

Synergetic effects of encapsulated phthalocyanine complexes in MIL-101 for the selective aerobic oxidation of tetralin

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Experimental part:

Synthesis of MIL-101

Mesoporous MIL-101 was prepared and purified by a modified synthesis introduced by *Ferey et al.*^{S1}

A solution containing 2.4 g chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9 \cdot \text{H}_2\text{O}$, Fluka, >97 %), 1.50 g 1,4-benzenedicarboxylic acid (H_2BDC) (Sigma-Aldrich, 98 %), 0.30 ml of hydrofluoric acid (40 % in water, Merck) and 30 ml deionised H_2O was introduced in a 48 ml Teflon-liner. The mixture was placed in an autoclave and was heated to 493 K for 9 h (heating ramp 25 K/h). After cooling period of 8 h, the reaction mixture was filtered through a large pore fritted glass filter (G 1) to eliminate excess of recrystallised terephthalic acid. The product was separated from water by centrifugation at 4000 rpm for 20 min. In order to remove incorporated 1,4-benzenedicarboxylic acid the as-synthesized product was first treated in 100 ml of ammonium fluoride solution in water/ethanol 1:1 v/v (3.7 g NH_4F (Sigma-Aldrich, $\geq 98\%$) for 24 h at 70 °C. Afterwards the halide salt excess was washed by an aqueous soxhlet-extraction for 20 h. Finally, the solid was dried at 423 K for 9 h and at reduced pressure to obtain activated, fine powdered MIL-101.

Synthesis of phthalocyanine complexes

Preparation of metal phthalocyanine complexes was performed according to published procedures: $\text{FePc}(\text{COOH})_4$ ², FePc^tBu_4 ³, $(\text{FePc}^t\text{Bu}_4)_2\text{N}$ ⁴, $\text{FePc}(\text{SO}_3\text{H})_4$ ⁵, FePcF_{16} ⁶, RuPcF_{16} ⁷, $\text{CoPc}(\text{COOH})_8$ ⁸.

Synthesis phthalocyanine complexes containing MIL-101

25 mg of MPcF_{16} (M=Fe, Ru) or $(\text{FePc}^t\text{Bu}_4)_2\text{N}$ complexes were dissolved in 25 ml of acetone (Acros Organics, >99 %) or dichloromethane, (Sigma-Aldrich, >99 %) respectively. 250 mg

of activated MIL-101 were added to intensively blue coloured solution and continuously stirred for 72 h. After complete solvent evaporation the composite materials were washed, stirred for 2 h and centrifuged at 4000 rpm for 20 min several times until the solutions remain colourless. Finally, solids were dried under air for 4 h at 423 K followed by drying at reduced pressure over night at the same temperature to obtain activated catalyst systems.

Catalytic tetralin oxidation

Catalytic tetralin oxidation under static pressure was carried out in parallel reactors with eight pressure stable micro-reaction-vessels (3 ml, Supelco) inside a temperature-controlled steel vessel. In a typical reaction a mixture of 2.5 ml of tetralin (Sigma-Aldrich, 99 %) and 1 mg of the pure complexes or 5 mg of the MIL-101 supported complex systems was placed into the batch reactor and heated under continuously stirring at 900 rpm to the desired temperature (50-130 °C) under static oxygen (Alphagaz 1, 99 %) or synthetic air pressure (Alphagaz 1, 99.999 %) up to 6-10 bar for 1-24 h. After cooling down to room temperature the reaction mixtures were depressurized and centrifuged. The conversion and selectivity of the oxidation reactions were subsequently analyzed by gas chromatography (Agilent technologies 6890N) using a HP-5 capillary column and a flame ionization detector (FID).

Catalytic oxidation of adamantane-1,3- d_2

Adamantane-1,3- d_2 (Ad- d_2) was prepared as previously described (ref. S6). Ad- d_2 (3.4 mg) was dissolved in 2.5 mL of acetonitrile and 5 mg of the FePcF₁₆-MIL-101 or RuPcF₁₆-MIL-101 materials were added. The resulting mixture was stirred at 90 °C at 8 bars of dioxygen for 6 h in the parallel batch reactors applied for tetralin oxidation. The reaction products were analyzed by GC-MS method (Hewlett Packard 5973/6890 system ; electron impact ionization at 70 eV, He carrier gas, 30 m x 0.25 mm cross-linked 5 % PHME (0.25 µm coating) capillary column, HP-5MS). The exact isotopic composition of 1-adamantanol was calculated by integration of all scans of the 1-adamantanol peak since AdOH- d_1 and AdOH- d_2 were partially separated on the GC column. KIEs were obtained from the intensities of molecular peak at $m/z=154$ (for AdOH- d_2) and $m/z=153$ (for AdOH- d_1) after correction on natural ¹³C abundance (1.08 % x 10 carbon atoms = 10.8 %).^{S6}

