Enhanced Photochemical Hydrogen Production catalyzed by a Molecular Catalyst Incorporated into a 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, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz for ^{1}H NMR). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS.

Experimental Procedures

*Synthesis of [FeFe]dcbdt(CO)$_6$ (**1**, dcbdt = 1,4-dicarboxylbenzene-2,3-dithiolate).* To tetramethylethylenediamine (3.12 mg, 21 mmol) was added n-BuLi (1.6 M, 13 mL, 21 mmol) under argon at 0 °C. The solution was stirred for 5 min and then benzenedithiol (0.5g, 3.5 mmol), dissolved in dry cyclohexane (30 mL) was added dropwise. The mixture was allowed to slowly warm up to ambient temperature and then stirred for 95 h. After cooling the suspension again to 0 °C, a stream of CO_2 gas (from dry ice, dried through P_2O_5) was led into the mixture over 3 h. The solvent was removed under vacuum and a yellow solid obtained.[1,2] The crude product was dissolved in dry THF (40 mL) and added to Fe_3CO_{12} (3.5g, 7 mmol). The dark green mixture was refluxed for 1h while turning red. The solvent was removed under reduced pressure and the crude product purified by flash chromatography on silica using a solvent gradient starting with hexane-ethylacetate 20:80 and ending with pure methanol. The product was obtained as red solid (0.2 g, 12%). Main byproducts are [FeFe](bdt)(CO)$_6$ and [FeFe](mcbdt)(CO)$_6$. Crystals for X-Ray analysis were grown by two-layer crystallization in methanol-pentane 20:80 at ambient temperature; ν_{max}/cm-1 (KBr) 2078, 2038, 2001, 1707, 1579; δH (300 MHz; CD3OD) 7.00 (s, 2H, CHarom).

Solvothermal synthesis of UiO-66. 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 solution was capped and sealed in a 20 mL vial, and allowed to react solvothermally at 120 °C for 24 h. After cooling, the mixture was centrifuged, then the solids were left to soak in MeOH for 3 d, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 d of soaking, the solids were centrifuged and dried under vacuum.

Solid-Liquid PSE between UiO-66 and [FeFe](dcbdt)(CO)$_6$. **1** (50.8 mg, 0.1 mmol) was dissolved in deoxygenated Millipore water (5 mL). Deoxygnation was performed bubbling Millipore water with N_2 (3×30 sec). This orange solution was centrifuged to remove the impurities, then added to UiO-66 (*ca.* 28 mg, 0.1 mmol equiv of –BDC) and the mixture was sonicated for 10 min to disperse UiO particles in the solution, then placed onto a place shaker to shake continuously for 24 h. After 24 h, the mixture was centrifuged and the solids were washed with copious amount of MeOH until the supernatant was colorless. Then the solids were left to soak in MeOH for 3 d, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 d of soaking, the solids were centrifuged and dried under vacuum.

PSE reaction between UiO-66 and [FeFe](bdt)(CO)$_6$ or [FeFe](dcbdt)(CO)$_6$. Fe complex (0.1 mmol; 51 mg for **1**, 42.0 mg for **2**) was dissolved in 4 mL of deoxygenated 50:50 (v:v) Millipore water/acetonitrile solution. Deoxygnation was achieved by bubbling the solution with N_2 (3×30 sec). The orange solution was centrifuged to remove the impurities, and was then added to solid UiO-66 (*ca.* 28 mg, 0.1 mmol equiv of –BDC) and the mixture was sonicated for 10 min to disperse the UiO-66 particles into the solution. The reaction mixture was placed onto a place shaker an agitated continuously for 24 h. After 24 h, the mixture was centrifuged and the solids were washed with copious amount of acetonitrile and MeOH until the supernatant was colorless. The resulting solids were left to soak in MeOH for 3 d, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 d of soaking, the solids were centrifuged and dried under vacuum.

