

Functionalization of Robust Zr(IV)-based Metal-Organic Framework Films via Postsynthetic Ligand Exchange

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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 (^1H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS.

Experimental Procedures

UiO-66 Film Synthesis. FTO glass was cut into small pieces with an average size of 0.5~0.75 cm^2 , then washed thoroughly with soap water, ethanol, and acetone, respectively for 15 min under sonication. After dried under air, cleaned FTO glass was pretreated in 1 mM terephthalic acid (bdc) in dimethylformamide (DMF) solution for overnight, with FTO facing upward. ZrCl_4 (35 mg, 0.15 mmol) and benzoic acid (1.35 g and 11 mmol) was dissolved in 8 mL DMF, and the mixture was Teflon-lined capped, and sealed in a 24 mL vial. The mixture was allowed to heat at 80 $^\circ\text{C}$ for 2 h. After cooling, dissolve H_2bdc (for thicker films 25 mg 0.15 mmol, for thinner films 16 mg 0.10 mmol) into the above solution via sonication. Then place one piece of bdc-pretreated FTO slide at the bottom of the vial with FTO side facing upwards. The vial was allowed to react solvothermally for 24 h. Cool down, carefully take out FTO glass coated with UiO-66 film, and incubate in DMF solution for 24 h, then incubate in methanol (MeOH) for further uses.

PSE of UiO-66 Film to Achieve [FeFe] Functionality. $[\text{FeFe}](\text{dcbdt})(\text{CO})_6$ (dcbdt=1,4-dicarboxylbenzene-2,3-dithiolate) was synthesized according to a previous publication.¹ $[\text{FeFe}](\text{dcbdt})(\text{CO})_6$ (50.8 mg, 0.1 mmol) was dissolved in deoxygenated Millipore water (2 mL), and the mixture was capped and sealed in a 24 mL vial. Deoxygenation was performed bubbling Millipore water with N_2 . A single piece of air-dried UiO-66 film on FTO glass was placed at the bottom of the vial with

MOF film side facing upwards. The mixture was allowed to react under room temperature for 24-72 h. After 24-72 h, the films were washed with copious amount of MeOH (3 x 10 mL), then incubate in MeOH for further uses.

PSE of UiO-66 Film to Achieve Catechol Functionality. CAT-bdc (20 mg, 0.1 mmol) were dissolved in 2 mL 4 % KOH solution under sonication, then titrate the solution with minimal amount of 1M HCl to pH=7. The aqueous solution was diluted with Millipore water to a volume of 10 mL, and transferred to a 20 mL scintillation vial. A single piece of air-dried UiO-66 film on FTO glass was placed at the bottom of the vial with MOF film side facing upwards. The mixture was incubated under room temperature for 24 h. After 24 h, the film was washed with copious amount of Millipore water (3 x 10 mL), then washed with ethanol/water (v:v=1:1) (3 x 10 mL), and incubated in ethanol/water (v:v=1:1) for 1 h. After 1 h, the film was washed with ethanol (3 x 10 mL) and incubated in ethanol for further uses.

Fe Metallation of UiO-66-CAT. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (13.5 mg, 0.05 mmol Fe) was dissolved in 10 mL deionized water, and the solution was transferred to a 20 mL scintillation vial. A single piece of vacuum-dried UiO-66-CAT film on FTO glass was placed at the bottom of the vial with MOF film side facing upwards. The mixture was incubated under room temperature for 24 h. After 24 h, the MOF film was washed profusely with Millipore water (4×10 mL), until the supernatant was colorless. The solids were then washed with ethanol/water (v:v=1:1) (3 x 10 mL), and incubated in ethanol/water (v:v=1:1) for 1 h. After 1 h, the film was washed with ethanol (3 x 10 mL) and incubated in ethanol for further uses.

Powder X-ray Diffraction (PXRD) Analysis. UiO-66 films were air-dried prior to PXRD analysis. PXRD data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu K α ($\lambda = 1.5418 \text{ \AA}$), 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). The experimental backgrounds were corrected using Jade 5.0 software package.

Digestion and Analysis by ^1H NMR. Approximately 5 mg of UiO-66 materials were sonicated off the slides, then was dried under vacuum and digested with sonication in 590 μL DMSO- d_6 (or 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 a Ir-sputter coating for 8 sec. 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.

