[FeFe] hydrogenase active site model chemistry in a UiO-66 Metal-Organic Framework

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Supporting Information

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General Methods

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Fisher Scientific, VWR and others). Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz). Chemical shifts are given in parts per million (ppm) and are referenced to the appropriate protic solvent peak or 0 ppm for TMS.

Experimental Procedures

Solvothermal Synthesis of UiO-66. UiO-66 was prepared according to the previously reported procedure:[1] A solid mixture of $ZrCl_4$ (16 mg, 0.07 mmol), terephthalic acid (11.6 mg, 0.07 mmol) and benzoic acid (427 mg, 3.5 mmol) was dissolved in DMF (4 mL). This mixture was capped and sealed in a 20 mL vial, sonicated for a few minutes until a clear solution was formed and allowed to react solvothermally at 120 °C for 24 h. After cooling, the mixture was centrifuged, and the solids were left to soak in MeOH for 3 days, during which time the solution was exchanged with fresh MeOH (10 mL) every 24 hours. After 3 days of soaking, the solids were centrifuged and dried under vacuum. Smaller crystals were prepared by the same procedure, using acetic acid (4.2 g, 7 mmol) as modulator instead of benzoic acid.

PSE of UiO-66 with [FeFe](dcbdt)$(CO)_6$. [FeFe](dcbdt)$(CO)_6$ (dcbdt=1,4-dicarboxylbenzene-2,3-dithiolate) was synthesized according to a previous publication.[1] [FeFe](dcbdt)$(CO)_6$ (50.8 mg, 0.1 mmol) was dissolved in deoxygenated Millipore water (2 mL), and the mixture added to a 24 mL vial. Deoxygenation was performed by bubbling Millipore water with argon. 28 mg of UiO-66 were added to the solution, the vial was capped, sealed and placed on a shaker. The mixture was allowed to react at ambient temperature for 24 hours. After 24 hours, the powder was washed with MeOH and soaked in MeOH for 3 d while exchanging the solvent every 24 h until the liquid remained clear. Then, the sample was dried under vacuum for further use.

Ligand exchange in the MOF. 5 mg of UiO-66-[FeFe](dcbdt)$(CO)_6$ and 1 mg Me_3NO were placed into a Schlenk flask under argon and 5 ml CH_3CN (dry, deoxygenated) was added. To this suspension, 1 ml of a 1.0 M THF solution of the respective phosphine ligand was added. (For PMe_3 and PEt_3 these solutions were purchased from Sigma Aldrich, for PPh_3, the solution was prepared from solid PPh_3). The reaction was stirred under argon for 12 hours up to 5 days. Solid MOFs were separated by centrifugation, washed extensively with CH_3CN and then dried under vacuum.

Synthesis of the reference complexes. The synthesis of the reference complexes was performed according to a literature procedure.[2] 50 mg of $Fe_2(bdt)(CO)_6$ was dissolved in 20 ml CH_3CN (dry, deoxygenated) in a Schlenk flask under argon. 25 mg Me_3NO was added and the mixture was stirred for 10 minutes at ambient temperature. Then, 0.2 ml of a 1.0 M THF solution of the respective phosphine ligand was added and the reaction mixture was stirred for 4 h until all the starting material was consumed as indicated by FT-IR. In case of PPh_3 ligand, the reaction was left for stirring overnight. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography yielding a red band. For the PMe_3 analogue, two fractions were isolated, one of which was a mononuclear complex $Fe(bdt)(CO)_2(PMe_3)_2$.

$Fe_2(bdt)(CO)_4(PMe_3)_2$: IR (CH_3CN) ν_{co} = 1991, 1948, 1924, 1917 (shoulder) cm^{-1}.

$Fe(bdt)(CO)_2(PMe_3)_2$: IR (CH_3CN) ν_{co} = 2009, 1954 cm^{-1}.

$Fe_2(bdt)(CO)_4(PEt_3)_2$: IR (CH_3CN) ν_{co} = 1992, 1947, 1929 cm^{-1}.

$Fe_2(bdt)(CO)_4(PPh_3)_2$: IR (CH_3CN) ν_{co} = 2001, 1957, 1941 cm^{-1}.