Powder X-ray Diffraction (PXRD) Analysis. Approximately 20-30 mg of UiO-66 samples were dried under vacuum prior to PXRD analysis. PXRD data were collected at ambient temperature on a Bruker D8 Advance 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 5~45° (sample dependent). The experimental backgrounds were corrected using Jade 5.0 software package.

Digestion and Analysis by ^1H NMR. Approximately 10 mg of UiO material was dried under vacuum and digested with sonication in 590 µL DMSO-d_6 and 10 µL of 40% HF.

Thermalgravimetric Analysis. Approximately 10-15 mg of UiO sample was used for TGA measurements, after BET analysis (activated). Samples were analyzed under a stream of N_2 using a TA Instrument Q600 SDT running from room temperature to 800 °C with a scan rate of 5 °C/min.

BET Surface Area Analysis. Approximately 50 mg of UiO sample was evacuated on a vacuum line overnight at room temperature. The sample was then transferred to a pre-weighed sample tube and degassed at room temperature on an Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mm Hg. The sample tube was re-weighed to obtain a consistent mass for the degassed exchanged MOF. BET surface area (m^2/g) measurements were collected at 77 K by N_2 on a Micromeritics ASAP 2020 Adsorption Analyzer using the volumetric technique. The sample was then manually degassed on the analysis port overnight at 30 °C for approximately 6 h. N_2 sorption isotherm were collected at 77 K.

Fourier-transformed Infrared (FTIR) Spectroscopy. Approximately 5 mg of UiO samples were dried under vacuum prior to FTIR analysis. FTIR data were collected at ambient temperature on a Bruker ALPHA FTIR Spectrometer from 4000 cm^{-1} and 450 cm^{-1}. The experimental backgrounds were corrected using OPUS software package.

Diffuse reflectance UV-Vis Spectroscopy. Approximately 20 mg of UiO samples were dried under vacuum prior to UV-Vis analysis. Solid-state UV-Vis data were collected on a StellarNet EPP 2000C spectrometer from 250 nm and 850 nm. The experimental backgrounds were corrected using SpectraWiz software package.

Scanning Electron Microscopy-Energy Dispersed X-ray Spectroscopy. Approximately 2-5 mg of activated UiO materials was transferred to conductive carbon tape on a sample holder disk, and coated using a Cr-sputter coating for 8 seconds. A Philips XL ESEM instrument was used for acquiring images using a 10 kV energy source under vacuum. Oxford EDX and Inca software are attached to determine elemental mapping of particle surfaces at a working distance at 10 mm. Around 19000X magnification images are collected.

X-ray Absorption Spectroscopy (XAS). XAS measurements were obtained at the Advanced Photon Source (APS) beamline 9-BM at Argonne National Laboratory. Beamline 9-BM is equipped withconsists of a Si(111) monochromator, and focusing is achieved with a rhodium-coated toriodal mirror. XAS was measured in transmittance mode and samples were maintained at room temperature. For each sample, approximately 20 mg were dried under vacuum for overnight, and brushed into a thin film sealed by Kapton tape. Three scans were accumulated and averaged for each sample, and the energy was calibrated by reference to the absorption of a Fe foil measured simultaneously.

Crystallographic Data. Crystallographic data sets were collected from single crystal samples mounted on a loop fiber and coated with N-paratone oil (Hampton Research). Collection was performed using a Bruker SMART APEX diffractometer equiped with an APEXII CCD detector, a graphite monochromator and a 3-circles goniometer. The crystal-to-detector distance was 5.0 cm, and the data collection was carried out in 512 x 512 pixel mode. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 10.0 degrees scan in 12 frames over three different parts of the reciprocal space (36 frames total) and re-refined with the whole data set of significant reflections. Cell refinement and data reduction were performed with SAINT V7.68A (Bruker AXS). Absorption correction was done by multi-scan methods using SADABS96 (Sheldrick). The structure was solved by direct methods and refined using SHELXL97 (Sheldrick). All non-H atoms were refined by full-matrix least-squares with anisotropic displacement parameters while hydrogen atoms were placed in idealized positions except for the hydrogens of the carboxylic acid which were placed at the singly bonded oxygen refined to a distance of 1.0 Å. The solvent molecule found in the large cavity shows significant disorder and was modelled over two positions with half occupancy. Further constraints to ADPs were applied. Refinement of F^2 was performed against all reflections. The weighted R-factor wR and goodness-of-fit are based on F^2. Complex [FeFe]dcbdt$(CO)_6$ forms in the solid state a linear chain along the crystallographic (010) axis through hydrogen bonding of the terephthalic acid fragments. The least-squares planes spanned by the carboxylic acid moieties are twisted with respect to the benzene ring by 24.6(3)° to 24.9(3)°.

