Supplementary Information

Iron tetrasulfophthalocyanine immobilized on metal organic framework MIL-101: synthesis, characterization and catalytic properties

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Experimental details

Catalysts and materials. Iron tetrasulfophthalocyanine FePcS was prepared according to the published procedure.[S1] MIL-101 was synthesized following a procedure described by Férey et al.[S2] The formula of $[Cr_3O(bdc)_3(H_2O)_2F_{0.72}(NO_3)_{0.28}]$ was assigned based on the elemental analysis data. $FePcS(Bu_4N)_4$ was obtained by replacement of sodium cation with tetrabutylammonium using tetrabutylammonium hydroxide.[S3] 2,3,6-Trimethylphenol, benzyl alcohol, 8-hydroxyquinoline and *tert*-butyl hydroperoxide were purchased from Aldrich. The other reactants were obtained commercially and used as received.

Immobilization of FePcS on MIL-101. The supported FePcS/MIL samples were prepared by dissolving a definite amount of FePcS (5÷15 mg) in water (3 mL), adding 100 mg of MIL-101, stirring for 3 h, filtering off, washing with water, and drying at 120°C until the weight remained constant. The immobilization process for controlled by UV-vis. The amount of immobilized FePcS was confirmed also by elemental analysis.

Adsorption measurements were carried out in a glass reactor at 25°C. The adsorbent (MIL-101, 10 mg) was placed into the reactor, and a FePcS solution in water (0.5 mL, 0.001÷0.01 M) was added. Samples of the solution were taken by a syringe (150 µL) after 16 h, diluted with water (50 mL), and then FePcS concentration in solution was determined by UV-vis ($\lambda = 635$ nm, $l = 10$ mm).

Desorption measurements were carried out in the same reactor at 25°C. Water (0.5 mL) was added to 10 mg of a MIL-101 sample containing FePcS (the amount of FePcS was determined from the adsorption measurements). Samples of the solution were taken by a syringe (150 µL) after 24 h, diluted with water (50 mL), and then FePcS concentration in the solution was determined from the UV-vis spectra using a calibration curve. The amount of FePcS irreversibly adsorbed on MIL-101 was determined from the point where the adsorption isotherm cuts axis Y. The results acquired from the adsorption study were in agreement with the ICP-AES elemental analysis data.

Ion exchange experiments. Treatment with an aqueous solution of $NaClO_4$ was performed at room temperature. 50 mg of 15 wt% FePcS/MIL-101 were added to 1 mL of 1 M $NaClO_4$ in water. The mixture was stirred for 2 h, then the solid was filtered off and FePcS concentration in the filtrate was determined by UV-vis. Similar experiments were performed using Bu_4NClO_4 in MeCN.

Catalytic experiments and product analysis. Catalytic oxidations were performed in thermostated glass vessels at 30-60°C under vigorous stirring (500 rpm). Typically, the reactions were initiated by adding 0.12-0.18 mmol of ^tBuOOH to a mixture containing 0.02-0.18 mmol of substrate and 4-6 mg (0.16-0.9 µmol Fe) of supported FePcS catalyst or 0.3-1.4 mg of $FePcS(Bu_4N)_4$ (0.16-0.9 µmol Fe) in 1 mL of solvent. The substrate conversions and product yields were quantified by GC using biphenyl as the internal standard as well as by ^1H NMR spectroscopy.

Instrumentation. FT-IR spectra were recorded on a BOMEM-MB-102 spectrometer. Raman spectra were collected using Fourier transform spectrometer RFS 100/S from Bruker. The 1064 nm line of Nd-YAG laser (100 mW) was used for the spectral excitation. All measurements were performed with a spectral resolution of 4 cm^{-1}. Nitrogen adsorption at 77 K was studied using an Autosorb-6B-Kr (Quantachrome) instrument within a partial pressure range of 10^{-5}–1.0 millitorr. Before measurements, the samples were degassed at room temperature under dynamic vacuum of 25 millitorr overnight. DR-UV-vis spectra were recorded on a Shimadzu UV-vis 2501PC. UV-vis spectra were run using a Cary 50 Varian spectrophotometer. XRD measurements were performed on an X-ray diffractometer DRON 3M using cupric radiation ($CuK_{\alpha1,2}$ 1.54060; 1.54439 Å). XPS measurements were carried out on a SPECS's machine equipped with a hemispherical electron energy analyzer PHOIBOS-150, an X-ray source XR-50 with a twin Al/Mg anode, and ions source IQE-11. Core-level spectra were obtained using Al $K\alpha$ radiation ($h\nu$ = 1486.6 eV). For calibration of the charge shift, C*1s* peak at 284.8 eV from adventitious hydrocarbon was used. The high-resolution TEM images of periodic structures were analyzed by the Fourier method. Local energy-dispersive X-ray analysis (EDXA) was carried out on an EDAX spectrometer (EDAX Co.) equipped with a Si (Li) detector with a resolution of 130 eV. Samples to be examined by HRTEM were prepared on a perforated carbon film mounted on a copper grid. GC analyses were performed using a Tsvet-500 gas chromatograph equipped with a flame ionization detector and DB-5MS capillary column (30 m×0.25 mm).