Characterization

N₂-physisorption:

Nitrogen and hydrogen physisorption isotherms were measured at -196°C using a Micromeritics 2020 apparatus. Prior to the measurement, the samples were activated in vacuum at 150°C for 24 hours. Specific surface areas were calculated using the BET equation ($p/p_o = 0.05\text{-}0.2$).

Powder X-ray diffraction:

Powder X-ray diffraction patterns were recorded using a Bruker D-5005 diffractometer (Bragg–Brentano geometry, graphite monochromator, Cu K α radiation).

SEM/EDS measurements:

FESEM (Field Emission Scanning Electron Microscopy) and EDS-analysis (Energy Dispersive Spectrometer) on complex containing MIL-101 catalysts were carried out with a Stereoscan 260 SEM with EDX analysis system using SE (Secondary Electrons) and BSE (Backscattered Electrons) detectors, respectively. Elemental analyses using EDX were obtained as a mean value of five measurements in a magnification of 3000.

(Diffusion reflection) UV-VIS spectroscopy:

UV-VIS experiments were carried in transmission (solutions) and diffuse reflectance mode (MPcX@MIL-101) using a Perkin-Elmer Lambda 35.

Elementary analysis (ICP-OES)

Elemental analysis was measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The samples were dissolved in a boiling sulphuric and nitric acid mixture under reflux conditions and metal contents were analyzed using ICP-OES Activa spectrometer (Jobin-Yvon).

Figures:

Table S1 Catalytic activity, selectivity, turnover number after 6 h and sizes of applied phthalocyanine complexes as homogeneous catalysts in tetralin oxidation.

Complex	FePc (COOH) ₄	FePc ^t Bu ₄	(FePc (^t Bu) ₄) ₂ N	FePc (SO ₃ H) ₄	FePc F ₁₆	RuPc F ₁₆	CoPc (COOH) ₈
X [%] ^a	0	27	25	0	21	38	0
S _{one} [%] ^b	-	68	69	-	68	70	-
TON ^c	0	3800	7400	0	3400	5200	0

^a Conversion of tetralin, ^b selectivity toward 1-tetralone, ^c turnover number for the tetralin oxidation into 1-tetralol and 1-tetralone after 6 h.