Photocatalysis. All components were added to the reaction flask. The determined total headspace of this flask was 88 mL and after adding 10 mL reaction solution, the headspace volume used for calculations was 78 mL. Before starting the experiment, the reaction mixture was purged with argon for 40 min. The H_2-sensor (HY-optima 740 high contaminant tolerant process analyzer) was turned on and activated by adding 0.5 mL pure H_2-gas into the reaction vessel. When a stable hydrogen content was detected, the LED (blue, 470 nm, 850 μE) was turned on and applied over up to 3h.

Calculation of number of moles of MOF catalyst. Based on the molecular formula and 15% replacement of bdt linkers by catalyst the molecular formula is defined as:
$Zr_6O_4(OH)_4\{(C_8H_4O_4) * 0.85 + (C_{14}H_2O_{10}Fe_2S_2) * 0.15\}_6$
The molar mass is calculated as:
$M_{\text{MOF total}} = 679.37\ \text{g/mol} + 6 * (164.11\ \text{g/mol} * 0.85 + 505.98 * 0.15) = 1971.71\ \text{g/mol}$
and the molar mass of catalyst incorporated into MOF:
$M_{\text{catalyst in MOF}} = (505.98\ \text{g/mol} * 0.15) * 6 = 455.38\ \text{g/mol}$
From these two values, a factor x_{cat} is defined as:
$x_{\text{cat}} = M_{\text{catalyst in MOF}} / M_{\text{MOF total}} = 0.231$
For 1 mg MOF is then:
$n_{\text{MOF total}} = 1\ \text{mg} / 1971.71\ \text{mg / mmol} = 0.51\ \mu\text{mol}$
and
$n_{\text{catalyst in MOF}} = x_{\text{cat}} * n_{\text{MOF total}} = 0.231 * 0.51\ \mu\text{mol} = 0.118\ \mu\text{mol}$

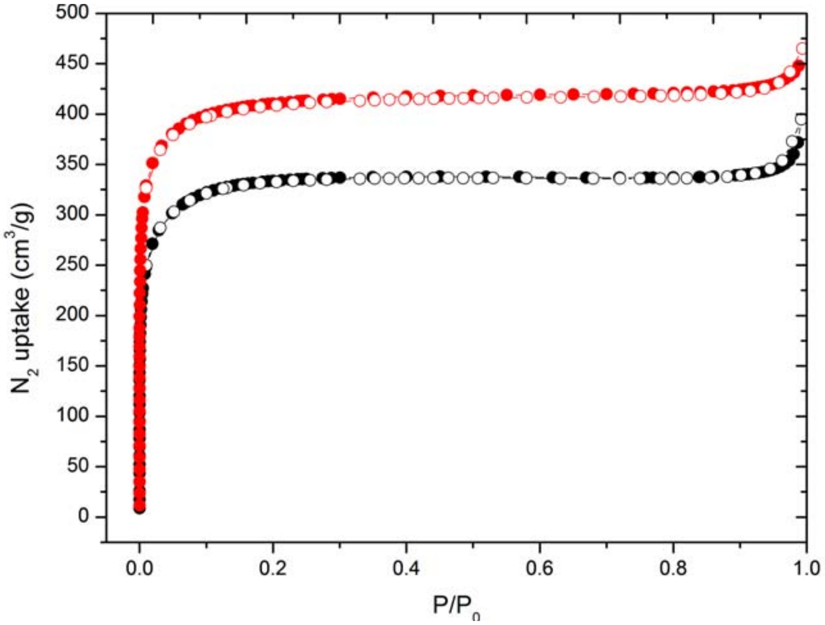

Figure S1. N_2 absorption (filled symbols) and desorption (open symbols) isotherms for UiO-66 (red) and UiO-66-[FeFe]dcbdt$(CO)_6$ (black).

