Electronic Supplementary Material (ESI) for Chemical Science.

Supplemental Information

On the limit of proton-coupled electronic doping in a Ti(IV)-containing MOF

Jenna L. Mancuso, Kevin Fabrizio, Carl K. Brozek*, Christopher H. Hendon*

Department of Chemistry and Biochemistry, University of Oregon, Eugene, Oregon 97403, United States

Table S1: Compilation of total energy changes in two node unit cell with increasing numbers of hydrogen atoms (*i.e* PCET events) paired at bridging oxo pairs between titanium atoms (Figure 3a) in a computational unit cell containing two inorganic nodes, computed on a PBEsol optimized structure at the HSEsol06 level.

H* pairs / cell	**ΔE from empty (eV)**	**ΔE from empty per pair (eV)**	**ΔE to release single H_2 (eV)**
2	-0.67	-0.67	0.67
4 – same node	-1.38	-0.69	0.72
6	-1.76	-0.59	0.38
8 – same node	-0.41	-0.10	**-1.34**
4 – 2 per node	-1.40	-0.70	
8 – 4 per node	-2.16	-0.54	
16 – 8 per node	-3.12	-0.39	

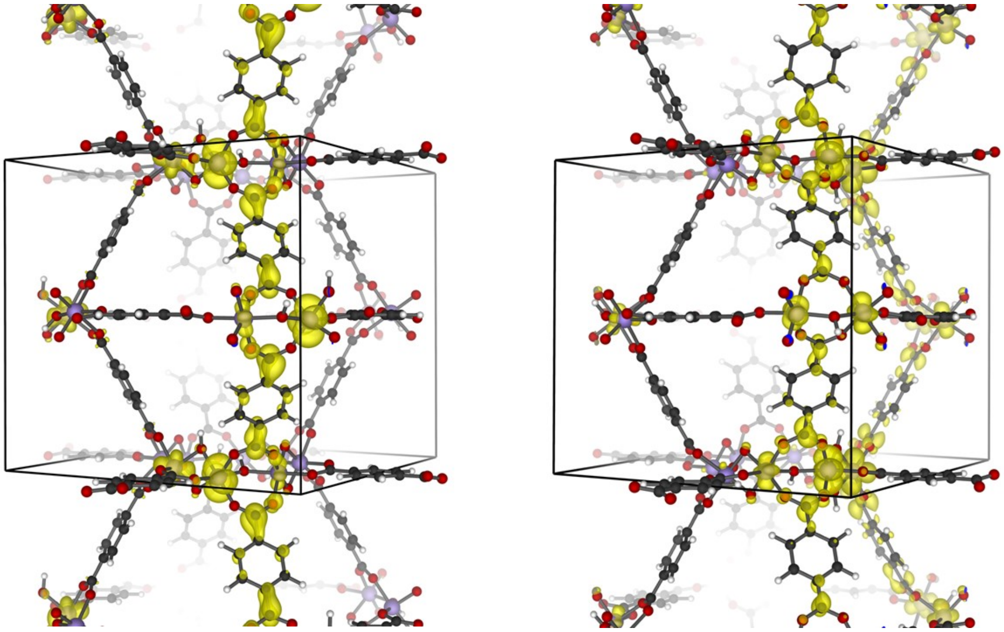

Figure S1. The spin density associated with the radical after two PCET events occur at separate μ^2-oxo pairs in separate nodes (left), compared with the localization of spin-density on a single node with paired transfers (right) within the node.

The coupling of unpaired H*-donated radicals through BDC antibonds is made more apparent at higher loadings. If four PCET events occur at the same node (**Figure 4**, equivalent to 2 e^{-1}/node throughout the material) each titanium is partially reduced and the conduction band states are nearly entirely localized within the node; in contrast, isolating the PCET events between different titanium pairs forces spin density through the linker antibonds onto the metals of adjacent nodes, **Figure S3**.

