

Electronic Supplementary Information (ESI)

A nanoscale Fe(II) metal-organic framework with bipyridinedicarboxylate ligand as high performance heterogeneous Fenton catalyst

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Experimental details

Materials and methods

$\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ (98%) and 4-chlorophenol (99%) were supplied by J&K Scientific Ltd. (Beijing, P.R. China). 2,2'-Bipyridine-5,5'-dicarboxylic acid was purchased from Jinan Henghua Sci.&Tec. Co., Ltd. (Jinan, Shandong, P.R. China). Phenol, H_2O_2 (30%), methylene blue, DMF, *o*- and *p*-benzenediols were all of analytical grade and obtained from Aladdin Industrial Inc. (Shanghai, P.R. China). Acetonitrile used in HPLC analysis was of chromatographic pure and purchased from Merger Co., Ltd. (Shanghai, P.R. China). Horseradish peroxidase (POD), which was used in the measurement of H_2O_2 , was obtained from Huamei Biologic Engineering Co. (Luoyang, Henan, China), and *N,N*-dialkyl-*p*-phenylenediamine (DPD) was from Merk (p.a.) (Whitehouse Station, NJ, USA). 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from Sigma–Aldrich Co. (Shanghai, P.R. China). All the chemicals were used as received without further purification.

Scanning electron microscope (SEM) images were taken with a JEOL JSM-7500F scanning electron microscope. The powder X-ray diffraction (PXRD) spectra were recorded on a Rigaku D/Max-2500 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at 40 kV and 100 mA. Fourier transform infrared spectroscopy (FT-IR) was measured by a MAGNA-560 Fourier transform infrared spectrometer with nujol mull method. Elemental analysis (C, H, and N) was carried out on a Perkin-Elmer 240C analyzer. Thermogravimetric analysis (TGA) was performed on a Rigaku standard TG-DTA analyzer from ambient temperature to 700 °C with a heating rate of 10 °C min^{-1} in the air, and an empty Al_2O_3 crucible was used as the reference. The concentrations of substrate and formed intermediates in the reacted solution were analyzed by HPLC method (Agilent LC 1200) with C-18 column. Acetonitrile/ H_2O (3/7) was used as the eluent in HPLC analysis, and the aqueous phase was adjusted by H_3PO_4 to pH = 2.4. Each species was quantified at its absorption maximum (270 nm for phenol, 230 nm for 4-chlorophenol and 210 nm for the hydroxylated intermediates of phenol) and compared with authentic sample. ESR spectra were obtained using a Bruker model EPR 300E spectrometer.

Synthesis of Fe-bpydc

2,2'-bipyridine-5,5'-dicarboxylic acid (0.5 mmol) was dissolved in the solvent of DMF (40 mL), and added to 40 mL of the aqueous solution of $\text{Fe}(\text{ClO}_4)_2$ (1 mmol). The resulting mixture was heated in an oil bath at 120 °C under vigorous agitation for 4 h. After cooling down to room temperature, the formed precipitate was separated by centrifugation, washed sequentially by water and ethanol, and dried at 60 °C. The obtained sample was defined as Fe-bpydc.

Catalytic degradation experiments

In a typical procedure, Fe-bpydc (4 mg) and phenol (0.1 mmol) were dispersed in 400 mL of H₂O. This suspension was stirred for 2 h to reach the adsorption-desorption equilibrium, and then H₂O₂ (0.6 mmol) was added to start the reaction. After reacted for a given time, ca. 1 mL aliquot was collected, filtered to remove the catalyst and subject to HPLC analysis. The concentration of H₂O₂ was measured by the spectrophotometric DPD method.¹

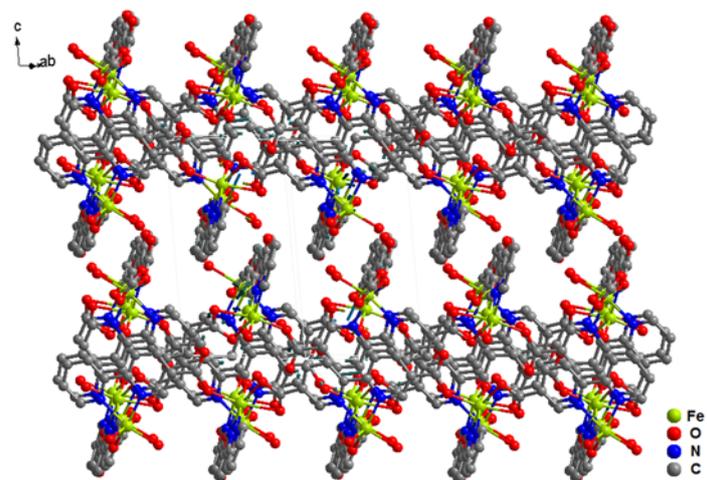


Fig. S1 Reported crystal structure of $\{[\text{Fe}(\text{bpydc})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$.²