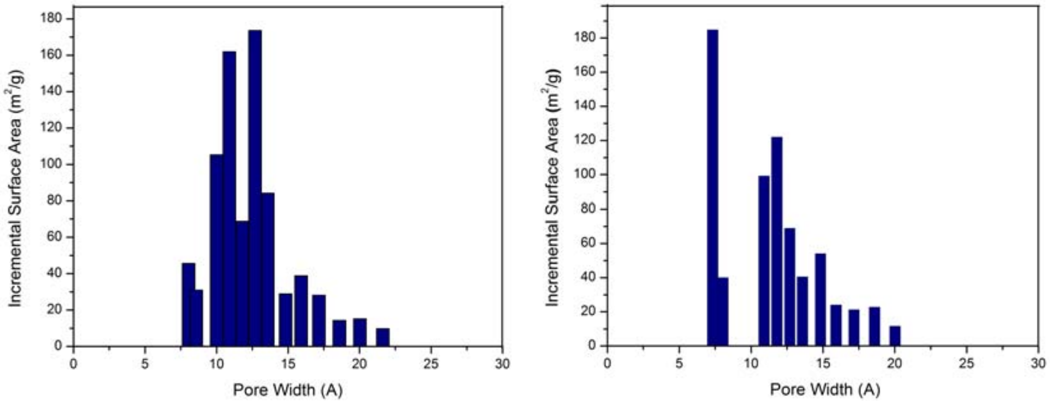

Figure S2. Pore size distribution of UiO-66 (left) and UiO-66-[FeFe]dcbdt$(CO)_6$ (right) obtained from N_2 gas sorption experiments.

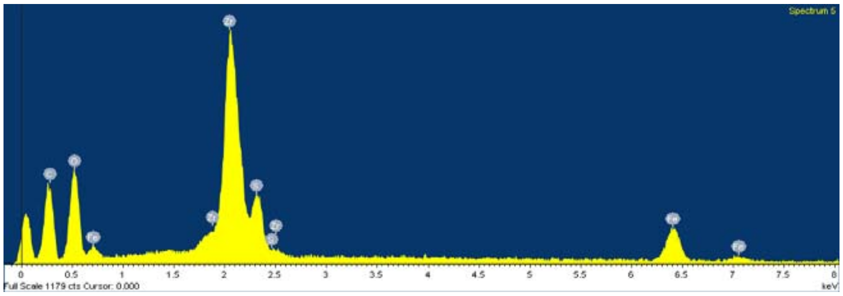

Figure S3. EDX analysis of UiO-66-[FeFe]dcbdt$(CO)_6$.

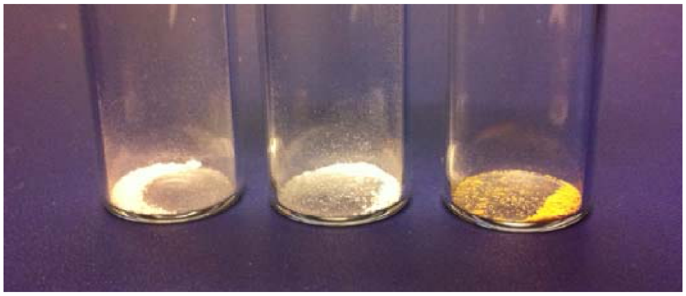

Figure S4. Photograph of pristine UiO-66 (left), UiO-66 after incubation with complex **2** and standard rinsing (middle), and UiO-66 after incubation with complex **1** and standard rinsing (right). Incorporation of **1** via PSE is evidence by the persistent color of the sample, indicating formation of UiO-66-[FeFe]dcbdt$(CO)_6$ (right).