References :

S1 J. H. Weber and D. H. Busch, *Inorg. Chem.*, 1965, **4**, 469.

S2 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science,* 2005, **309**, 2040.

S3 O. V. Zalomaeva and A. B. Sorokin, *New J. Chem.*, 2006, **30**, 1768.

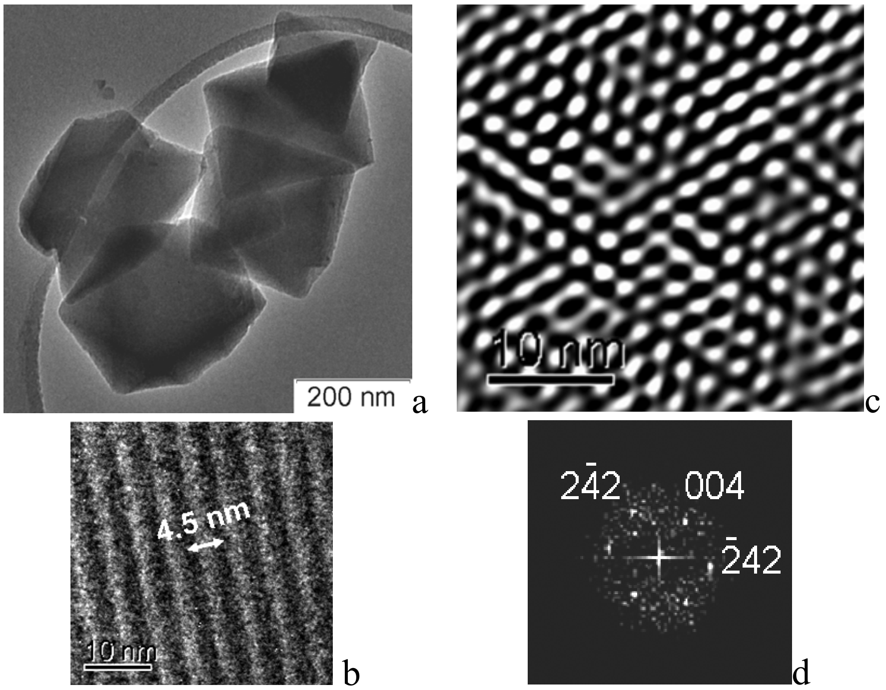

Figure S1. HRTEM micrographs of FePcS/MIL-101: a – morphology of sample particles; b – periodic image of lattice planes (002) of crystalline particles; c – HRTEM-image (Fourier-filtered) and d – corresponding Fourier pattern with Millers indexes for lattice planes (d_{242}≈2.0 nm, d_{004}≈2.3 nm). Planes of a crystal lattice on HRTEM micrographs correspond to maxima on XRD patterns.

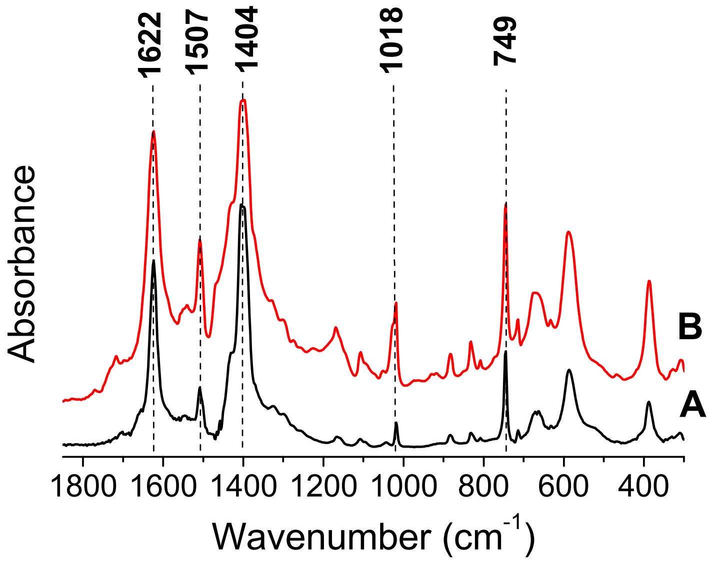

Figure S2. FT-IR spectra of (A) MIL-101 and (B) 15 wt% FePcS/MIL-101.