Sample preparation for PXRD after protonation. 20 mg UiO-66-[FeFe]$(CO)_{6-x}(PMe_3)_x$ was added to a solution of triflic acid in MeCN (11.3 mM, 20 mL) and kept for 15 minutes. Then the solid was centrifuged off and a PXRD was recorded.

Powder X-ray Diffraction (PXRD) Analysis. All UiO-66 samples were dried in vacuum prior to PXRD analysis. PXRD data were collected at ambient temperature on a D5000 Bruker diffractometer at 40 kV, 40 mA for Cu Kα (λ= 1.5418 Å), with a scan speed of 1 sec/step, a step size of 0.02° in 2θ, and a 2θ range of ~5 to 45° (sample dependent).

Digestion and Analysis by ^{1}H NMR. Approximately 5 mg of UiO-66 materials were digested with sonication in a mixture of 590 µL CD_3OD and 10 µL of 40% HF.

Scanning Electron Microscopy-Energy Dispersed X-ray Spectroscopy. UiO-66 films were transferred to conductive carbon tape on a sample holder disk, and coated using an Au/Pd-sputter coating for 60 sec. A Zeiss 1550 instrument was used for acquiring images using a 5 kV energy source under vacuum.

Fourier-transformed Infrared (FTIR) Spectroscopy. IR absorption spectra were recorded on a Bruker FT-IR spectrometer. A liquid sample cell (Bruker A140) with CaF_2 windows and path-length 0.5 mm was used. For reference complexes, 1 mM solutions were prepared in CH_3CN (spectroscopic grade). For the MOF samples, 1 mg of UiO-66 material was suspended in 1 mL CH_3CN. FTIR data were collected at ambient temperature from 4000 cm^{-1} and 850 cm^{-1}.

Electrochemical analysis. Electrochemical data were obtained by cyclic voltammetry using an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). A three-electrode setup was used with a glassy carbon counter electrode, an Ag/$AgNO_3$ reference (CH Instruments, 0.01 $AgNO_3$ in acetonitrile) and modified glassy carbon working electrode. For electrode fabrication, an ink solution was prepared by mixing the MOF (1 mg) and carbon black (4 mg) in an aliquot (0.5 mL) of the 2-propanol solution, which contains 0.5% v/v of Nafion® 117, followed by ultra-sound sonication for 1 h. The ink solution (10 µL) was drop-casted on a polished glassy carbon electrode (geometrical surface area 0.38 cm^2) and dried in air for 24 h. Control experiments were performed with glassy carbon disc for voltammetry (diameter 3, freshly polished). All measurements were conducted with degassed anhydrous CH_3CN and tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Fluka, electrochemical grade) as supporting electrolyte (0.1 M).