Diffuse reflectance UV-Vis Spectroscopy. UiO-66 films were air-dried 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.

Fourier-transformed Infrared (FTIR) Spectroscopy. ~ 5 mg of UiO-66 materials were sonicated off the slides, followed by drying 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.

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 graphite counter electrode, an Ag/AgNO_3 reference (CH Instruments, 0.01 AgNO_3 in acetonitrile) and modified FTO conducting glass as working electrode. Control experiments were performed with glassy carbon disc for voltammetry (diameter 3, freshly polished). All measurements were conducted with degassed anhydrous DMF and tetrabutylammonium hexafluorophosphate (TBAPF_6 , Fluka, electrochemical grade) as supporting electrolyte (0.1 M). Before analysis, PSE was proceeded for 72 h, then the films were washed extensively with MeOH and soaked in MeOH while exchanging the liquid until it remained colorless. Films were then dried in vacuum for 4h.

Supporting Figures and Tables

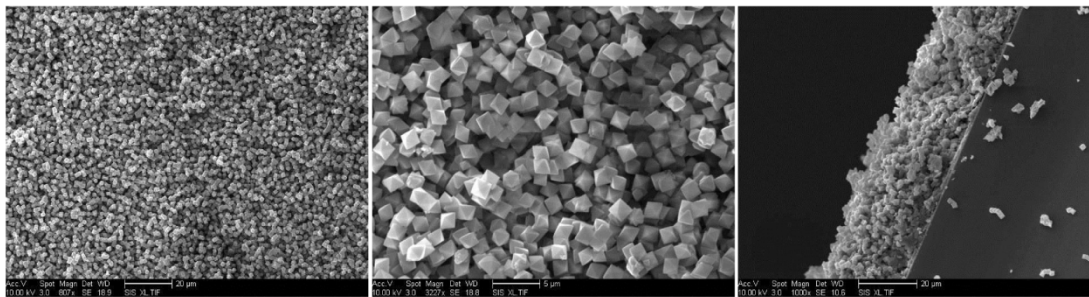


Figure S1. Top-view SEM images thicker films at different magnifications and cross-sectional SEM image showing film thickness of $\sim 20\ \mu\text{m}$.

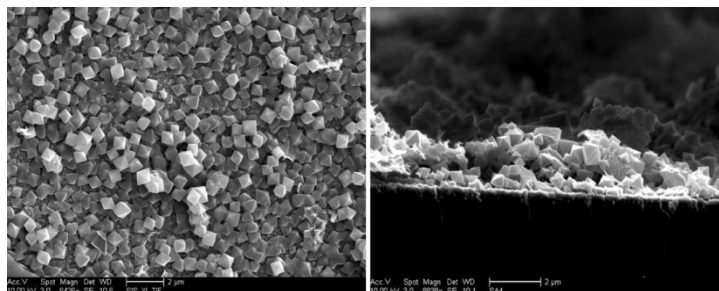


Figure S2. Left: Top-view SEM image of thinner film. Right: Cross-sectional SEM image showing film thickness of $2\text{--}5\ \mu\text{m}$.

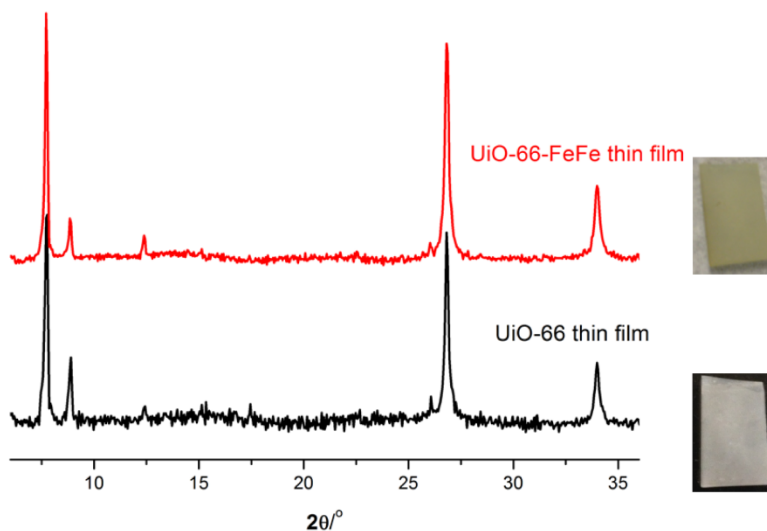


Figure S3. PXRD of thinner UiO-66 film (black) and corresponding film (red) after 72 h of PSE with $\text{Fe}_2(\text{dcbdt})(\text{CO})_6$.

