

Supporting Information

Novel crystalline nanoporous iron phosphonate based metal-organic framework as an efficient anode material for lithium ion batteries

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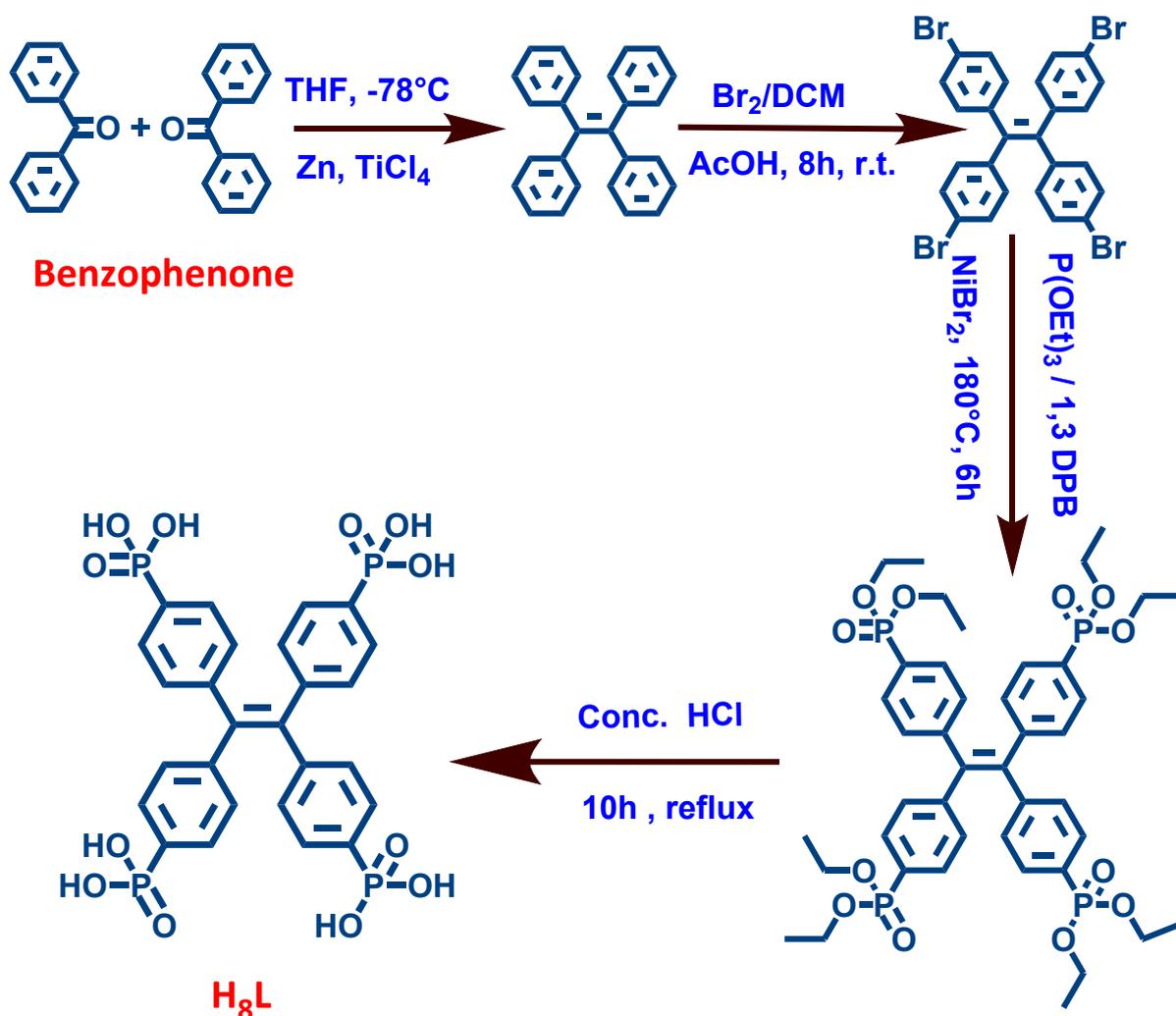
Material characterizations

Powder X-ray diffraction analysis of H₈L-Fe-MOF was carried out in a Bruker AXS D-8 Advanced SWAX diffractometer using *Cu-K α* ($\lambda = 1.5406 \text{ \AA}$) radiation. Diffraction patterns were recorded in the 2θ region (4° - 50°) at a scan rate of 0.4° per min. The crystal structure solution and the extended framework in capped stick model of the MOF were carried out by using the EXPO2014 and VESTA crystallography softwares. Ultra high resolution transmission electron microscopic (TEM) images of the MOF was taken by using a UHR-FEG TEM system (JEOL JEM 2100F) transmission electron microscope operating at 200 kV electron source. Sample was prepared by dropping a sonicated ethanolic solution of the H₈L-Fe-MOF material over a carbon coated copper grid followed by drying under high vacuum. N₂ adsorption/desorption isotherm of both the materials were obtained at 77 K from the Autosorb-iQ surface area analyzer of Quantachrome Instruments, USA. Pore size distribution plot was obtained by employing non local density functional theory (NLDFT) taking N₂ sorption at 77 K on carbon with slit pore model as reference. Prior to the sorption measurement, the powder sample was Soxhlet extracted for 24 h using anhydrous MeOH as dispersion medium and dried under vacuum at 150°C . Prior to all the adsorption study, the samples were degassed at 423 K for 12 h under high vacuum conditions. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/DTA 851e TA-SDT Q-600 instruments. The EPR (electron paramagnetic resonance) spectroscopic analysis has been done for the freshly synthesized H₈L-Fe-MOF at room temperature using a JES-FA200 ESR spectrometer (JEOL). FTIR spectra of both the H₈L ligand and H₈L-Fe-MOF were recorded from Perkin Elmer Spectrum 100 spectrophotometer. The solid state UV-VIS spectra of the four armed phosphonate ligand and the novel iron phosphonate MOF were recorded using UV-VIS recording spectrophotometer (UV-2401PC, Shimadzu, Japan) in the diffuse reflectance mode. The self-assembled morphology as well as the particle size of the material was analyzed by a JEOL JSM-7500F field emission scanning electron microscope.