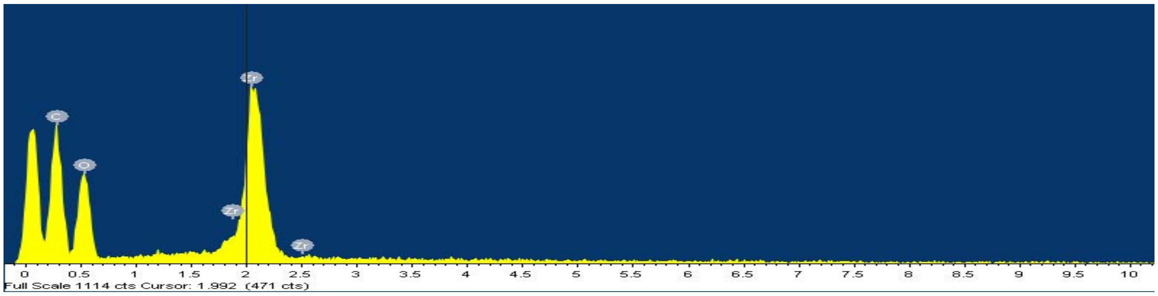

Figure S5. EDX analysis of UiO-66 after exposure to an aqueous solution of **2**. The iron content of the sample is very low, indicating that **2** does not remain trapped in the pores of the MOF.

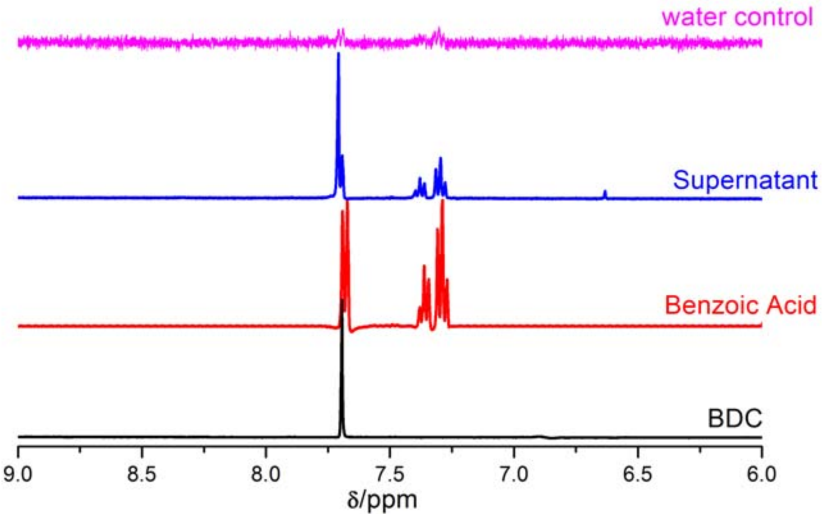

Figure S6. ^{1}H NMR of the PSE solution containing UiO-66 and **1** in D_2O (blue) showing the leaching of benzoic acid (modulator) and BDC (linker) from the MOF. ^{1}H NMR spectra of benzoic acid (red) and BDC (black) are shown for reference (10 mg dissolved in 600 μL of D_2O and 100 μL of 4 % KOH). A control experiment under the same solution conditions, but in the absence of compound **1** (magenta), shows that benzoic acid and BDC do not significantly leach from the MOF in the absence of PSE.

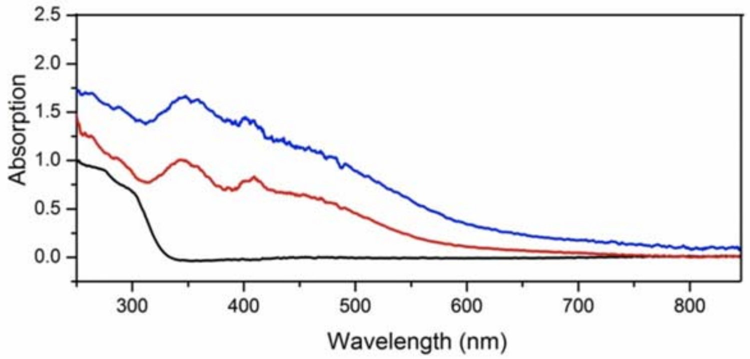

Figure S7. Diffuse reflectance solid-state UV-Vis of UiO-66 (black), [FeFe]dcbdt(CO)$_6$ (blue) and UiO-66-[FeFe]dcbdt(CO)$_6$.