Supporting Figures and Tables

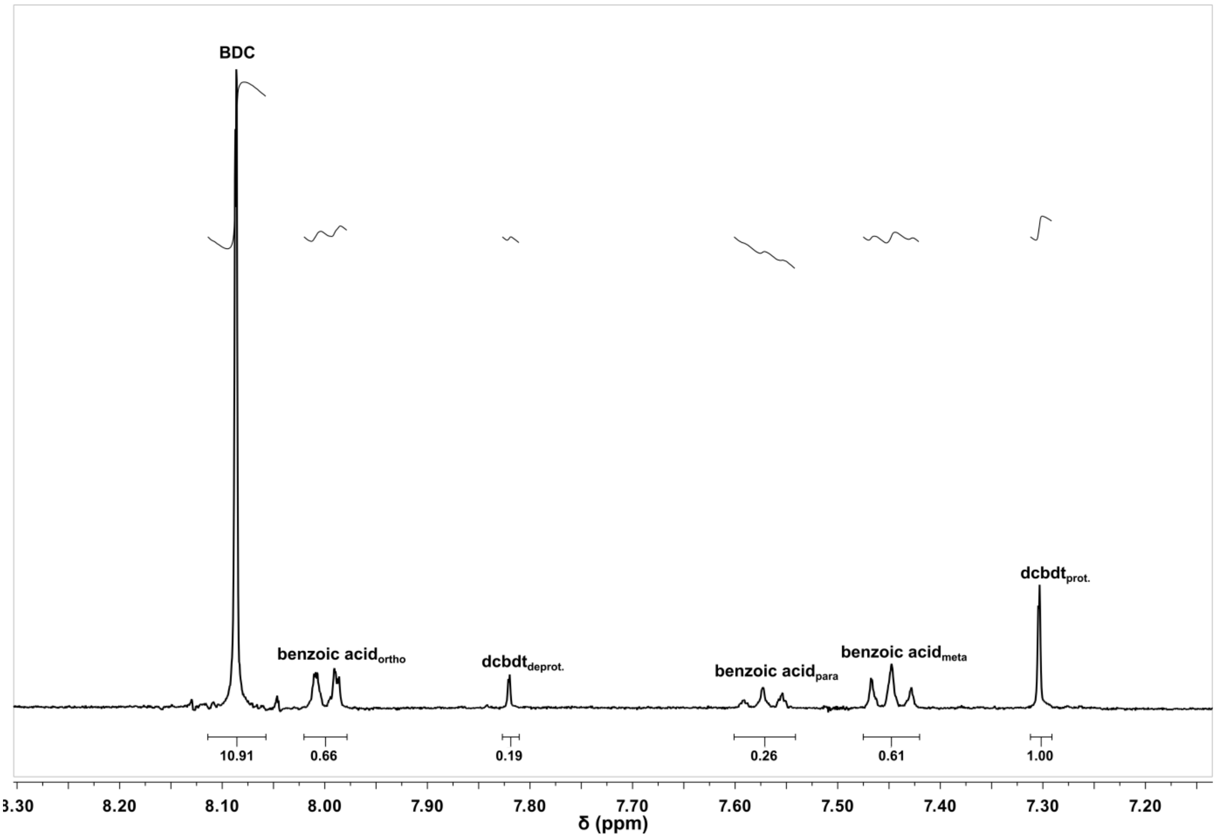

Figure S1. ^{1}H-NMR of digested UiO-66-[FeFe](dcbdt)(CO)$_6$. BDC = 1,4-benzenedicarboxylate, dcbdt = 1,4-dicarboxy 2,3-benzenedithiolate and mod. = benzoic acid modulator. Two singlets are visible for the dcbdt ligand due to different protonation states of the compound. The two singlet can be observed also in the ^{1}H-NMR spectrum of isolated [FeFe](dcbdt)(CO)$_6$.

Calculation of PSE:
BDC 10.91/4H = 2.73
benz.(ortho) 0.66/2H = 0.33
benz.(para) 0.26/1H = 0.26
benz.(meta) 0.61/2H = 0.305

dcbdt 1.19/2H = 0.595

total of 4.2175
Percentage dcbdt of total linker content:
0.595/4.2175 = 0.141 = 14.1%