Chemicals

Zinc powder, titanium (IV) chloride, potassium carbonate, Na₂S₂O₃, MgSO₄, benzophenone, bromine, 1,3-diisopropylbenzene, anhydrous nickel(II) bromide, triethylphosphite, FeCl₃, are purchased from Sigma-Aldrich, Loba Chemie and Merck, India. Anhydrous THF, DCM, acetic acid and solvents are bought from Spectrochem. 1,3 di-isopropyl benzene was purchased from TCI chemicals. All these reagents and solvents are used without further purification.

Schematic presentation of the H₈L Ligand



Scheme 1. Synthesis of H₈L ligand starting from simple benzophenone.

Experimental

Synthesis of TPE: The whole synthesis of 1,1,2,2-tetraphenylethane (TPE)¹ were performed using the dry glass apparatus and under the nitrogen atmosphere. In a 500 mL two-neck round bottom flask, we had taken zinc powder (45 g, 612 mmol) and anhydrous tetrahydrofuran (200 mL). Then the mixture was degassed for 40 min purging with nitrogen gas. It was stirred in a -40°C reaction bath by using dry ice/CH₃CN bath. After few minutes, titanium tetrachloride (35 mL, 304 mmol) was added very carefully to the former cold system with moderately stirring condition. After the full addition of that metal precursor, the mixture was allowed to achieve the room temperature. Then after attending the room temperature, the reaction mixture was allowed to reflux at 90°C for two hours. After the reflux the mixture was allowed to cool down to 0°C and benzophenone (31 g, 168 mmol) was poured into the cold mixture by mixing with anhydrous THF. Finally, the mixture was refluxed at 90 °C for overnight. Then, it was cooled at room temperature and poured into a 1.0 L glass beaker. Potassium carbonate (10% wt, 500 mL) solution was added into this beaker to get the final precipitate. After that, the mixture was

filtered to get the residue and this was air-dried for overnight. This air dried sample was dissolved in DCM and the insoluble solid was revoked from the mixture by filtration. Finally, the solvent was evaporated under reduced pressure and we get the desired tetraphenyl ethylene product (pure white solid, 26 g, 95% yield). This TPE was characterised by $^1\text{H NMR}$ (500 MHz, CDCl_3 , 298 K, **Fig. S1**) $\delta = 7.03\text{-}7.06$ ppm (m, 8H), $7.09\text{-}7.13$ ppm (m, 12H).

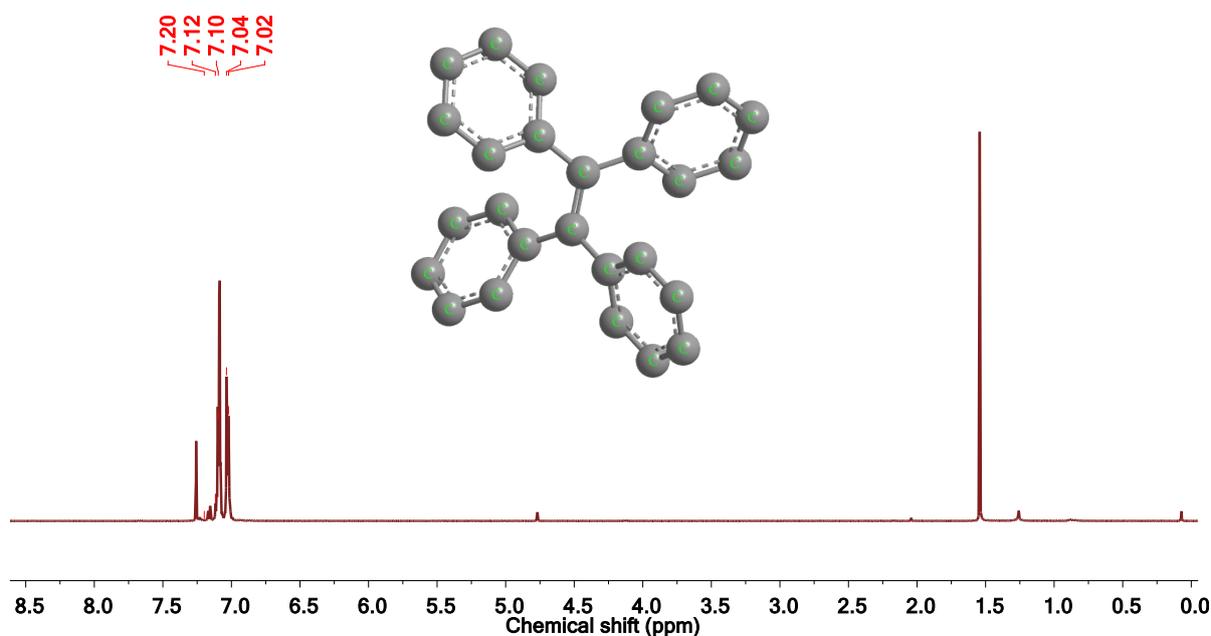


Fig. S1. $^1\text{H NMR}$ spectrum of TPE.

