

**1. General Methods and Materials:** [Cu<sub>3</sub>(4,4'-bpy)<sub>3</sub>] [HSiW<sub>12</sub>O<sub>40</sub>].(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)(HSiW-MOF), [Cu<sub>3</sub>(4,4'-bpy)<sub>3</sub>] [PMo<sub>12</sub>O<sub>40</sub>].(C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>).0.5H<sub>2</sub>O(PMo-MOF), [Cu<sub>2</sub>(4,4'-bpy)<sub>2</sub>][HPMo<sub>12</sub>O<sub>40</sub>].(C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>)(HPMo-MOF) and [Cu(Phen)(4,4'-bpy)(H<sub>2</sub>O)]<sub>2</sub>[PW<sub>12</sub>O<sub>40</sub>].(4,4'-bpy) (PW-MOF) (C<sub>3</sub>H<sub>4</sub>N<sub>2</sub> = imidazole, C<sub>5</sub>H<sub>6</sub>N<sub>2</sub> = 2-aminopyridine, bpy = bipyridine, Phen = 1,10-phenanthroline) were synthesized according to published procedures and their syntheses were confirmed by elemental analysis, infrared spectroscopy, and XRD.[1]

All common laboratory chemicals were reagent grade, purchased from commercial sources, and used without further purification. Elemental analyses for C, H, Si, W, Cu, N, P and Mo were carried

out on a Perkin-Elmer 7300 DV and Leco, CHNS-932 elemental analyzer. Infrared spectra (KBr pellets) were recorded on a JASCO, FT/IR-6300 instrument. The oxidation products were quantitatively analyzed by gas chromatography (GC) on a Chrompack CP 9001 instrument using a SIL-5CB column (50m, 32mm, 5 $\mu$ m) and FID detector(oven temperature, 60~120 °C; Injection temperature, 200 °C; Detector temperature, 200 °C). The yield of products were calculated from the peak areas by using an internal standard method. Powder X-ray diffraction (XRD) data were obtained on a D8 Advanced Bruker using Cu K $\alpha$  radiation ( $2\theta = 5-40^\circ$ ). The CV studies are performed at  $25 \pm 2$  °C using a three-electrode assembly in 10 mL glass cell including a Ag/AgCl (3 M KCl) electrode as the reference, a Pt plate as the counter electrode, and the glassy carbon electrode (GCE) as the working electrode. All the potentials were measured and reported vs. Ag/AgCl (3MKCl). The CV measurements were carried out on Autolab/Potentiostat/Galvanostat-302 N, and controlled by a Nova 1.8 software (Eco Chemie, Utrecht, Netherlands). UV–vis spectra were recorded on JASCO V-670 UV–vis spectrophotometer (190–2700 nm).

## 1.2. Catalytic recycling

A typical recycling experiment was carried out as follows:

The round-bottom flask was cooled to room temperature after the required reaction time, followed by the catalyst and reaction solution separated by filtration. Then, the catalyst was thoroughly washed with acetonitrile and acetone and afterwards dried in vacuum at room temperature.

## 2. Preparation and Catalysts analysis data[1]:

**2.1. Preparation of [Cu<sub>3</sub>(4,4'-bpy)<sub>3</sub>] [HSiW<sub>12</sub>O<sub>40</sub>].(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)(HSiW-MOF).** HSiW-MOF was synthesized hydrothermally from a mixture of H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O (FW  $\approx$  2878.17, 0.4 g, 0.14 mmol), CuCl<sub>2</sub>·2H<sub>2</sub>O (0.23 g, 1.33 mmol), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (0.41 g, 3.25 mmol), im (im = imidazole, 0.027 g, 0.4 mmol), 4,4'-bpy (0.101 g, 0.65 mmol) and distilled water (20 ml). The

pH of the mixture was necessarily adjusted to 4 with  $\text{NH}_3\cdot\text{H}_2\text{O}$  solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature. Dark red block crystals could be isolated. in about 51% yield (based on W). Elemental analyses (%) calcd.: W, 61.24; Si, 0.78; Cu, 5.29; C, 11.00; H, 0.81; N, 3.11. Found: W, 62.2; Si, 0.87; Cu, 5.04; C, 9.85; N, 2.94, H, 0.75