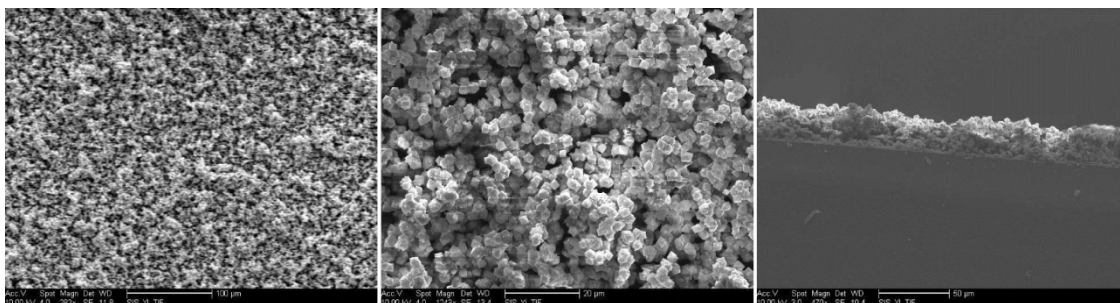


Figure S4. Top-view (left and middle) and cross-sectional (right) SEM images of UiO-66-CAT film.

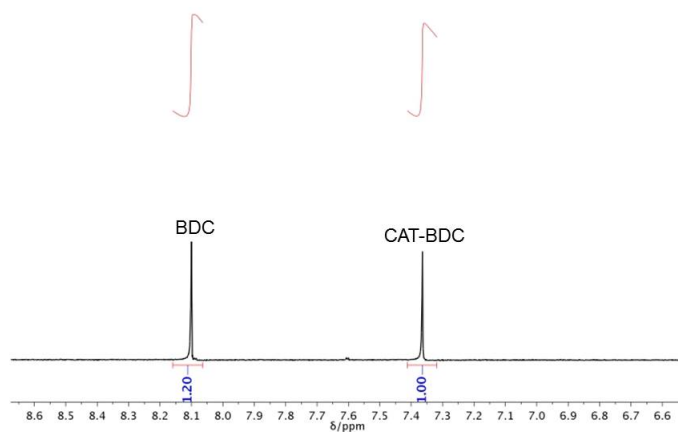


Figure S5. ^1H NMR of UiO-66-CAT film digested with diluted $\text{HF}/\text{CD}_3\text{OD}$.

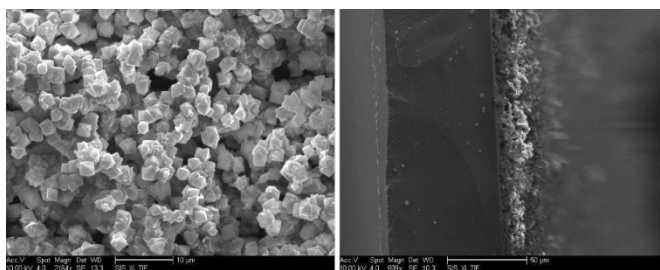


Figure S6. Top-view (left) and cross-sectional (right) SEM images of UiO-66-FeCAT film.