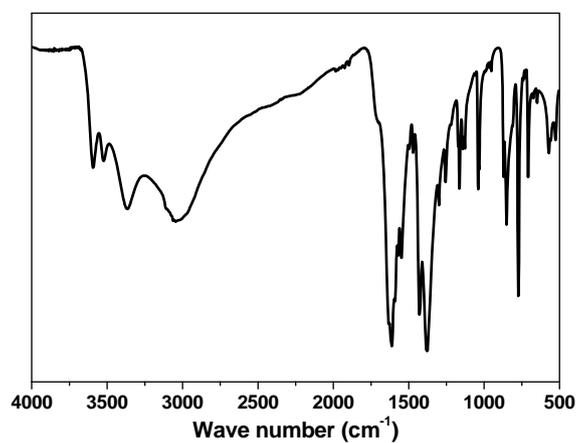


Fig. S2 FT-IR spectrum of the as-prepared Fe-bpydc sample.

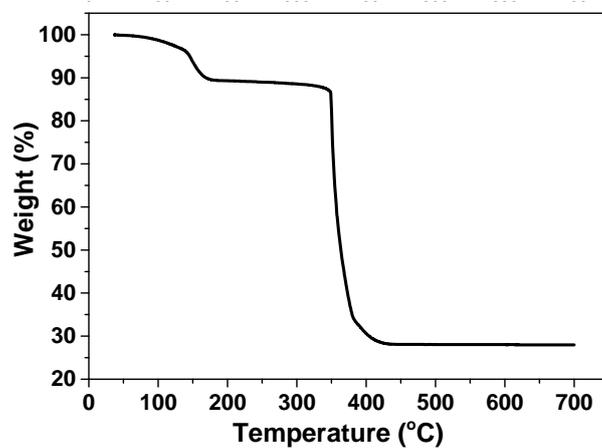


Fig. S3 TGA curve of the as-prepared Fe-bpydc sample.

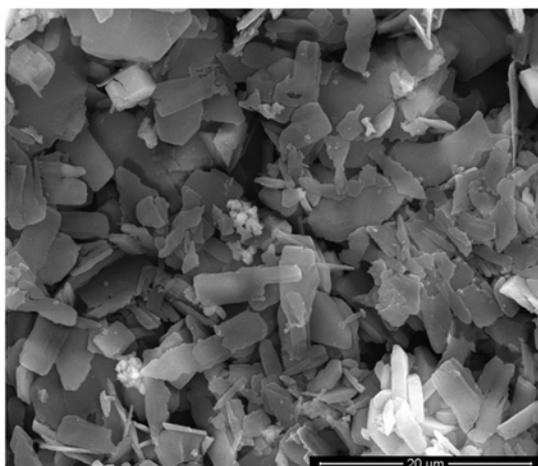


Fig. S4 The SEM image of the Fe-bpydc catalyst after the degradation of phenol.

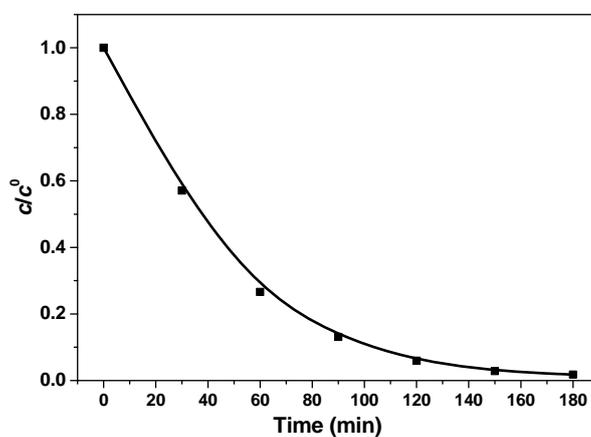


Fig. S5 Degradation kinetics of 4-chlorophenol (4-CP) in the catalytic oxidation system of Fe-bpydc. 0.01 g L^{-1} Fe-bpydc, $c_{4\text{-CP}}^0 = 0.25 \text{ mM}$, $c_{\text{H}_2\text{O}_2}^0 = 1.5 \text{ mM}$, $400 \text{ mL H}_2\text{O}$.