## **2.2. Preparation of $[\text{Cu}_3(4,4'\text{-bpy})_3][\text{PMo}_{12}\text{O}_{40}]\cdot(\text{C}_5\text{H}_6\text{N}_2)\cdot 0.5\text{H}_2\text{O}(\text{PMo-MOF})$ :**

PMo-MOF was synthesized hydrothermally from a mixture of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$  (FW $\approx$ 1825.25, 0.5 g, 0.274mmol),  $\text{NH}_4\text{VO}_3$  (0.234 g, 2.0mmol),  $\text{C}_8\text{H}_6\text{O}_4$  (isophthalic acid) (0.30 g, 1.81mmol),  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (0.333 g, 1.953 mmol), 4,4'-bpy (0.166 g, 0.864 mmol),  $\text{C}_5\text{H}_6\text{N}_2$  (2-aminopyridine) (0.10 g, 1.062mmol) and distilled water (25 ml). The pH of the mixture was necessarily adjusted to 6.5 with  $\text{NH}_3\cdot\text{H}_2\text{O}$  solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature. Dark block crystals could be isolated in about 61% yield (based on Mo). Elemental analyses (%) calcd.: Mo, 44.54; P, 1.20; Cu, 7.38; C, 16.26; H, 1.21; N, 4.34. Found: Mo, 43.75; P, 1.02; Cu, 7.14; C, 16.7; N, 4.25; H: 1.18

## **2.3. Preparation of $[\text{Cu}_2(4,4'\text{-bpy})_2][\text{HPMo}_{12}\text{O}_{40}]\cdot(\text{C}_5\text{H}_6\text{N}_2)(\text{HPMo-MOF})$ .**

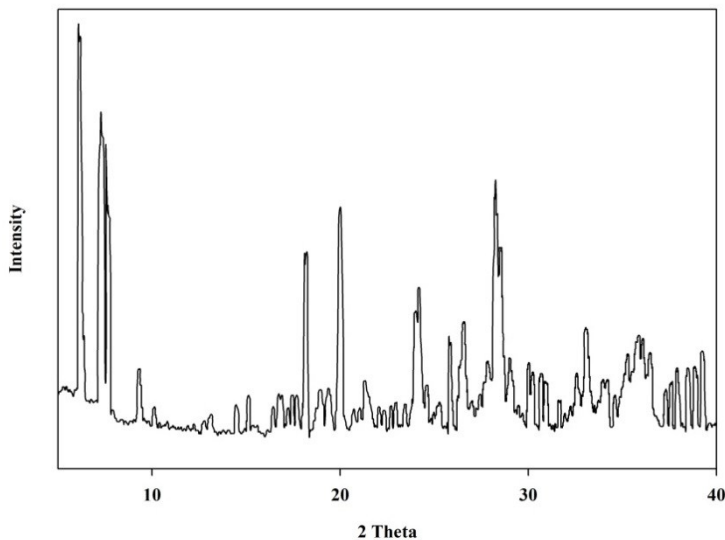
HPMo-MOF was synthesized hydrothermally from a mixture of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$  (FW  $\approx$  1825.25, 0.5 g, 0.274 mmol),  $\text{C}_6\text{H}_5\text{NO}_2$  (2-picolinic acid) (0.16, 1.357 mmol),  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (0.333 g, 1.953 mmol), 4,4'-bpy (0.20 g, 1.04 mmol),  $\text{C}_5\text{H}_6\text{N}_2$ (2-aminopyridine) (0.10 g, 1.062 mmol) and distilled water (25 ml). The pH of the mixture was necessarily adjusted to 6 with  $\text{NH}_3\cdot\text{H}_2\text{O}$  solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature. Dark block crystals could be isolated in about 58% yield (based on Mo). Elemental analyses (%) calcd.: Mo, 48.85; P, 1.31; Cu, 5.39; C, 12.74; H, 0.98; N, 3.57. Found: Mo, 48.70; P, 1.18; Cu, 5.11; C, 12.87; N, 3.54; H, 0.89

#### 2.4. Preparation of [Cu(Phen)(4,4'-bpy)(H<sub>2</sub>O)]<sub>2</sub>[PW<sub>12</sub>O<sub>40</sub>].(4,4'-bpy) (PW-MOF).