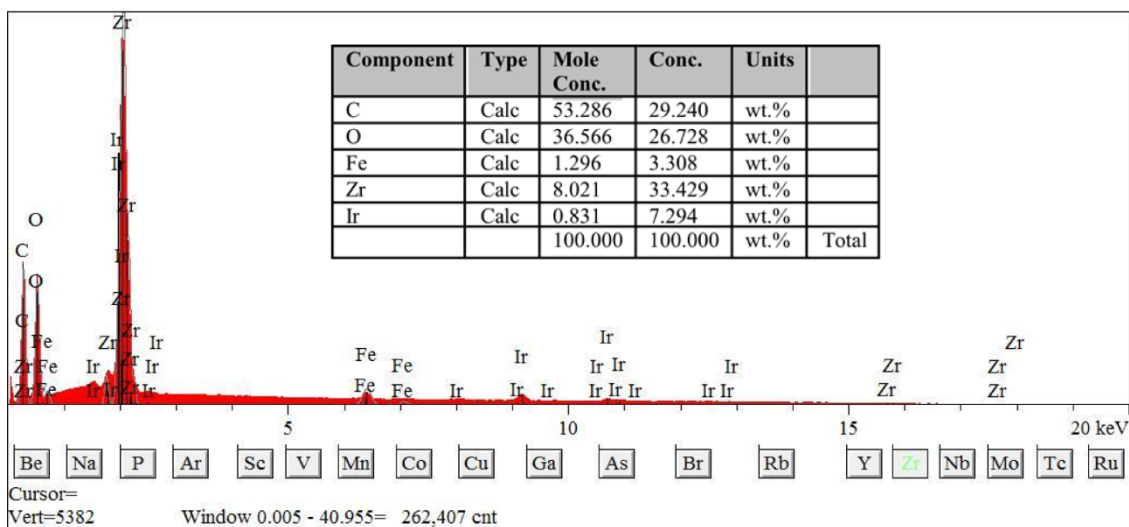


Figure S7. EDX of UiO-66-FeCAT film, indicating an atomic ratio of 8.021:1.296 (Zr:Fe).

Table S1. Overview over degree of PSE in powder materials versus thin films.

MOF-type	PSE powder (%)	PSE thin film (%)
UiO-66-CAT	36(3) ^a	62(6) ^a
UiO-66-[FeFe](dcbdt)(CO) ₆	14(2) ^a	32(5) ^a

^aThe values in the parentheses is the errors based on 2~3 independent samples.

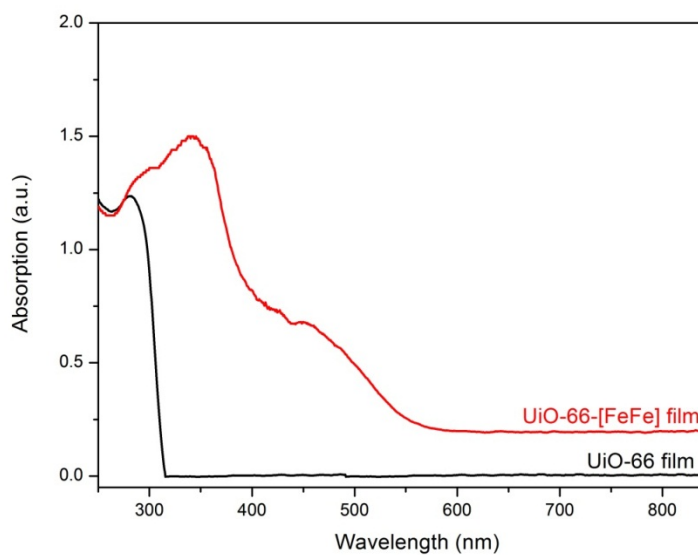


Figure S8. Diffuse reflectance UV-Vis spectra of UiO-66 film and UiO-66-[FeFe](dcbdt)(CO)₆ film.