Synthesis of TPE-Br

The electrophilic bromination reaction of the aromatic compound TPE was performed following a previously reported procedure.² At first we have taken the previously synthesized white solid TPE compound (6 g, 18 mmol) in a 250 ml round bottom flask (RB) with 100 ml dichloromethane and 50 ml glacial acetic acid. Wrapping with an aluminium foil, the mixture was placed in an ice and mineral salt bath to attain the very lower temperature. After achieving the 0°C temperature of that mixture, liquid bromine (6 g, 75 mmol) was added to that mixture very slowly using dropping funnel. After fully addition, the mixture was stirred at room temperature for eight hours. Then the mixture was poured into a 500 ml beaker, which contained $\text{Na}_2\text{S}_2\text{O}_3$ solution for removing excess bromine. Finally, it was extracted with DCM using separating funnel. The DCM solvent was evaporated under reduced pressure to get the desired TPE-Br product (10 g, 95% yield). This TPE-Br was characterised by $^1\text{H NMR}$ (400 MHz, CDCl_3 , 298 K, **Fig. S2**) $\delta = 6.77\text{-}6.78$ ppm (d, 8H), $7.19\text{-}7.20$ ppm (d, 8H).

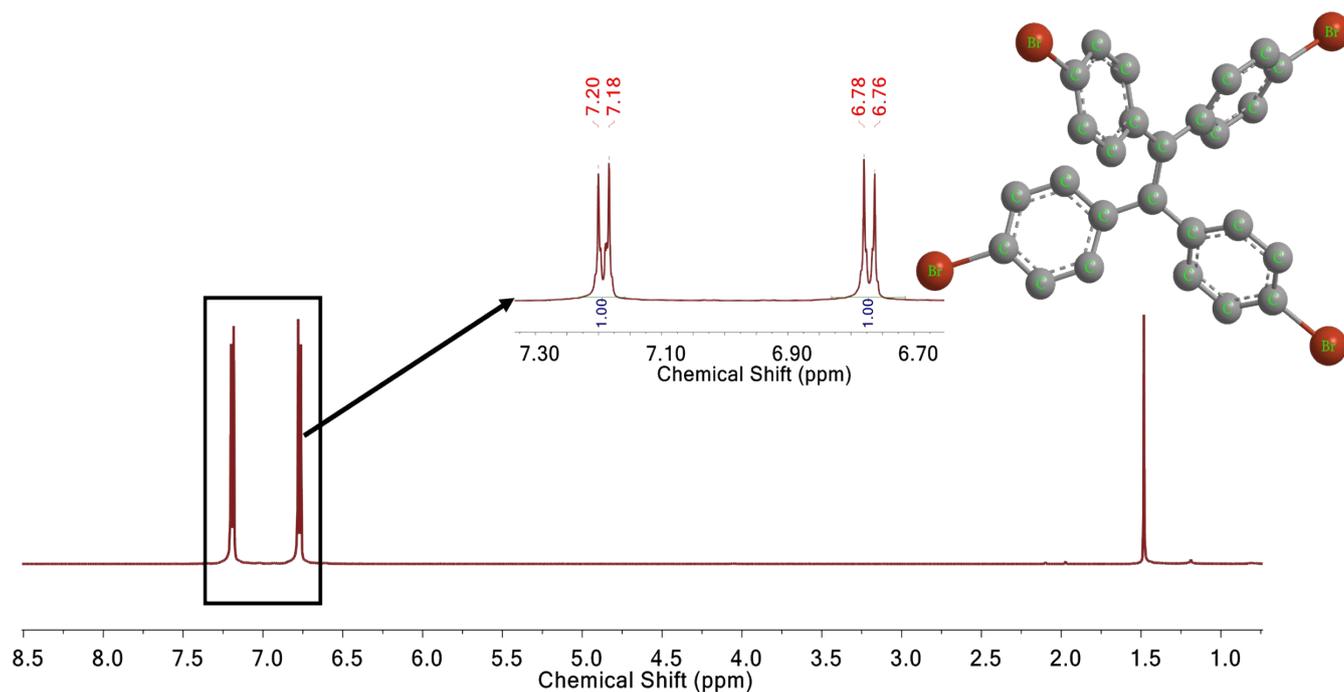
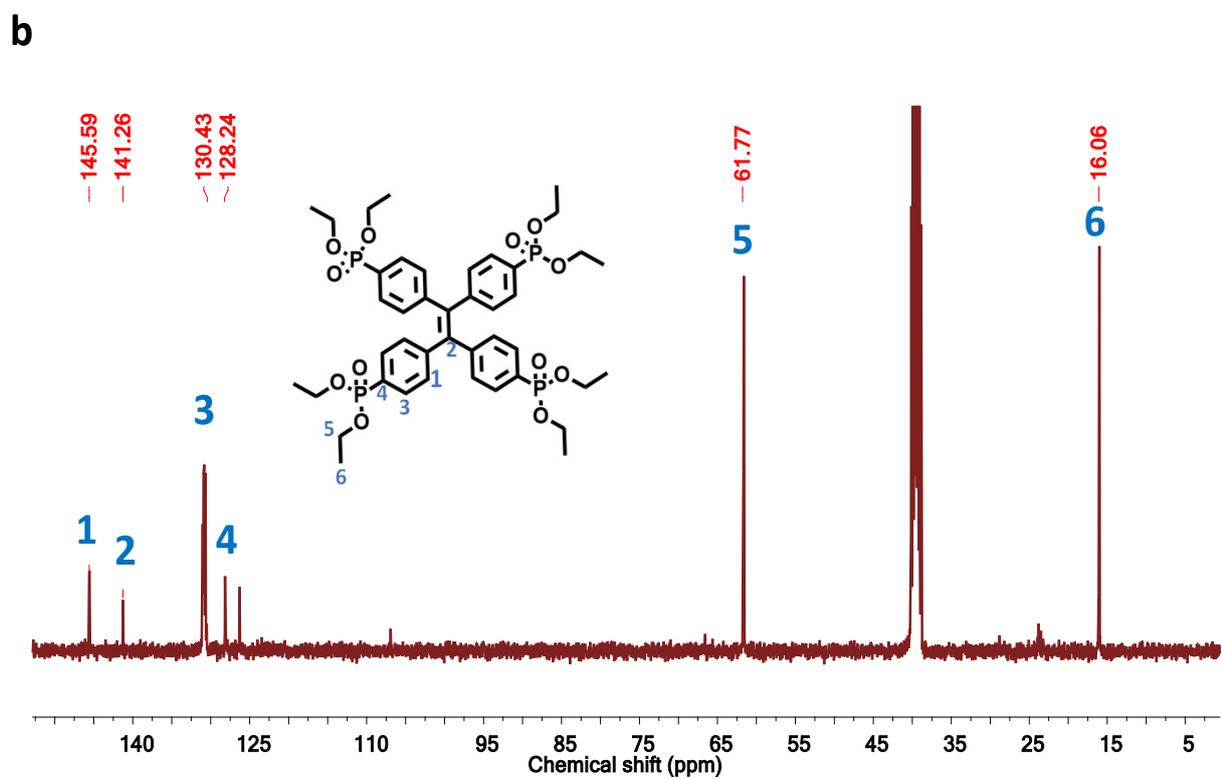
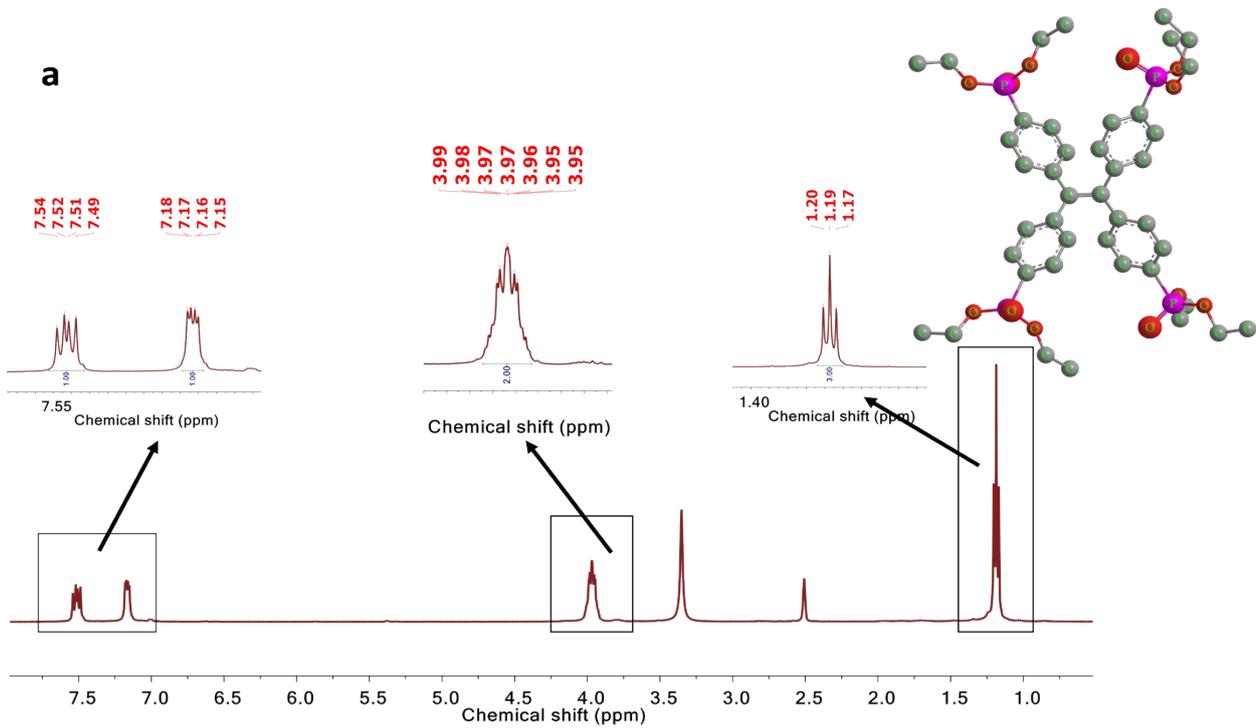