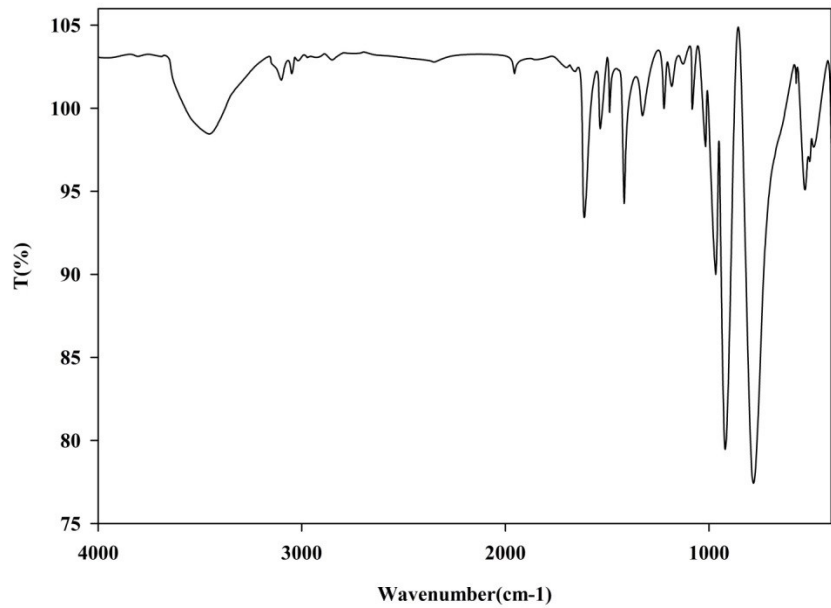
PW-MOF was synthesized hydrothermally from a mixture of Na<sub>2</sub>WO<sub>4</sub>.2H<sub>2</sub>O(0.5g, 1.516 mmol), H<sub>3</sub>PO<sub>4</sub> (0.20 ml, 85%), C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (isonicotinic acid) (0.1 g, 0.812 mmol), CuCl<sub>2</sub>.2H<sub>2</sub>O (0.201 g, 1.179 mmol), Phen (0.133 g, 0.671 mmol), 4,4'-bpy (0.052 g, 0.271 mmol) and distilled water (25 ml). The pH of the mixture was necessarily adjusted to 5 with NH<sub>3</sub>.H<sub>2</sub>O solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature. Blue block crystals could be isolated in about 45% yield (based on W). Elemental analyses (%) calcd.: W, 57.02; P, 0.80; Cu, 3.28; C, 16.76; H, 1.15; N, 3.62. Found: W, 56.12; P, 0.81; Cu, 3.51; C, 16.47; N, 3.37; H, 0.99.