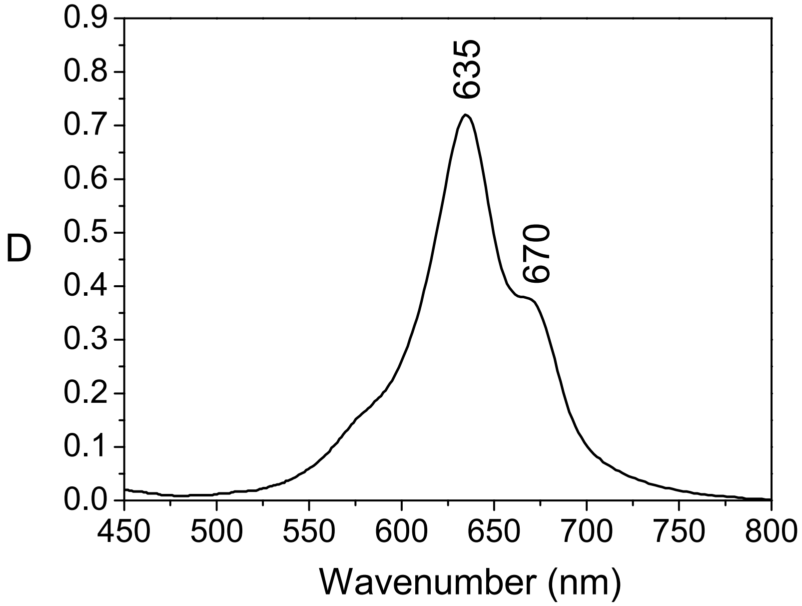

Figure S3. UV-vis spectrum of FePcS in H_2O ($1 \cdot 10^{-5}$ M).

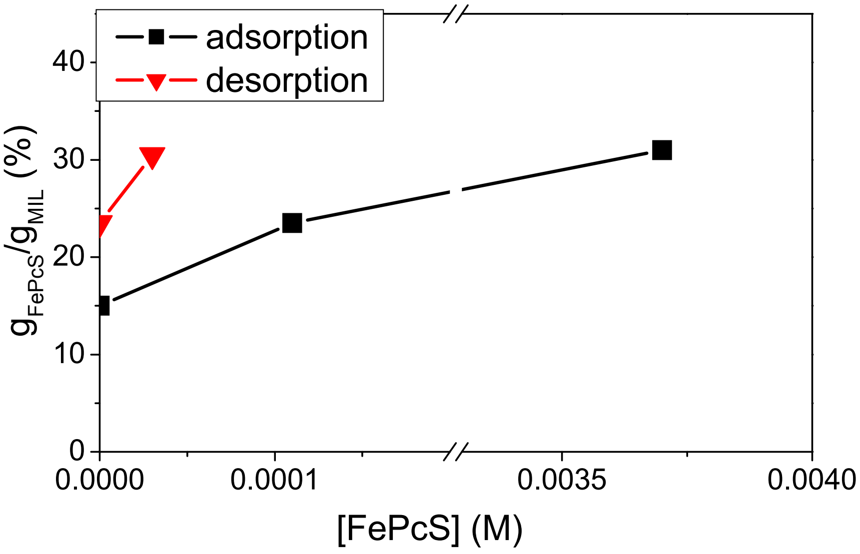

Figure S4. Adsorption/desorption isotherms for FePcS on MIL-101 (H_2O, 25°C). Adsorption is marked by ■, desorption is marked by ▼.

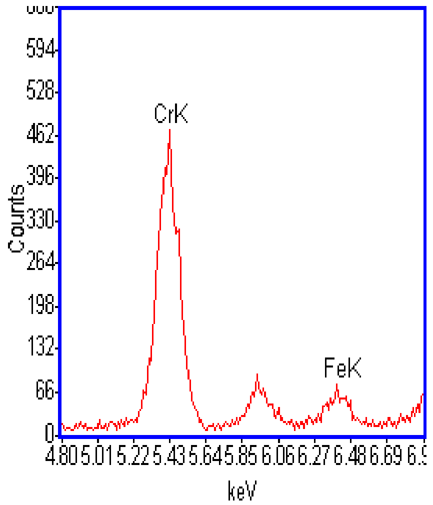

Figure S5. Typical EDX spectra from a narrow area (~10 nm in diameter) of FePcS/MIL-101 particles (Cr*Kα*, Cr*Kβ* and Fe*Kα* – very similar signals are observed independently of the electron probe position).