Fig. S2. ^1H NMR spectrum of TPE-Br.

Synthesis of TPE-Ester

The esterification of the bromo aromatic compound using C-P coupling method was reported previously.³ Formally synthesized bromo derivative compound (4.5 g) of TPE was dissolved in 75 ml 1, 3-diisopropyl benzene by warming at 120°C maintaining the inert condition for two hours. After that, the temperature was decreased slowly and when it was 70°C, we added the anhydrous nickel (II) bromide (330 mg) to this mixture under inert atmosphere. After the fully addition of that metal precursor, the mixture was refluxed at 180°C. After sometimes, triethyl phosphite (3.5 mL) was added dropwise, and the addition was continued for 3 h. Finally, the mixture was allowed to reflux for overnight at 190°C. After completion of the reaction, vacuum distillation was performed for removing the volatile component and high boiling 1,3-diisopropyl solvent. The dark viscous liquid was allowed for column chromatography by using chloroform and methanol mixture [CHCl_3 : MeOH = 10: 1 (v/v)]. After the solvent evaporation under reduced pressure, we get the desired phosphonate ester compound (2.5 g, 40% yield). This TPE-Ester was characterised by ^1H NMR (400 MHz, DMSO-d_6 , 298 K) δ = 7.15-7.18 ppm (dd, 8H), 7.49-7.54 ppm (dd, 8H), 3.95-3.99 ppm (m, 16H), and 1.17-1.20 ppm (t, 24H) (**Fig. S3a**), ^{13}C NMR (**Fig. S3b**) and ^{31}P NMR δ = 17.23 ppm (**Fig. S3c**)