#### Catalysts analysis data (Fig 1-10):

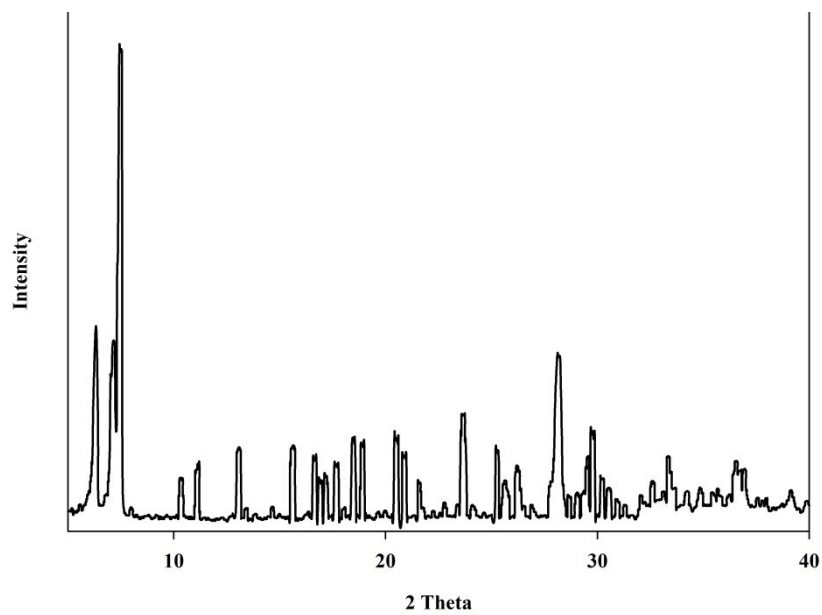
HSiW-MOF



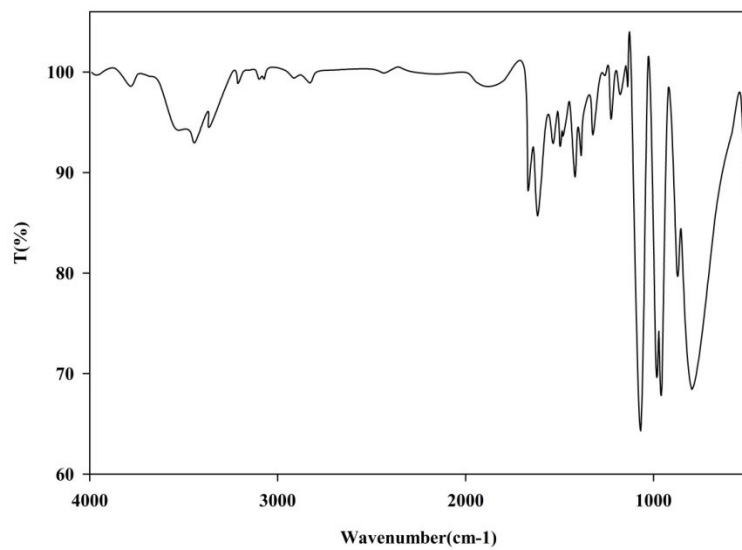
**Fig 1.** XRD pattern of HSiW-MOF



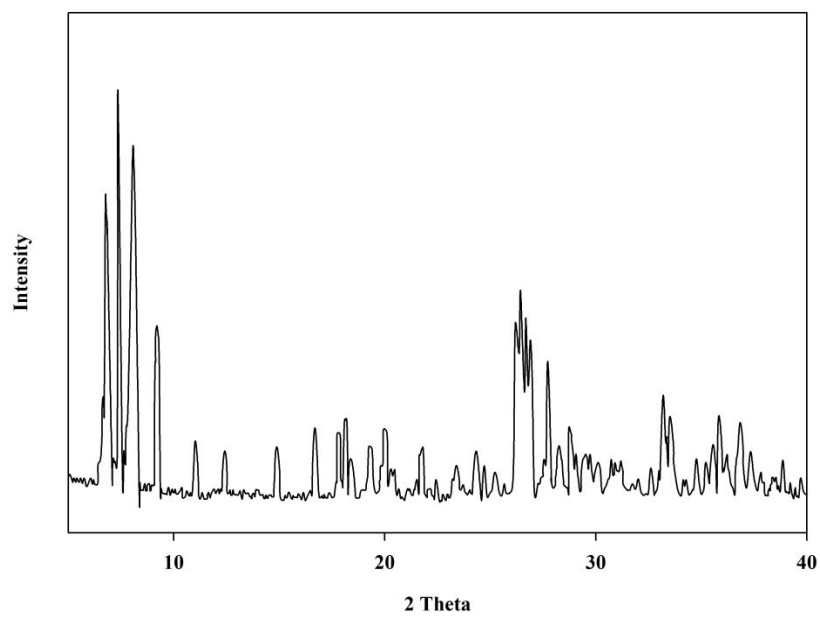
**Fig 2.** IR Spectrum of HSiW-MOF



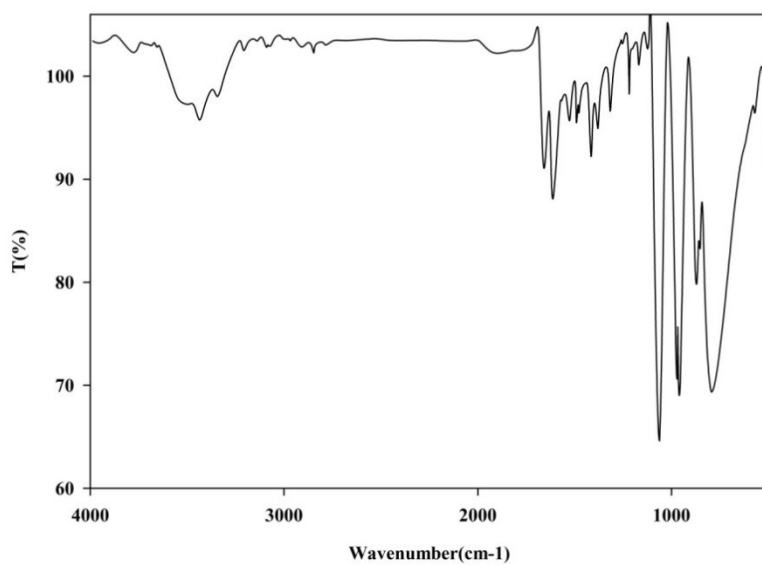