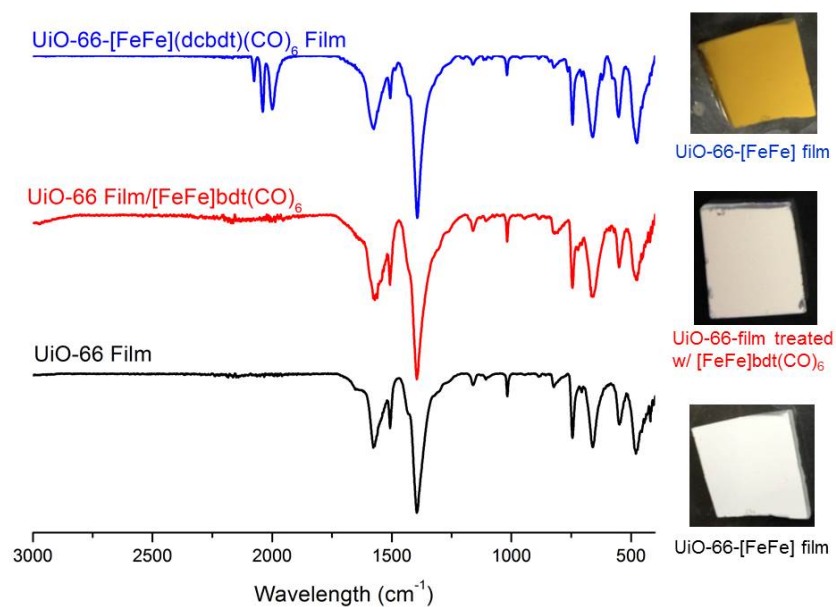


Figure S9. FTIR (left) and photograph (right) of thicker UiO-66 film (black), UiO-66 film treated with $[\text{FeFe}]\text{bdt}(\text{CO})_6$ (red), and corresponding UiO-66- $[\text{FeFe}](\text{dcbdt})(\text{CO})_6$ film.

Table S2. C/H/N/S elemental analysis of UiO-66- $[\text{FeFe}](\text{dcbdt})(\text{CO})_6$ with an expected molecular formula as $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_4([\text{FeFe}](\text{dcbdt})(\text{CO})_6)_2(\text{DMF})_2(\text{CH}_3\text{OH})_2$.

	C (%)	H (%)	N (%)	S (%)
Observed	29.22	2.93	1.36	5.40
Calculated	31.94	1.81	1.09	4.97

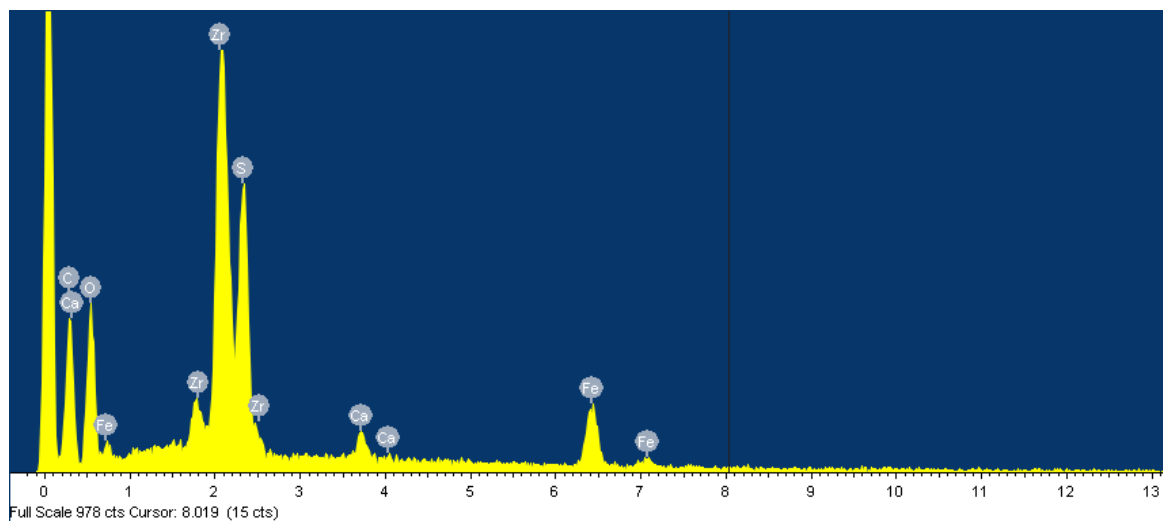
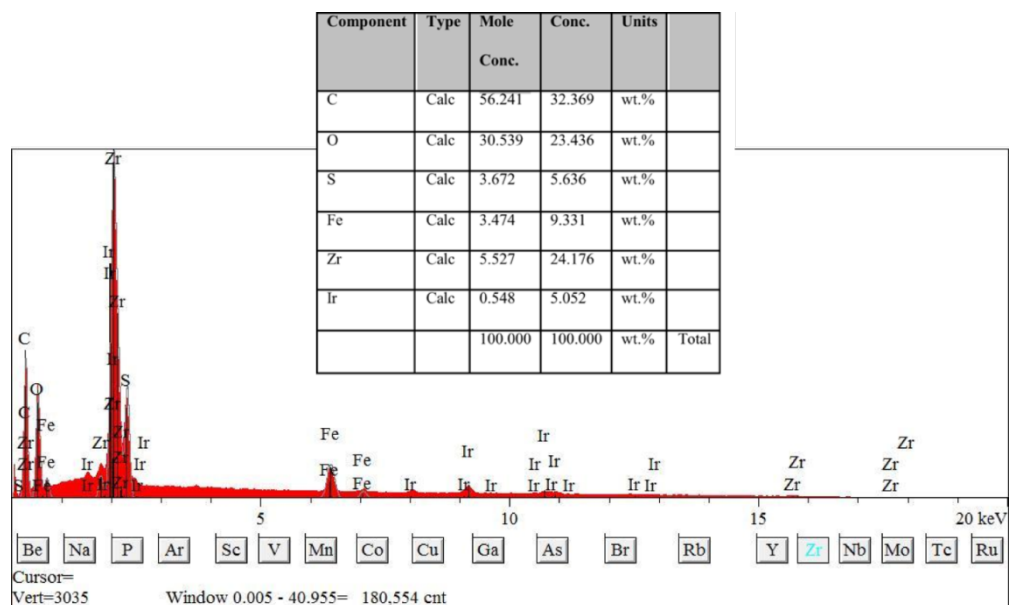