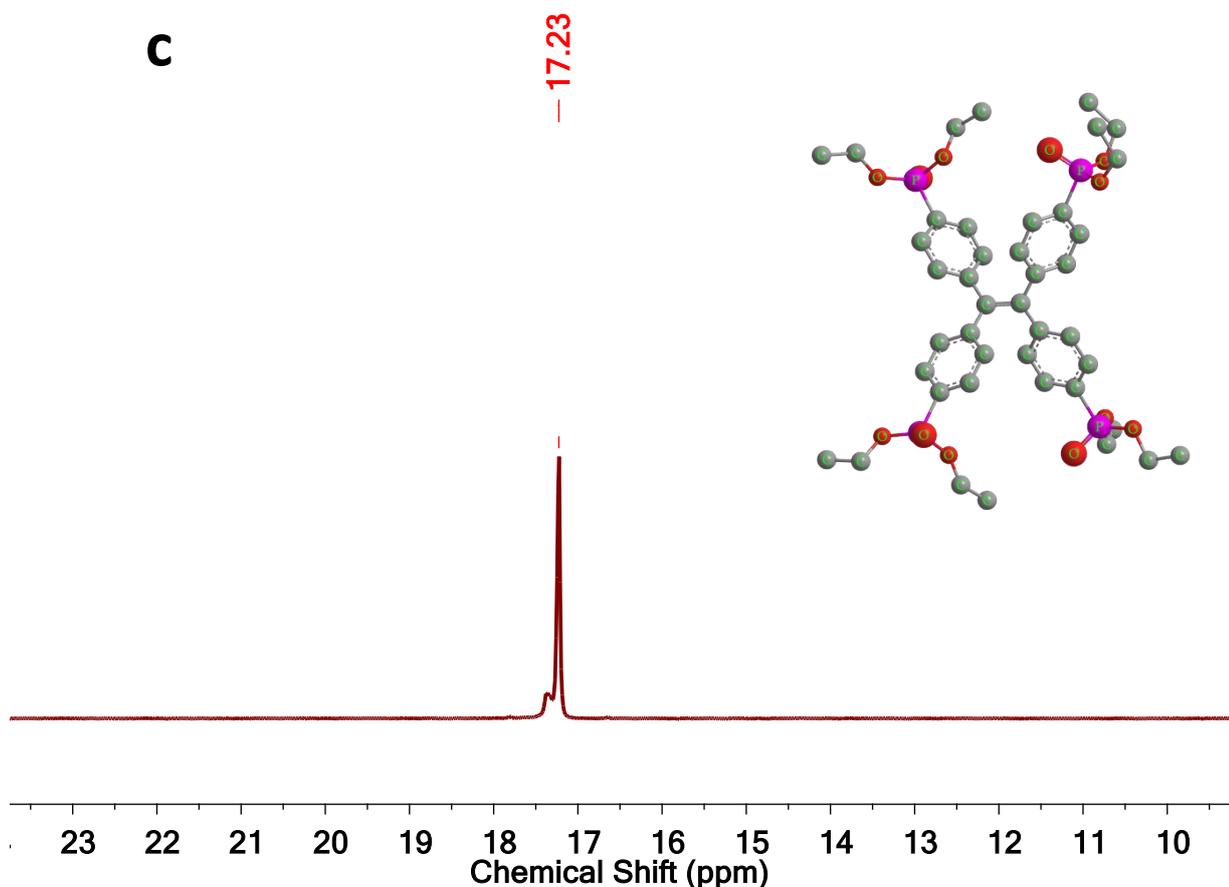


Fig. S3. ^1H (a), ^{13}C (b) and ^{31}P (c) NMR spectra of TPE-Ester.

Synthesis of TPE-Acid (H_8L -Ligand)

Now the last step is the ester hydrolysis under acidic condition. We had taken around 2.5 g of previously synthesized TPE-Ester into a 100 mL round bottom flask with 50 ml concentrated HCl. Then the acidic solution was refluxed at 100 °C for overnight. After completion of the hydrolysis reaction, the acidic solution was removed by vacuum distillation and finally we get the white crude product. This crude product was dissolved in 20 mL distilled water and decolorized by activated charcoal. After the filtration the solvent was evaporated under reduced pressure and we ultimately get the desired TPE-Acid ligand (H_8L). After that, it was recrystallized from ethanol solvent. Finally, we get the 1.71 g of white solid H_8L ligand (92% yield). The compound was characterized by ^1H , ^{31}P NMR. ^1H NMR (500 MHz, $\text{D}_2\text{O} + \text{K}_2\text{CO}_3$, at 298K) $\delta = 7.15\text{-}7.18$ ppm (dd, 8H); $7.44\text{-}7.49$ ppm (dd, 8H) (**Fig. S4a**), ^{31}P NMR (500 MHz, $\text{D}_2\text{O} + \text{K}_2\text{CO}_3$, at 298K) $\delta = 13.13$ ppm (**Fig. S4b**).