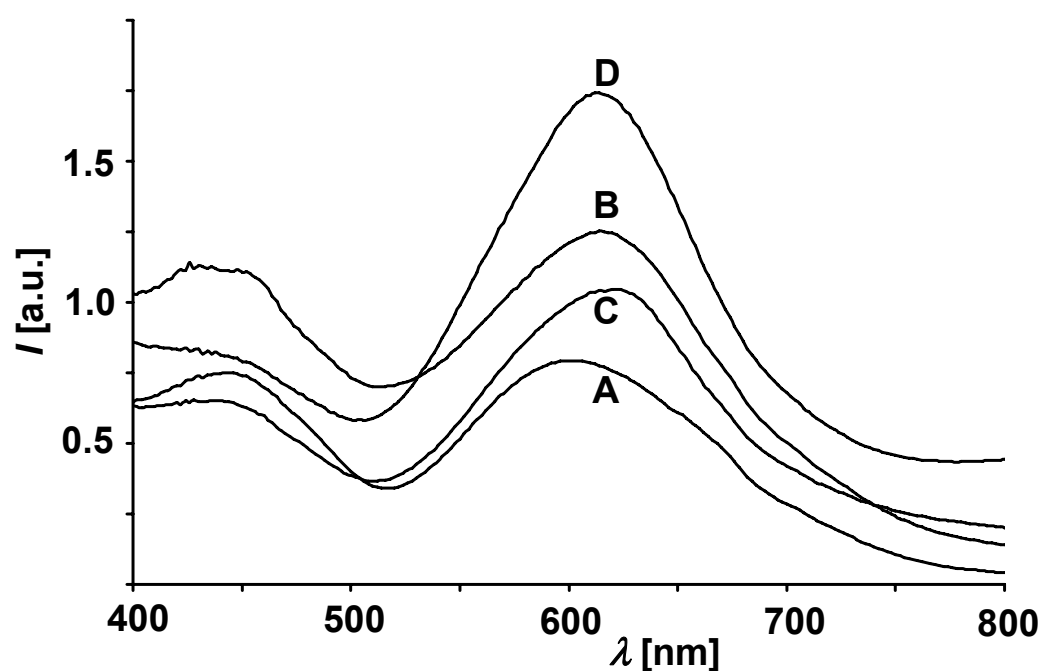


Fig. S1 Diffuse reflectance UV-VIS spectra of non-loaded MIL-101 (A), (FePc^tBu₄)₂N@MIL-101 (B), FePcF₁₆@MIL-101 (C) and RuPcF₁₆@MIL-101(D).

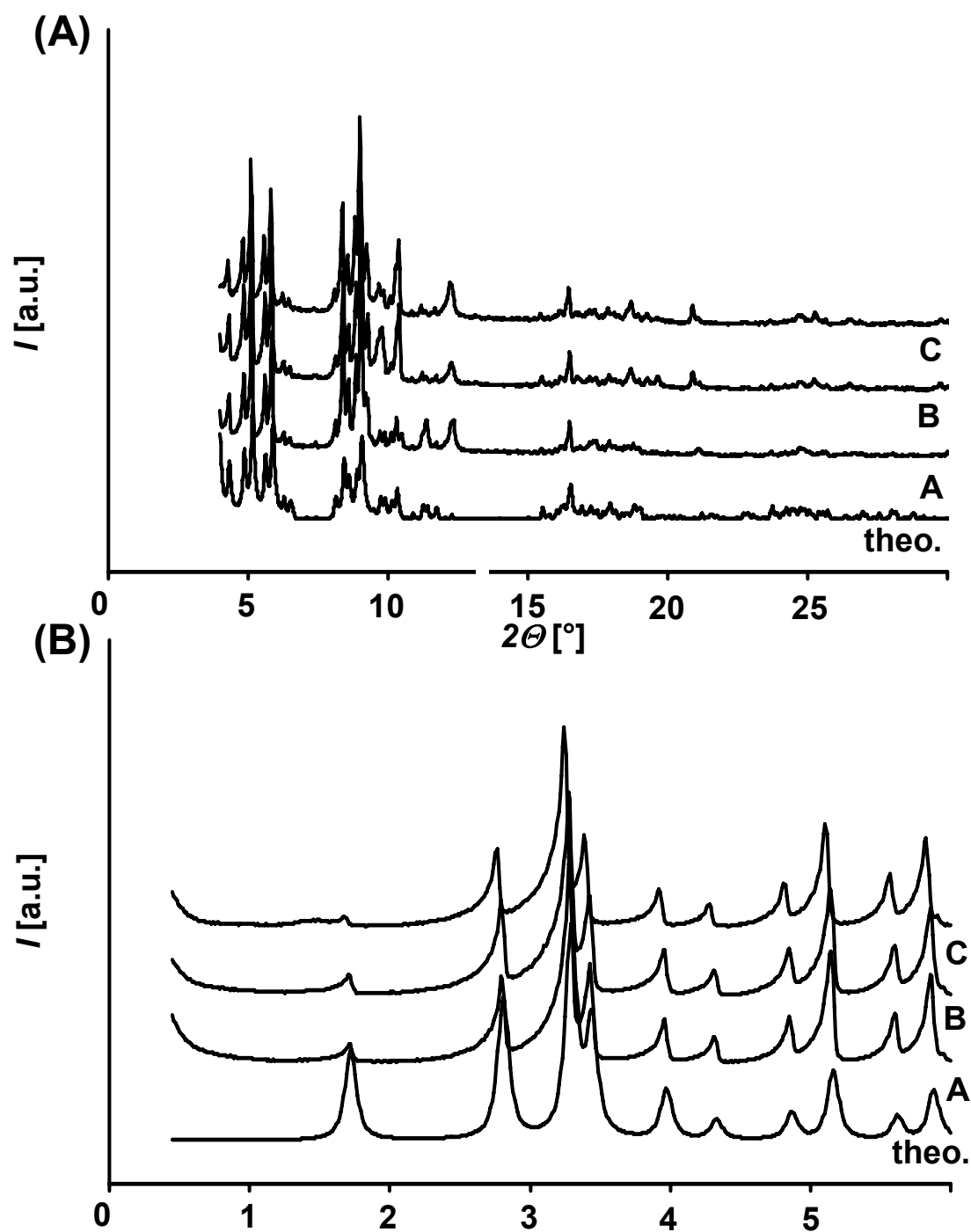


Fig. S2 Nitrogen physisorption isotherms and X-ray powder diffraction patterns of non-loaded MIL-101 (A), FePcF₁₆@MIL-101 (B) and RuPcF₁₆@MIL-101 (C).