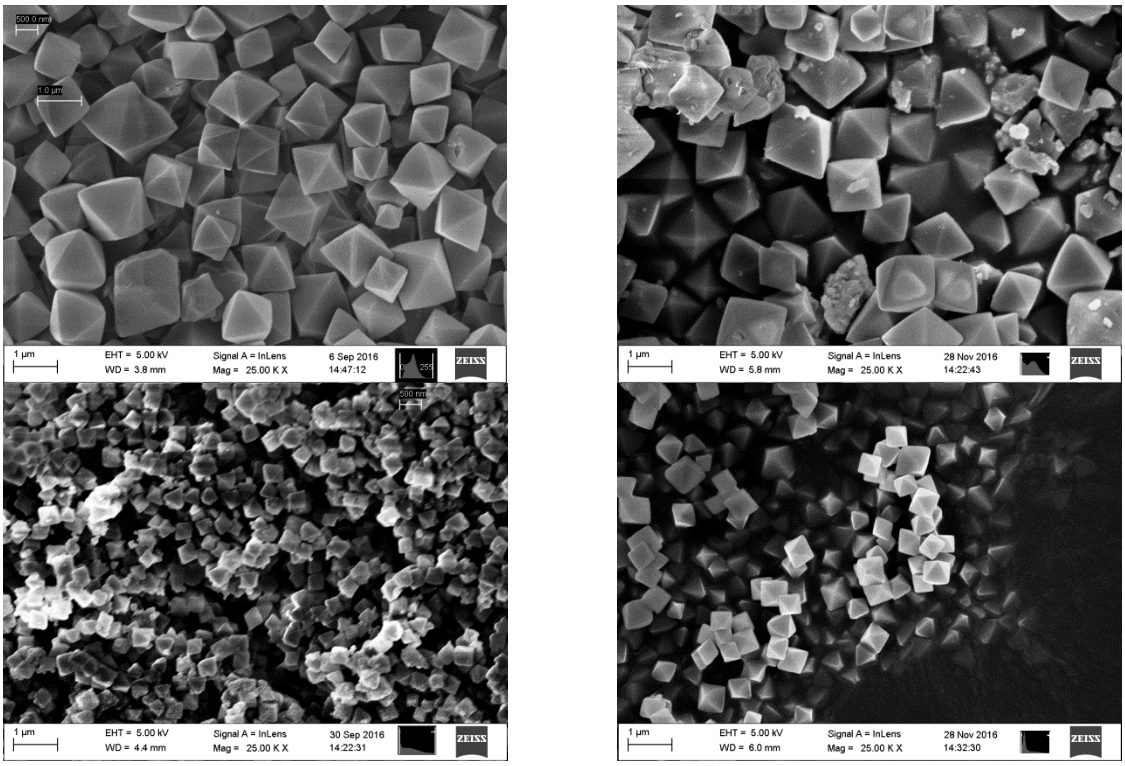

Figure S2. Top-view SEM images. Top-Left: UiO-66-[FeFe](dcbdt)$(CO)_6$ prepared with benzoic acid modulator. Bottom-Left: UiO-66-[FeFe](dcbdt)$(CO)_6$ prepared with acetic acid modulator. Right: corresponding UiO-66-[FeFe](dcbdt)$(CO)_6(PMe_3)_2$.

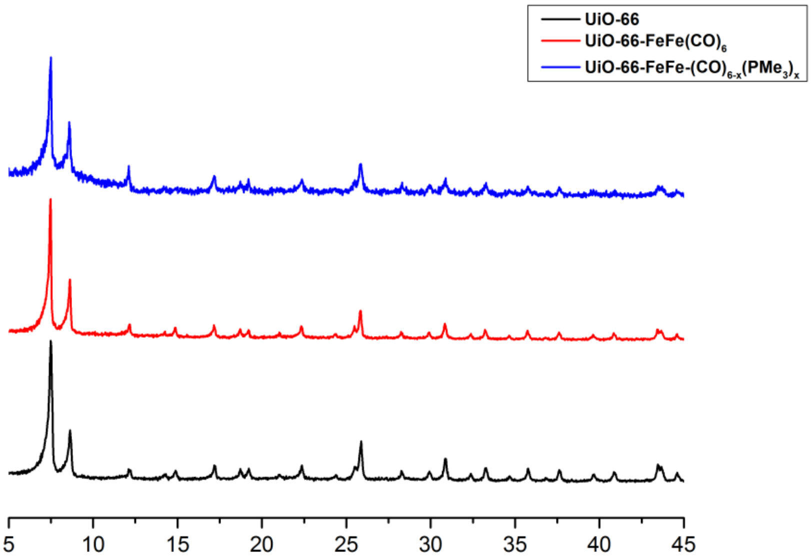

Figure S3. PXRD of UiO-66, UiO-66-[FeFe](dcbdt)$(CO)_6$ and the ligand exchange product UiO-66-[FeFe]$(CO)_{6-x}(PMe_3)_x$.

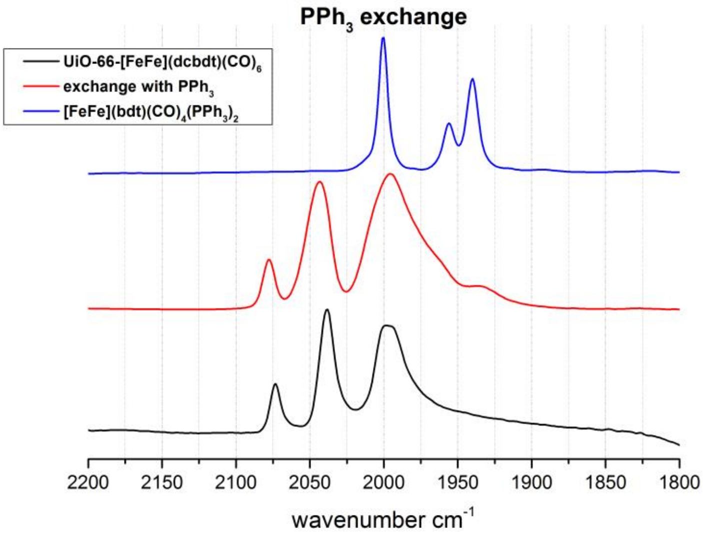

Figure S4. IR spectrum for ligand exchange reaction with PPh_3.