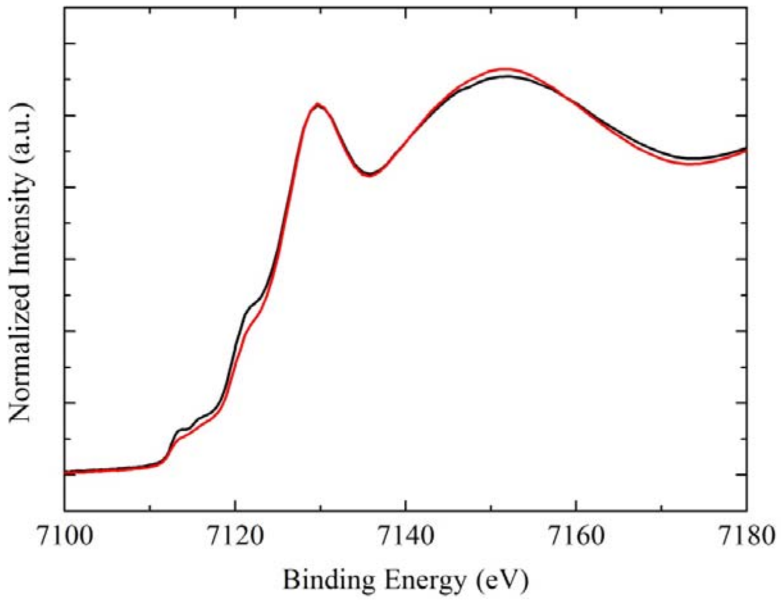

Figure S8. XANES spectra of [FeFe]dcbdt$(CO)_6$ (black) and UiO-66-[FeFe]dcbdt$(CO)_6$ (red).

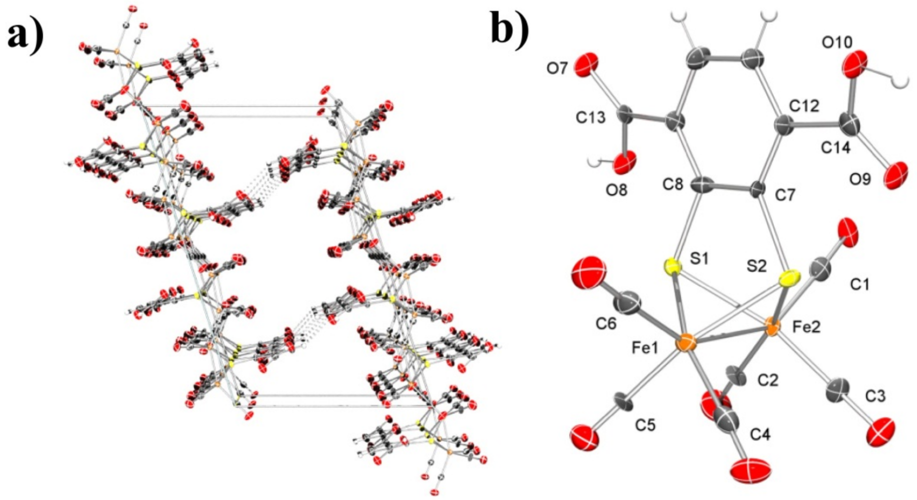

Figure S9. Crystallographic analysis of compound **1**. a) View along the crystallographic (010) axis. The disordered pentane molecule in the central void is omitted for clarity. b) Asymmetric unit of the dinuclear iron complex. ORTEP plots of [FeFe]dcbdt(CO) (probability level of 50%).