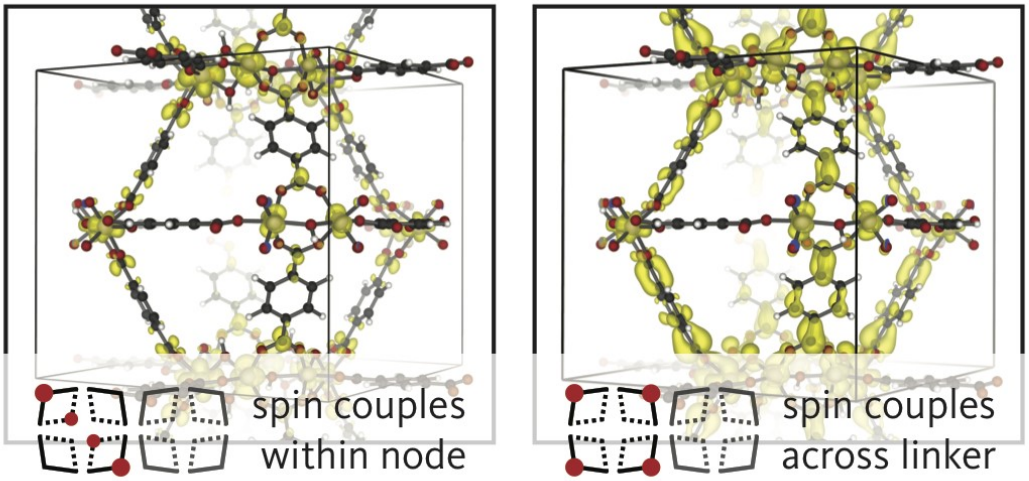

Figure S2. The spin density for all four conduction band electrons when four PCET events occur on a single node a) localizes within the node when matched between disparate sets of titanium pairs, but b) fill organic antibonding orbitals when the individual PCET are spread across each μ^2-oxo pair within the node.

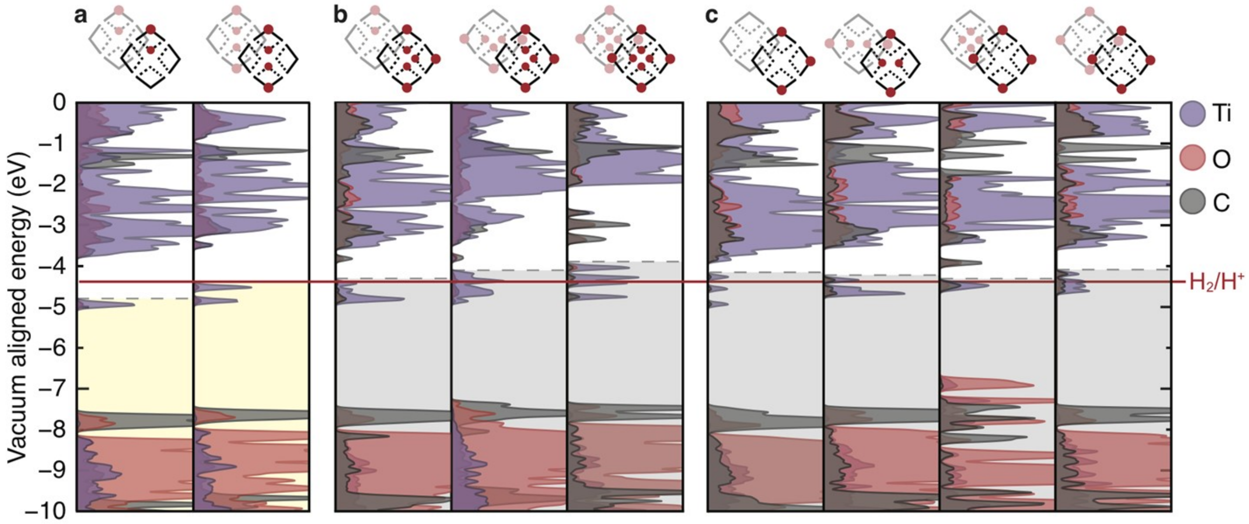

Figure S3. Atom-projected density of states for a range of configurations and dopant concentrations sampled for this study that were otherwise not discussed in the body of the article—the most favorable conformations occur when bridging oxo pairs are both protonated during subsequent/concurrent PCET events as is apparent in the purple and red sections depicting a range of two and four PCET event possibilities.