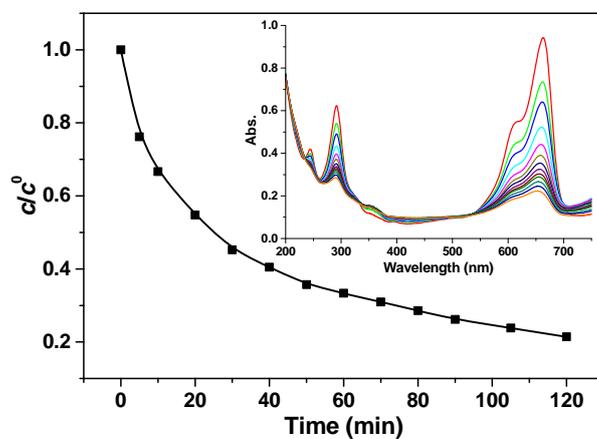


Fig. S6 Degradation kinetics of methylene blue (MB) in the catalytic oxidation system of Fe-bpydc. 0.01 g L^{-1} Fe-bpydc, 4 mg L^{-1} MB, $c_{\text{H}_2\text{O}_2}^0 = 1.5 \text{ mM}$, $400 \text{ mL H}_2\text{O}$. Inset: the change of absorption spectrum of the reacted solution.

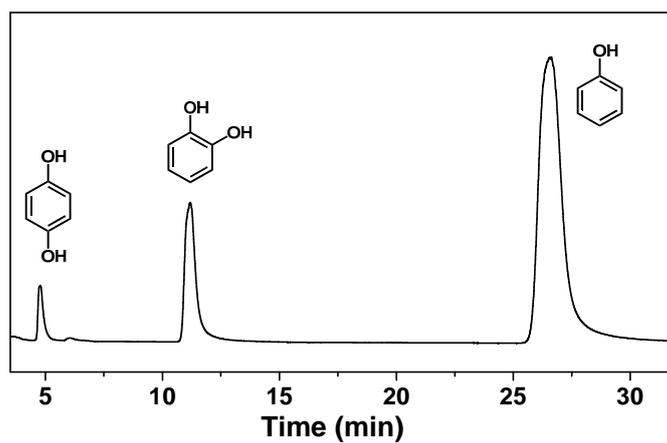


Fig. S7 Typical HPLC chromatogram of the reacted solution of phenol.

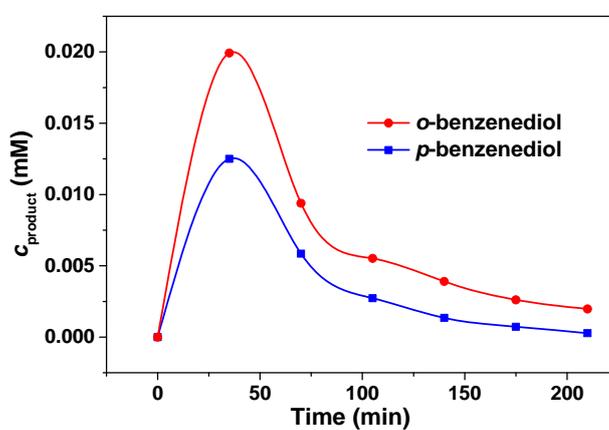


Fig. S8 Concentration change of *o*- and *p*-benzenediols during the catalytic degradation of phenol. $0.01 \text{ g L}^{-1} \text{ Fe-bpydc}$, $c_{\text{phenol}}^0 = 0.25 \text{ mM}$, $c_{\text{H}_2\text{O}_2}^0 = 1.5 \text{ mM}$.

References

- 1 H. Bader, V. Sturzenegger and J. Hoigné, *Water Res.*, 1988, **22**, 1109–1115.
- 2 R. C. Finn and J. Zubieta, *Solid State Sci.*, 2002, **4**, 83–86.