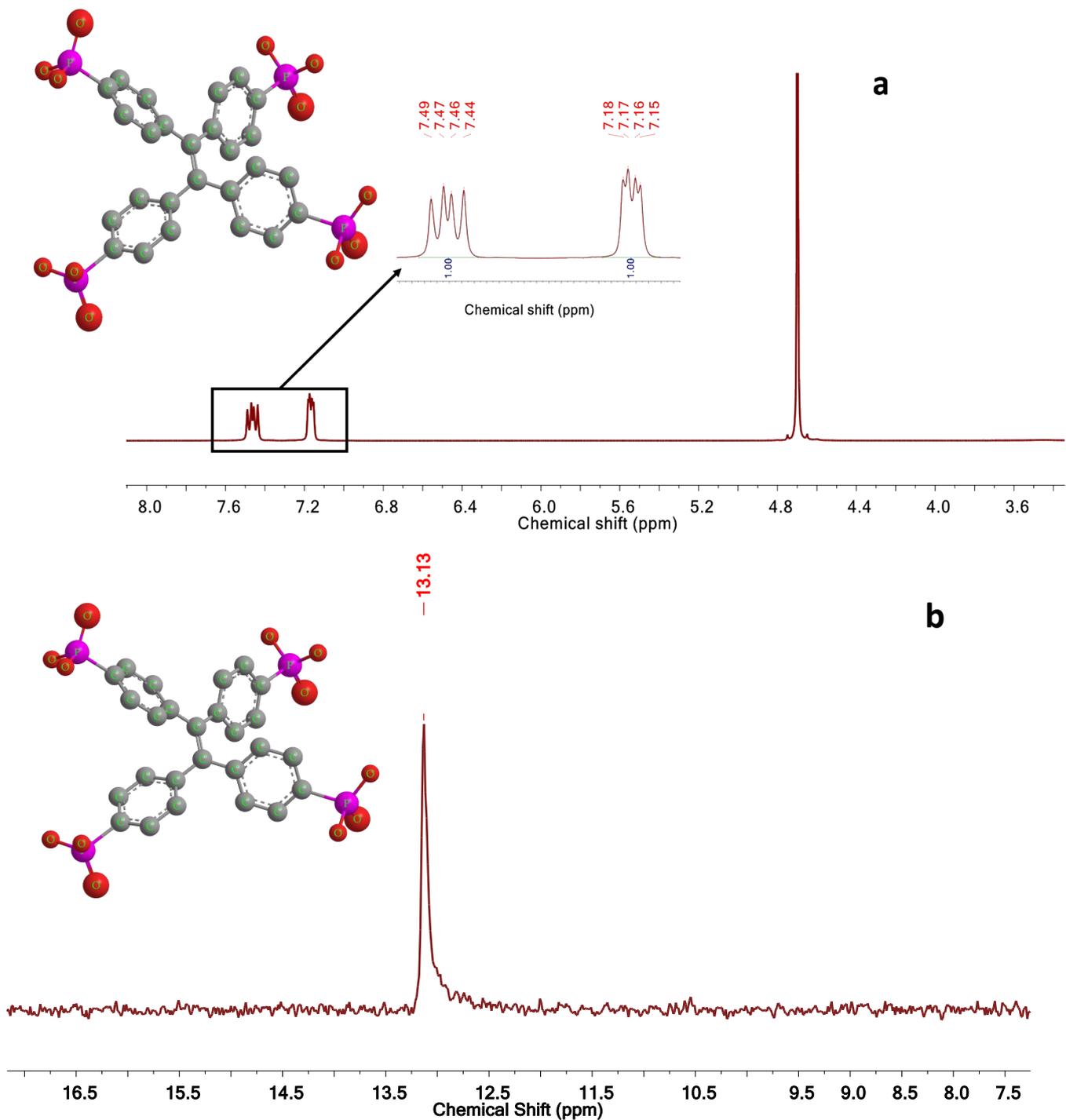


Fig. S4. ^1H (a) and ^{31}P (b) NMR spectra of TPE-Acid (H_8L).

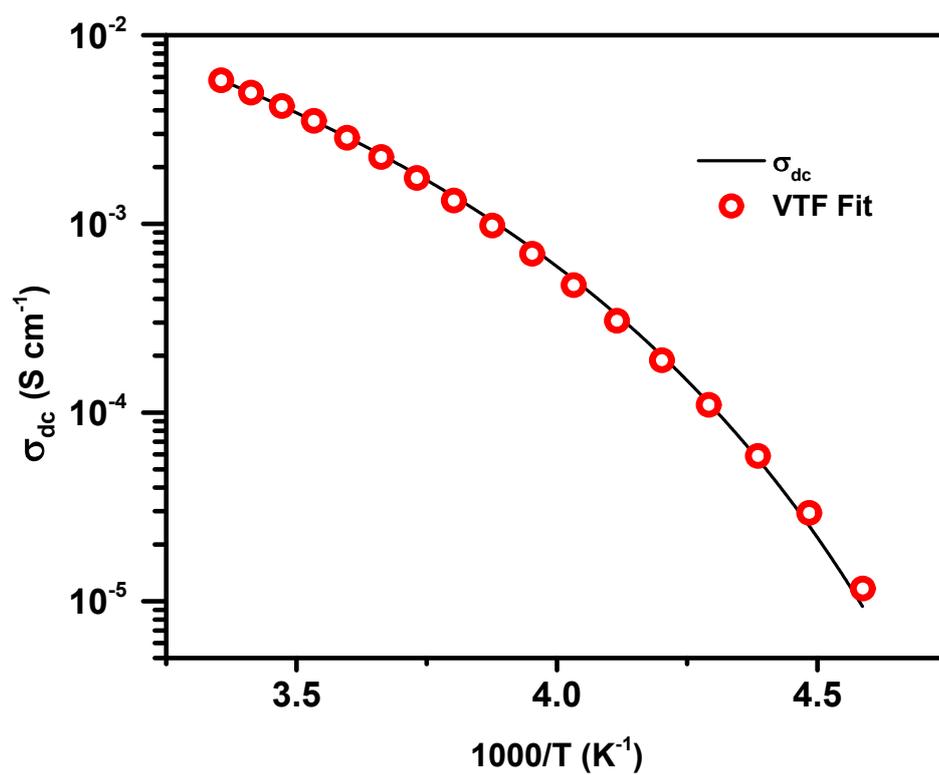


Fig. S5. DC conductivity of GPE membrane as a function of temperature in inverse scale with VTF fitting.