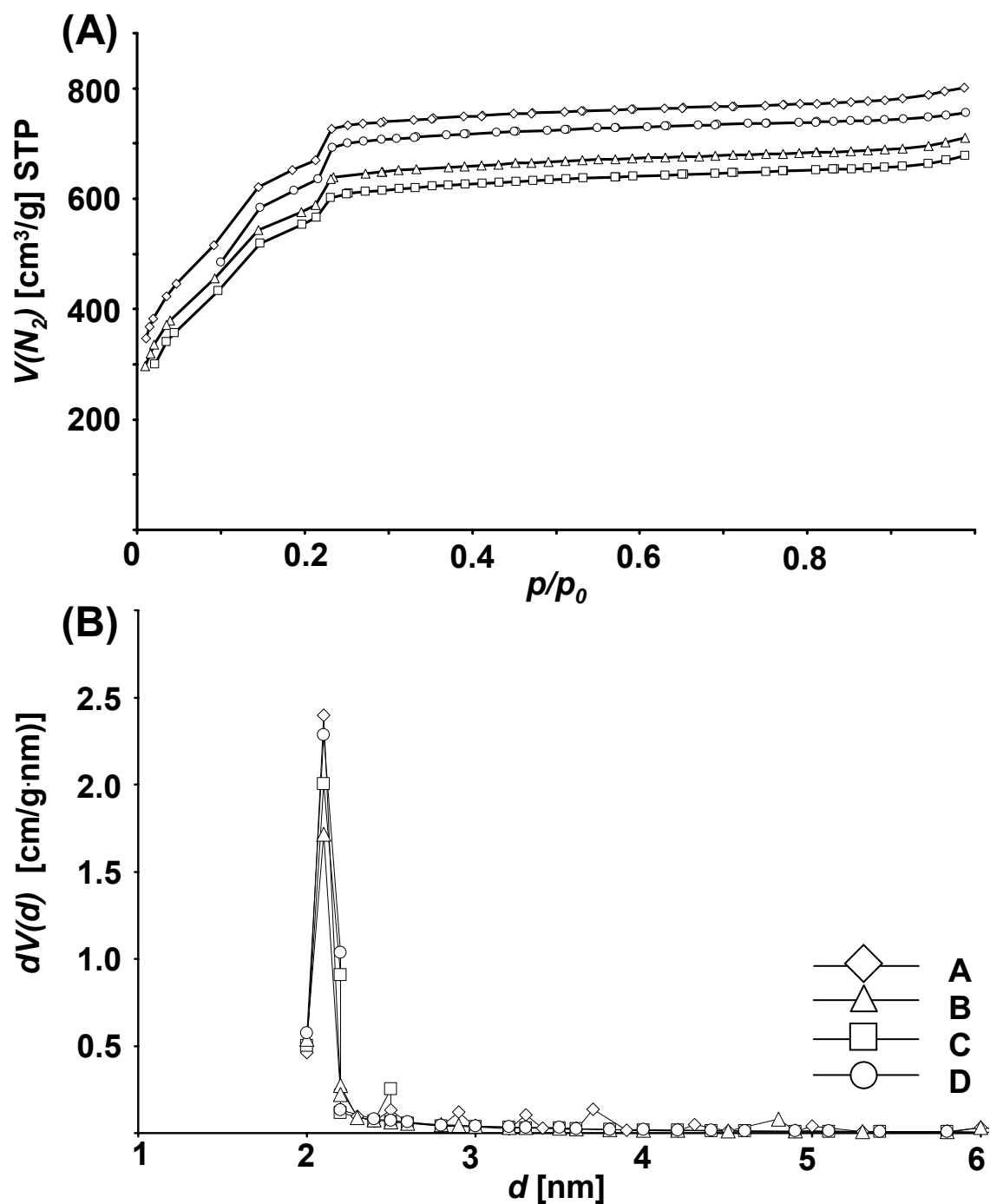


Fig. S3 Nitrogen physisorption isotherms patterns of non-loaded MIL-101 (A), FePcF₁₆@MIL-101 (B), RuPcF₁₆@MIL-101 (C) and (FePc^tBu₄)₂N@MIL-101 (D).