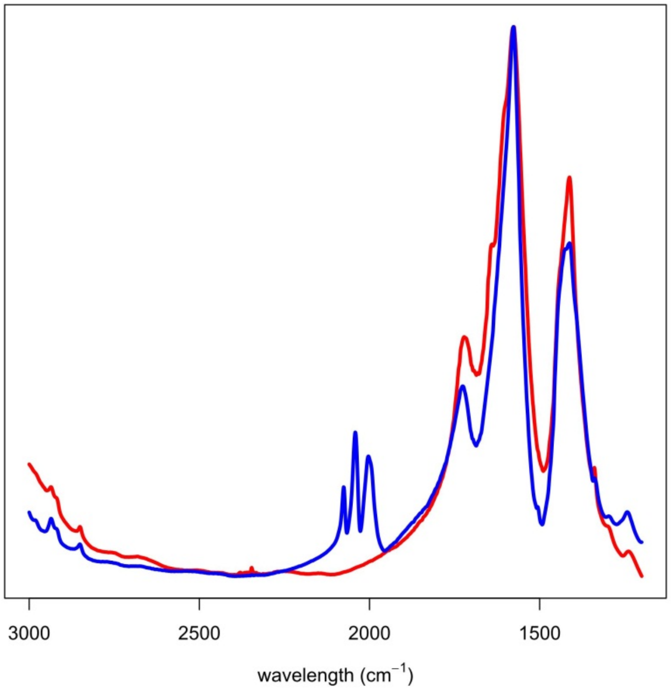

Figure S10. FTIR spectrum of UiO-66-[FeFe]dcbdt$(CO)_6$ (blue) recovered after exposure for one hour under the photo-catalysis conditions (pH 5 acetate buffer). In red is the FTIR spectrum of the material recovered from the reaction with free (dissolved in solution, homogenous) [FeFe]dcbdt$(CO)_6$ (red) under identical conditions. The molecular integrity of the Fe_2 complex in UiO-66-[FeFe]dcbdt$(CO)_6$ is proven by the characteristic IR absorption of the CO ligands around 2000 cm^{-1}. Complete decomposition is observed for the catalyst in solution.

Table S1. Crystallographic data for compound **1**.

Identification code	[FeFe]dcbdt(CO)
Empirical formula	C14 H4 Fe2 O10 S2, C5 H12
Formula weight	580.14
Crystal description	Red blocks
Crystal size [mm]	0.10 x 0.12 x 0.14
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions: a	12.641(7)
b	9.564(5)
c	20.250(10)
β	107.43(2)
Volume [Å^3]	2336(2)
Z	4
Calculated density [Mg/m^3]	1.650
F(000)	1176
Linear absorption coefficient μ	1.472
Absorption correction	Multi-scan
Min. and max. transmission	0.5857, 0.7457
Temperature	100(2)
Diffractometer	Bruker D8 –APEX-II
Radiation source	Mo K_α
Radiation and wavelength	0.71073
Scan type	ω-scan
Range for data collection Θ	1.69 - 28.51
Index ranges	-16 <h 11, -11 <k 12, -26 < l 27
Reflections collected / unique	34815, 5831
Significant unique reflections	4431
R(int), R(sigma)	0.0914, 0.0752
Completeness	0.984
Θ-max	28.51
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restraints	5831 / 276 / 51
Goodness-of-fit on F^2	1.239
Final R indices [I > (I)]σ2	0.1485
R indices (all data)	0.3398
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P=(F_o^2+2F_c^2)/3$
Weighting scheme parameters a, b	0.0535, 96.0107
Largest σ/Δ in last cycle	0.00
Largest difference peak and hole	3.370 , -1.884
Structure Solution Program	ShelXS-97
Structure Refinement Program	ShelXL-97

References

(1) Seidel, W. W.; Hahn, F. E.; Lügger, T. *Inorg. Chem.* **1998**, *37*, 6587.

(2) Sellmann, D.; Becker, T.; Knoch, F. *Chem. Ber.* **1996**, *129*, 509.