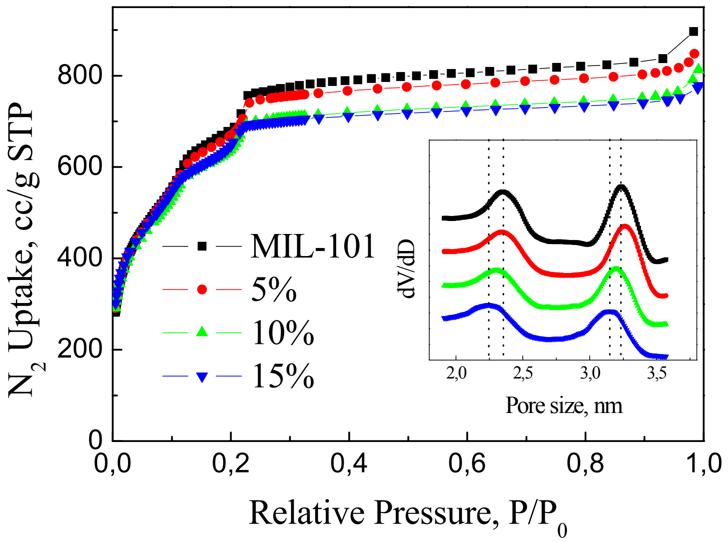

Figure S6. N_2 adsorption isotherms measured at 77K: initial MIL-101, 5, 10 and 15 wt% FePcS/MIL-101. Insert: pore volume-size distributions calculated from the N_2 adsorption isotherms using the Saito-Foley method.

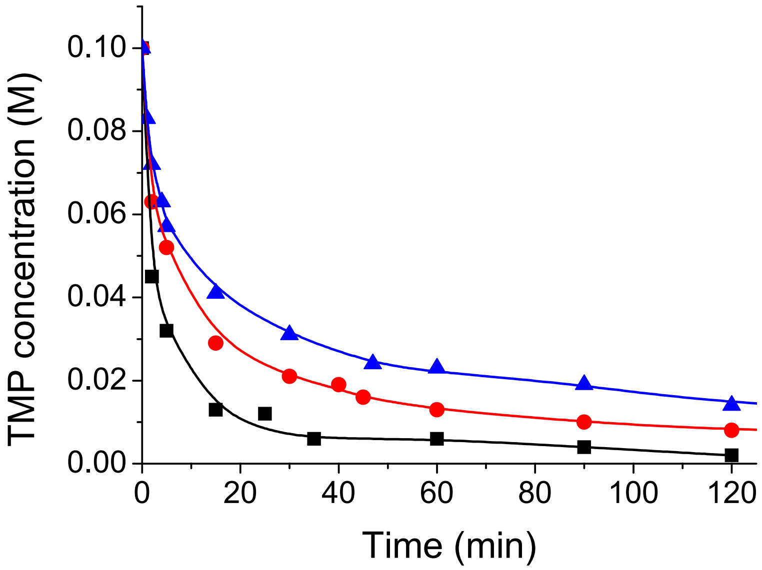

Figure S7. Kinetic profiles for TMP oxidation in the presence of FePcS/MIL-101 with different FePcS loading: (■) 5 wt%, (●) 10 wt% and (▲) 15 wt%. Reaction conditions: [TMP] = 0.1 M; 0.14 mol.% Fe; [^{t}BuOOH] = 0.3 M (used as 70 wt% aqueous solution); 30°C; MeCN.