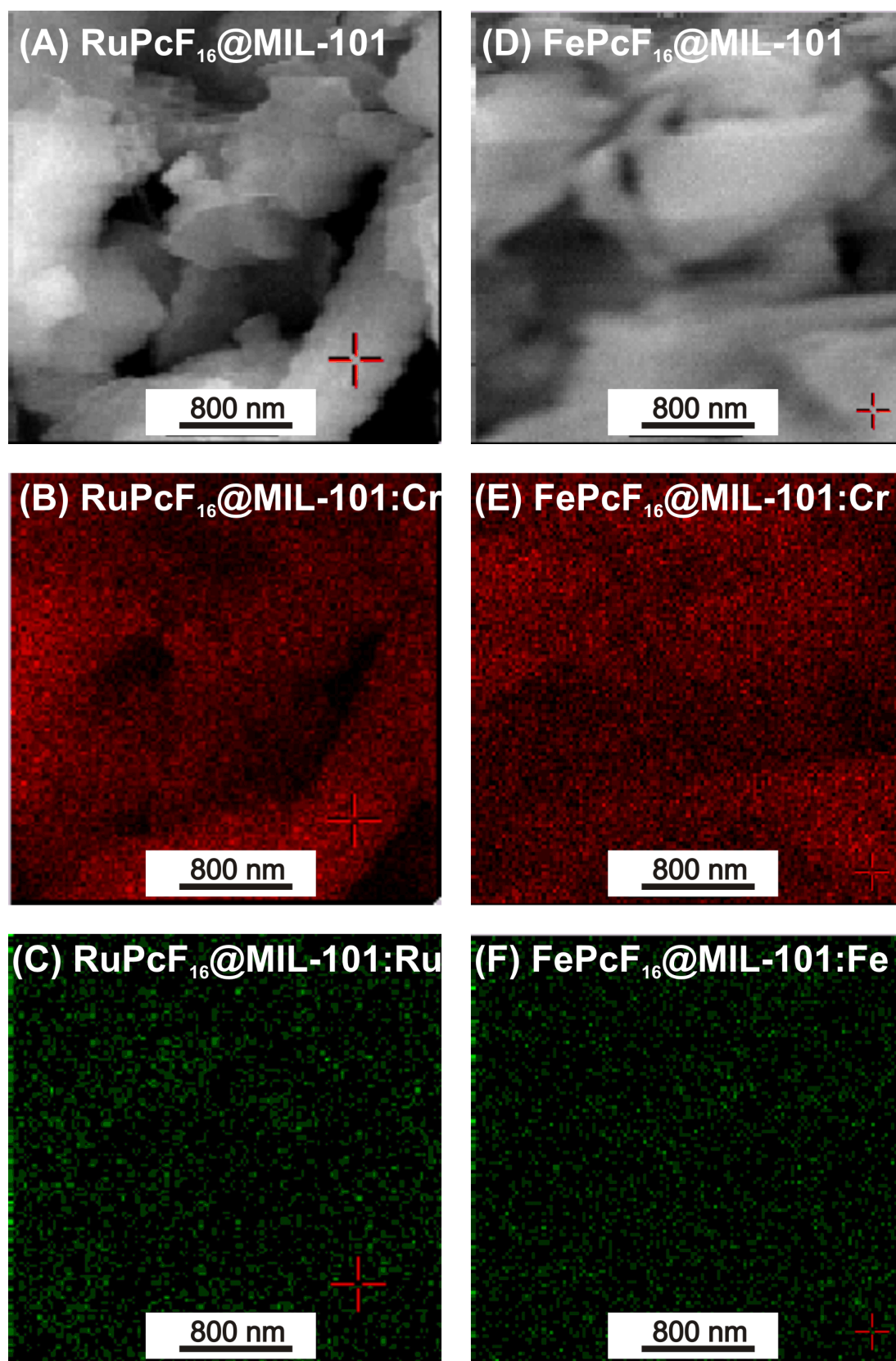


Fig. S4 EDS analysis of iron and ruthenium perfluorophthalocyanines containing Cr-MIL-101

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