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Electronic Supplementary Information (ESI)

Fe(II) metal-organic framework as visible responsive photo-Fenton catalyst for the degradation of organophosphates

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Experimental details

Materials and methods

All used chemicals were obtained commercially and used as received without further purification. SEM images were taken with a JEOL JSM-7500F scanning electron microscope. A Rigaku D/Max-2500 diffractometer with Cu K α radiation (λ = 0.15406 nm) was applied to get the powder X-ray diffraction (PXRD) patterns of samples at 40 kV and 100 mA. Fourier transform infrared (FT-IR) spectra were recorded with KBr pellet by a Nicolet Magna-IR 560 Fourier transform infrared spectrometer. The elemental compositions (C, H, and N) were measured by a Perkin-Elmer 240C analyzer. Thermogravimetric analysis (TGA) was performed with 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. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 VG Lited XPS using Al K α radiation (hv = 1486.6 eV), and binding energies were referred to the C 1s at 285.0 eV. Absorption spectra of solid and solution samples were measured by USA Cary 5000 and Shimadzu UV-2450 spectrophotometers, respectively. The photocatalytic experiments were carried out under the irradiation from a CEL-HX F300/CEL-HX UV300 xenon lamp, and a 420 nm cut-off filter was applied to remove the UV component. The concentrations of substrate and intermediates formed during photocatalytic degradation were determined by HPLC method (Agilent LC 1200). The ions (PO_4^{3-}, NO_3^{-}) were quantified by an ion chromatography (Dionex ICS-900) equipped with an lonpac ASII-HC column (4×250 mm, Dionex), an eluent generator (Dionex EGCIII KOH) and a conductivity detector. The total organic carbon (TOC) of the degraded solution was measured by Analytic jena multi N/C 2100 TOC analyzer. Electron spin resonance (ESR) spectra were obtained using a Brucker model EPR 300E spectrometer.

Synthesis of Fe-pydc

FeSO₄ (0.2782 g, 1 mmol) and H₂pydc (0.1672 g, 1 mmol) were dissolved respectively in 100 mL H₂O and 100 mL DMF. These two solutions were well-mixed at room temperature in a 250 mL round-bottom flask and then heated at 130 °C for 4 h in oil bath. After cooling down to room temperature, the resulting orange precipitate was collected by centrifugation, washed with H₂O, DMF and ethanol in sequence , and then dried at 60 °C in a vacuum drying oven.

Photocatalytic degradation experiments

In a typical procedure, 2 mg of Fe-pydc was ultrasonically dispersed in 200 mL aqueous solution

of organophosphate (0.05 mM) and placed in a 250 mL beaker. The suspension was stirred for 2 h before reaction to reach the adsorption-desorption equilibrium. The irradiation was started immediately after the addition of H_2O_2 (1.25 mM). At the given reaction time intervals, samples (~5 mL) were taken out and filtered to remove the catalyst. The filtrates were subjected to HPLC, ion chromatography and TOC analysis.



Fig. S1 Framework structure of [Mn(pydc)·2H₂O].



Fig. S2 Thermogravimetric curve of as-synthesized Fe-pydc sample.



Fig. S3 UV-vis diffuse reflectance spectrum of Fe-pydc. The absorption spectra of Fe²⁺ ion and pydc²⁻ ligand in solutions were provided for comparison.



Fig. S4 Degradation kinetics of (a) DENP and (b) TNPP in the catalytic system of Fe-pydc. 0.01 g L^{-1} Fe-pydc, $c_{substrate^0} = 0.05$ mM, $c_{H_{2}O_2^0} = 1.25$ mM, 200 mL H₂O, irradiated by a 300 W Xe lamp cutoff below 420 nm.



Fig. S5 ESR spectra of DMPO-radical adducts formed in Fe-pydc systems. 0.01 g L⁻¹ Fe-pydc, $c_{\text{BNPP}^0} = 0.05 \text{ mM}, c_{\text{H}_2\text{O}_2^0} = 1.25 \text{ mM}.$