Figure S10. Top: EDX of UiO-66-[FeFe](dcbdt)(CO)₆ thicker film, indicating an atomic ratio of 5.53:3.47:3.67 (Zr:Fe:S). Bottom: EDX of UiO-66-[FeFe](dcbdt)(CO)₆ thicker film, indicating an atomic ratio of 4.11:2.69:2.88 (Zr:Fe:S).

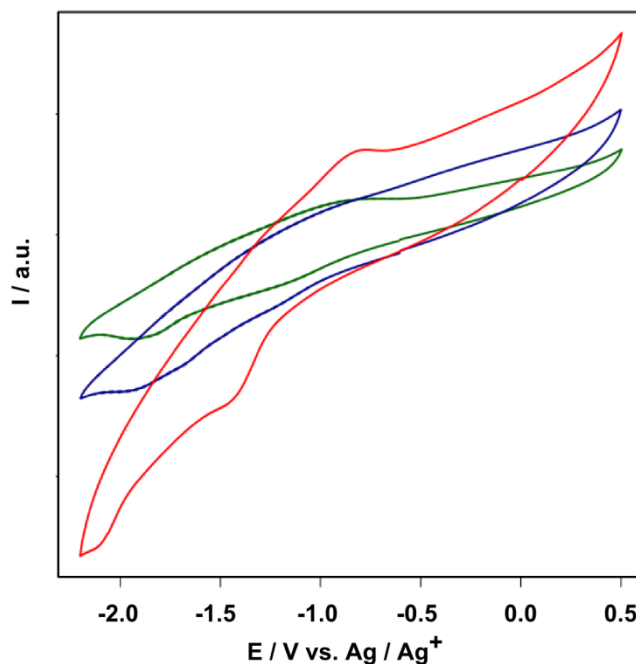


Figure S11. Electrochemistry control experiment: FTO (green), SAM-FTO (blue) and UiO-66 thin film (2-5 μm) (red) treated under identical PSE condition (20 mM $\text{Fe}_2(\text{dcbdt})(\text{CO})_6$ in water for 72 h, then washed with MeOH and soaked in MeOH for 24 h). Cyclic voltammogram in 0.1 M TBAPF₆ supporting electrolyte in DMF versus Ag/Ag⁺.

References

- (1) Pullen, S.; Fei, H.; Orthaber, A.; Cohen, S. M.; Ott, S. *J. Am. Chem. Soc.* **2013**, *135*, 16997.
- (2) Fei, H.; Shin, J.; Meng, Y. S.; Adelhardt, M.; Sutter, J.; Meyer, K.; Cohen, S. M. *J. Am. Chem. Soc.* **2014**, *136*, 4965.