**Fig 3.** XRD pattern of PMo-MOF



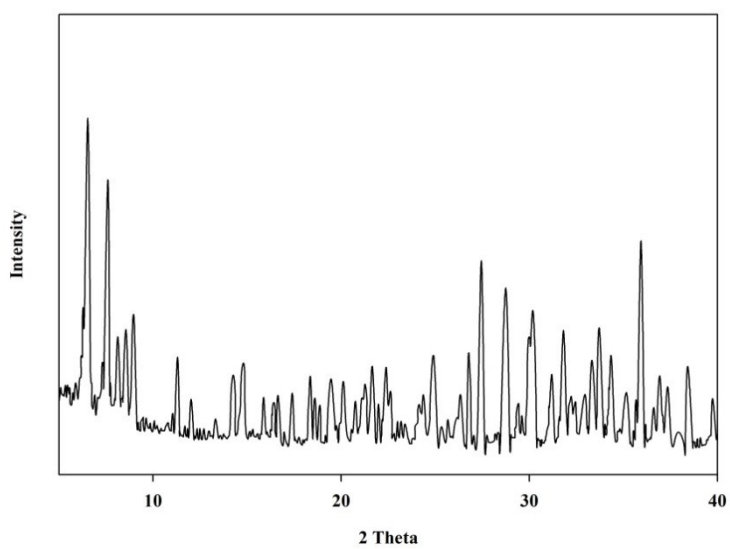
**Fig 4.** IR Spectrum of PMo-MOF



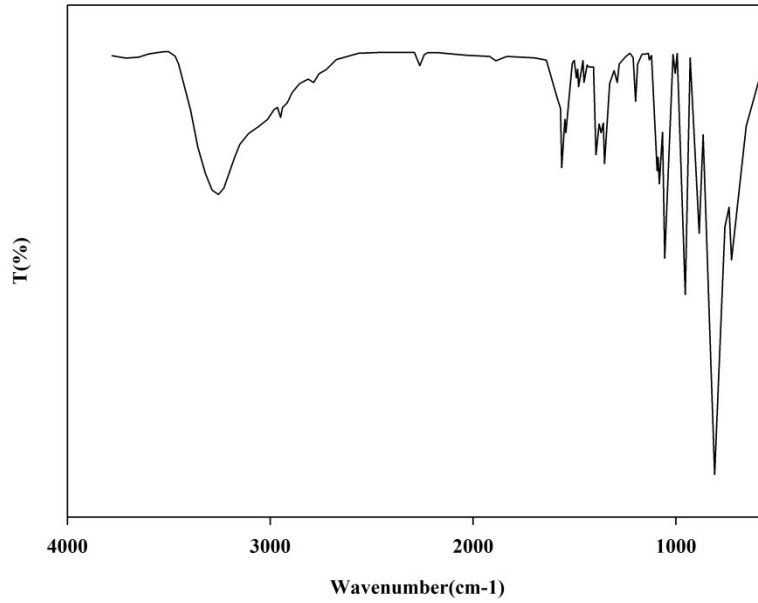
**Fig 5.** XRD pattern of HPMo-MOF



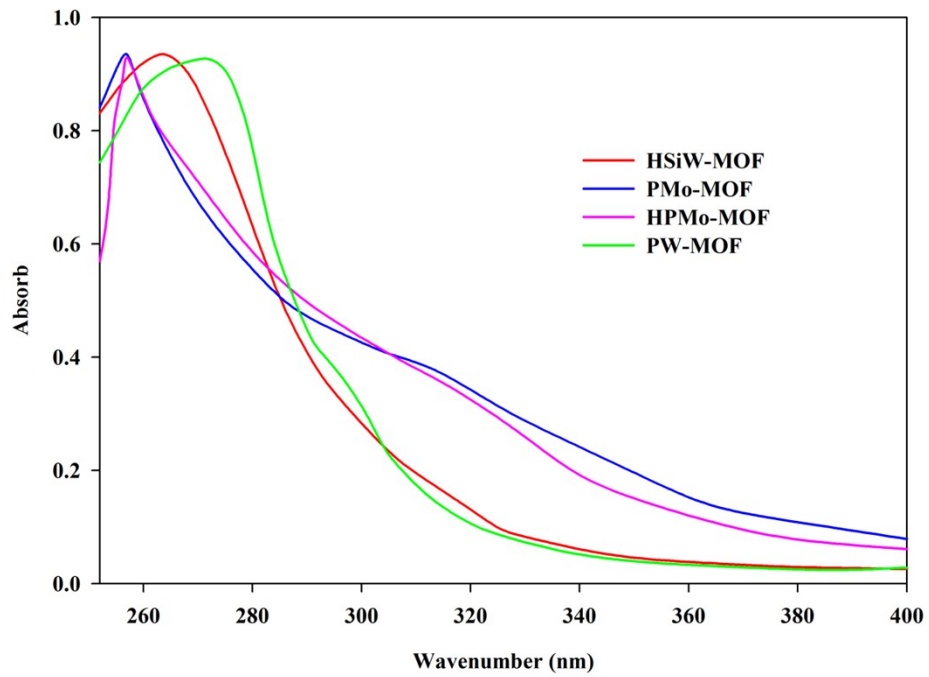
**Fig 6.** IR spectrum of HPMo-MOF



**Fig 7** XRD pattern of PW-MOF

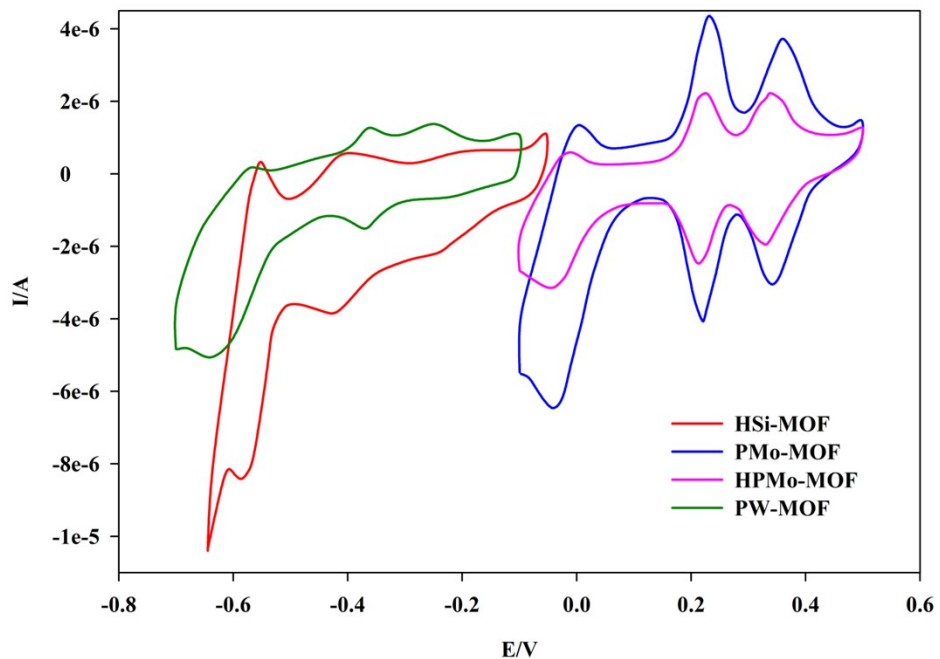


**Fig 8.** IR spectrum of PW-MOF



**Fig 9.** UV-vis spectra of HSiW-MOF, PMo-MOF, HPMo-MOF and PW-MOF in dimethyl sulfoxide





**Fig 10.** cyclic voltammograms of DMSO solutions of HSiW-MOF, PMo-MOF, HPMo-MOF and PW-MOF

## Reference

- [1] L. Xiao, L. Wang, X. Shan, H. Guo, L. Fu, Y. Hu, X. Cui, K. Li and J. Xu, *Cryst Eng Comm*, 2015, **17**, 1336.