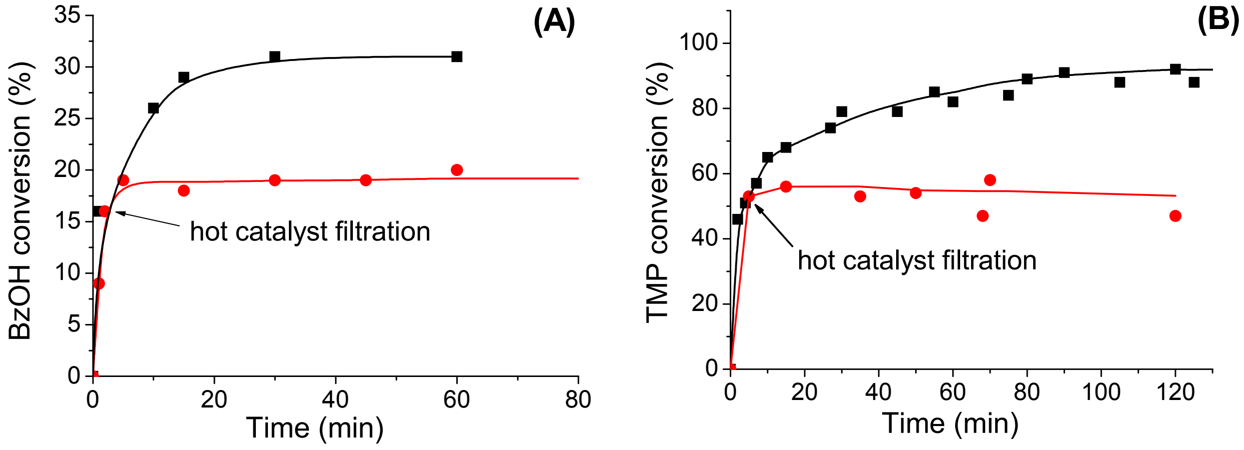

Figure S8. (A) Oxidation of BzOH with ^{t}BuOOH over 15 wt% FePcS/MIL-101. Reaction conditions: [BzOH] = 0.18 M; 0.5 mol.% Fe (15 wt.% FePcS/MIL-101); [^{t}BuOOH] = 0.18 M (70 wt.% aqueous solution); 60°C; MeCN. (B) Oxidation of TMP with ^{t}BuOOH over 15 wt% FePcS/MIL-101. Reaction conditions: [TMP] = 0.1 M; 0.14 mol% Fe; [^{t}BuOOH] = 0.5 M (70 wt% aqueous solution); 30°C; MeCN.

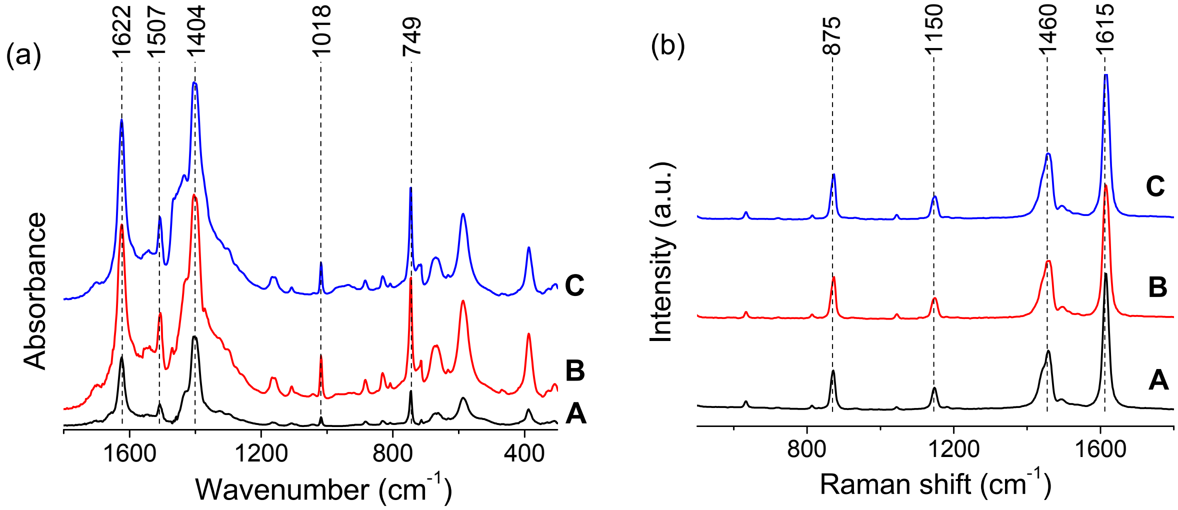

Figure S9. (a) FT-IR and (b) Raman spectra of MIL-101: (A) initial, (B) after treatment of 10 mg MIL-101 with 0.4 M ^{t}BuOOH in 2 mL MeCN at 25°C for 5 h and (C) after treatment of 10 mg MIL-101 with 0.2 M ^{t}BuOOH in 2 mL MeCN at 80°C for 5 h. ^{t}BuOOH was used as 70 wt% aqueous solution.