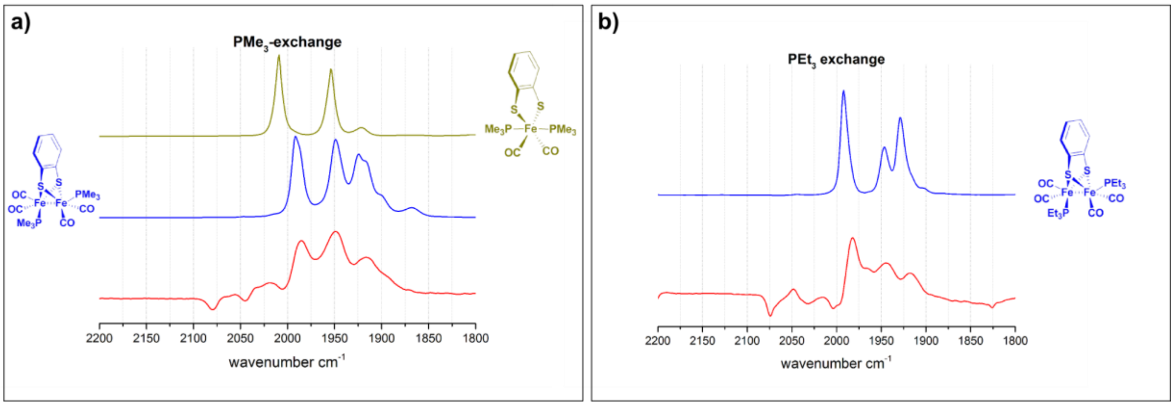

Figure S5. Difference IR spectra (red) obtained by subtracting the spectrum of UiO-66-[FeFe](dcbdt)$(CO)_6$ from the respective spectra after phosphine exchange with a) PMe_3 and b) PEt_3.

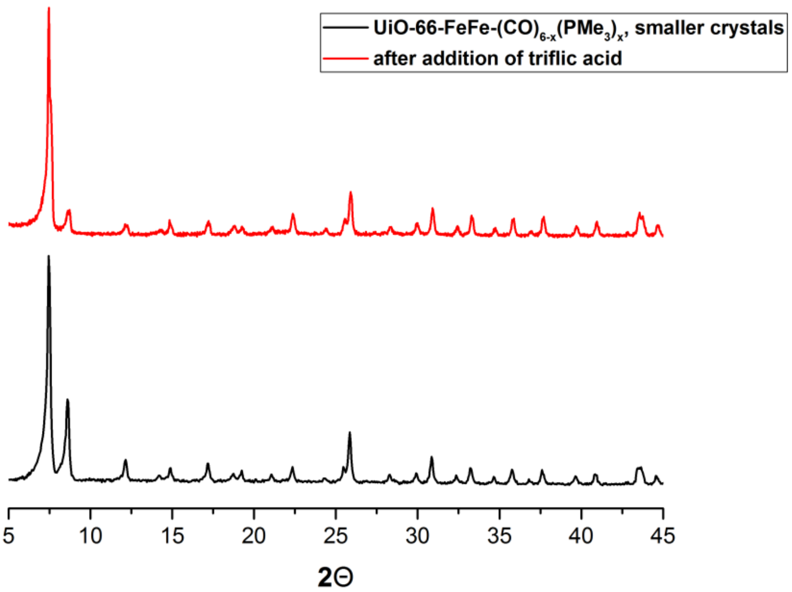

Figure S6. PXRD of UiO-66-[FeFe](CO)$_{6-x}$(PMe$_3$)$_x$ (smaller crystals) before (black) and after (red) protonation with triflic acid.

References

1. S. Pullen, H. Fei, A. Orthaber, S. M. Cohen and S. Ott, *J. Am. Chem. Soc.*, 2013, **135**, 16997-17003.
2. F. Gloaguen, J. D. Lawrence, M. Schmidt, S. R. Wilson and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 2001, **123**, 12518-12527.