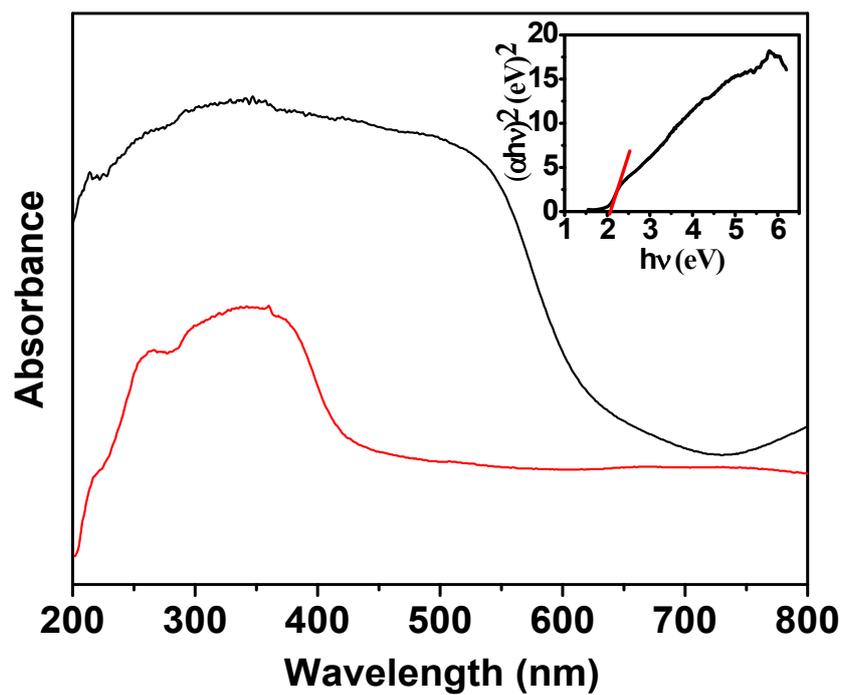


Fig. S6. UV-Vis DRS spectra of H₈L (red) and H₈L-Fe-MOF (black). Corresponding Tauc plot for direct band gap calculation of H₈L-Fe-MOF is shown in the inset.

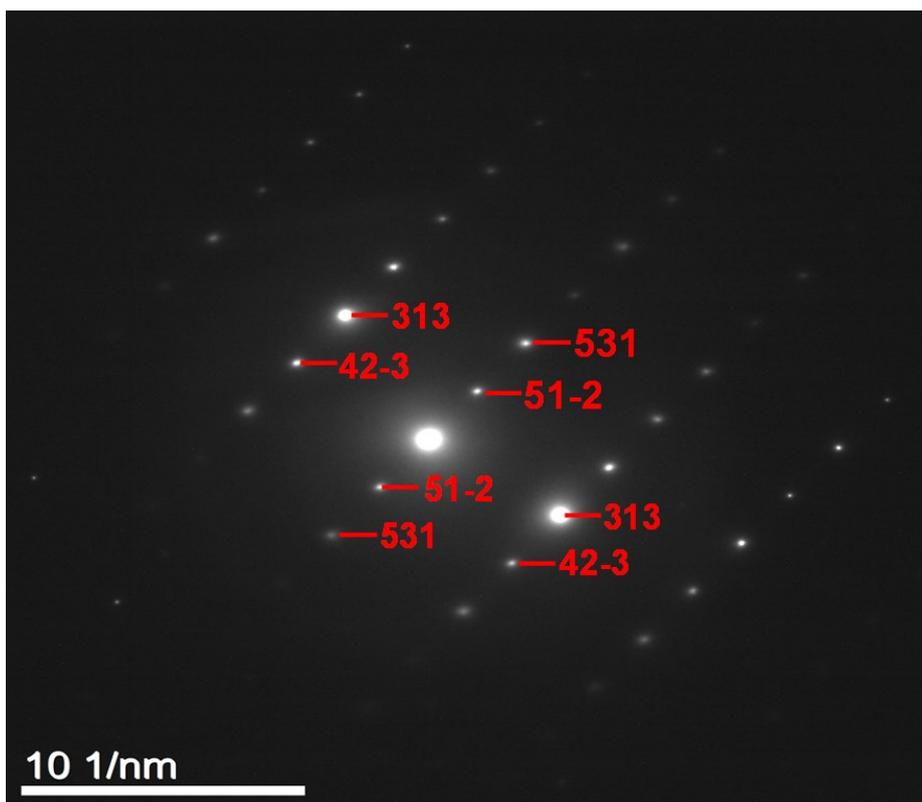


Fig. S7. Selected area electron diffraction (SAED) pattern and indexing of planes for the monoclinic crystal phase of H₈L-Fe-MOF.

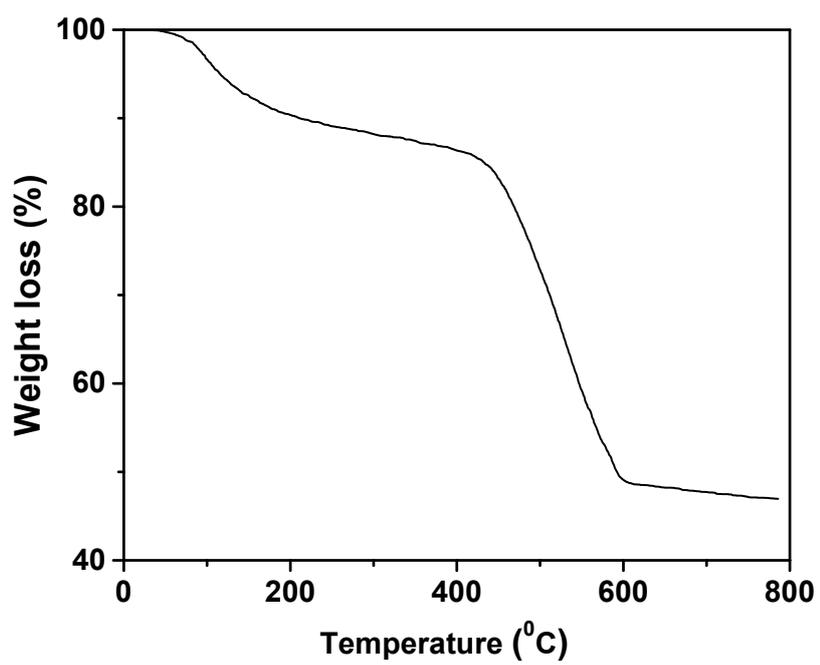


Fig. S8. Thermogravimetric weight loss of H₈L-Fe-MOF with temperature under N₂ flow.

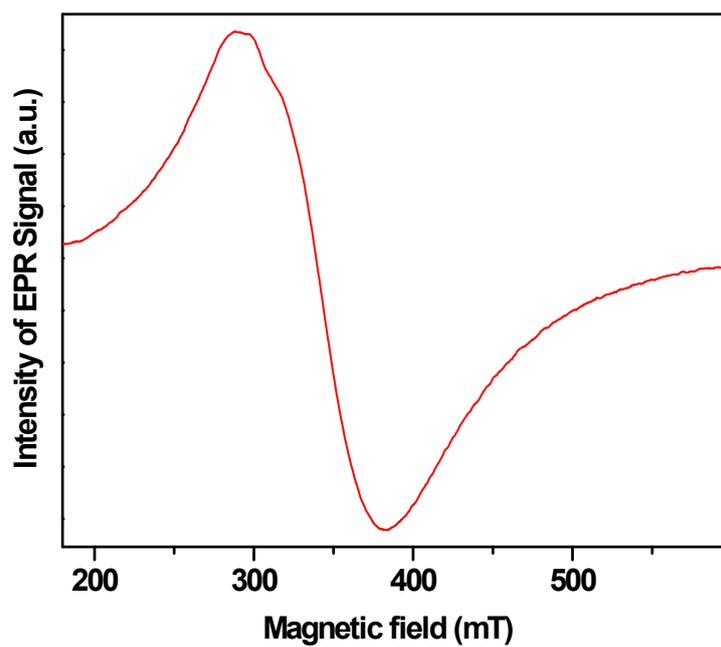


Fig. S9. Electron paramagnetic resonance spectrum of Fe^{+3} in $\text{H}_8\text{L-Fe-MOF}$.

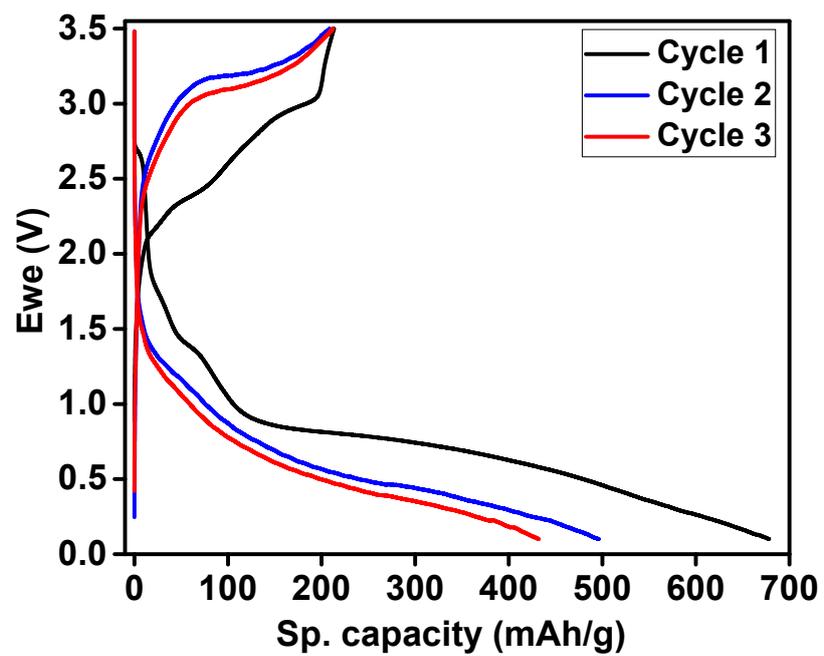


Fig. S10. Charge-discharge profile of the H₈L-Fe-MOF electrode up to three cycles.

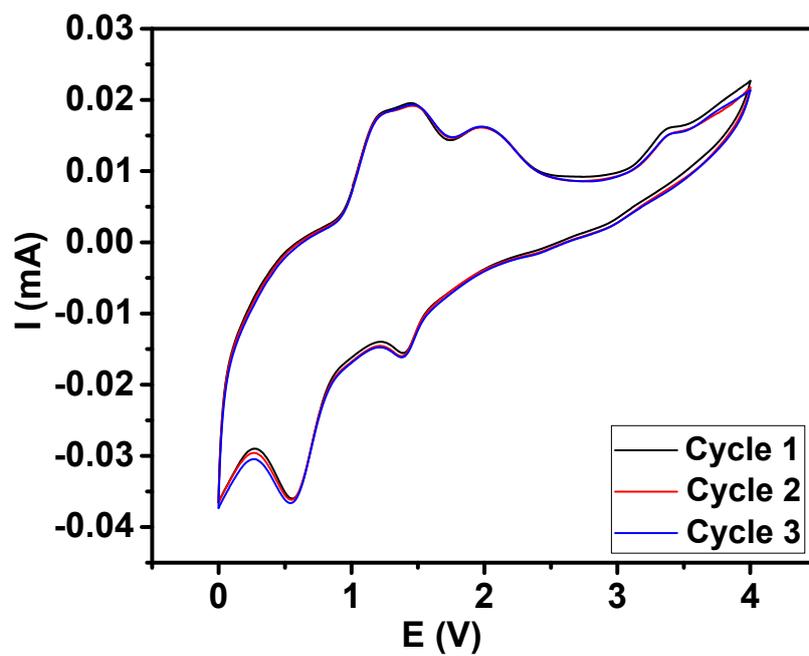


Fig. S11. Cyclic voltammograms of H₈l-Fe-MOF.

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