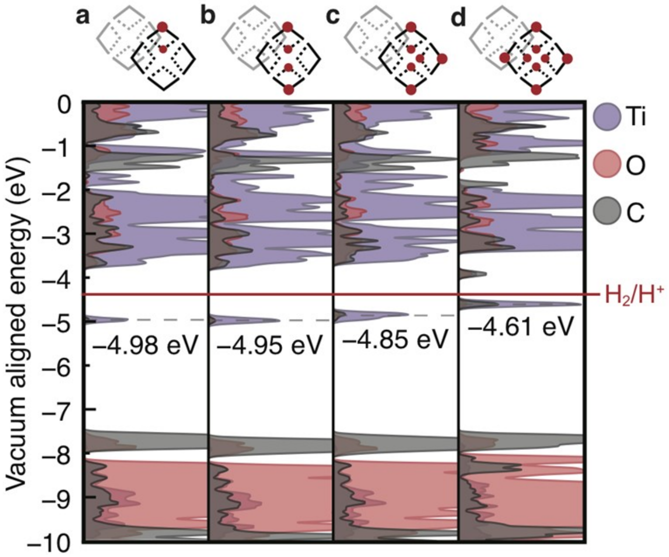

Figure S4. Atom-projected density of states for MIL-125 with (a) two, (b) four, (c) six, and (d) eight pairs of PCET events adding to the same bridging oxo pairs of the same node showing the reaction is net-favorable up to full saturation of the node – however this too can be forced by application of a chemical reductant and coordinating Na$^+$ counterions.[1]

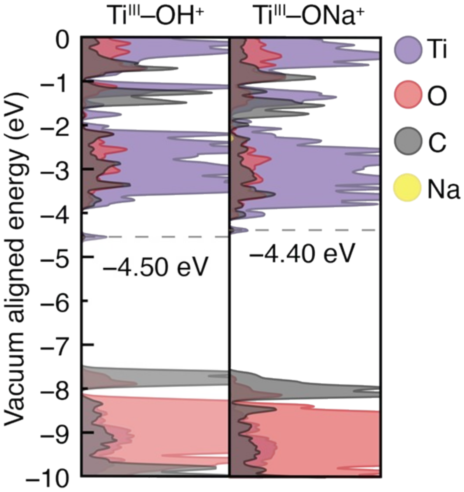

Figure S5. A comparison of proton-coupled and sodium coupled reduction of MIL-125.

Vacuum alignment procedure

All VASP-recovered energy values were referenced to the vacuum potential by subtracting the background potential applied to the unit cell as located within the center of the largest pore. This value was obtained using the open-source code MacroDensity[2] by sampling the potential at the origin of unit cell – a plateaued potential was identified at this location by performing a scan of the potential change across the diagonal of the unit cell.

Experimental Methods

Materials and Characterization

All commercial chemicals were used as received unless stated otherwise. Titanium (IV) ethoxide (99.99%-Ti, Strem Chemicals), terephthalic acid (98% Sigma Aldrich), *N,N*-dimethylformamide (DMF, ACS grade, Fisher Scientific), methanol (HPLC grade, Fisher Scientific), 1,3,5-trimethoxybenzene (99.0%, Sigma Aldrich), benzyl alcohol (BnOH, 100%, Alfa Aesar), and dimethyl sulfoxide-d6 (DMSO-d6, Cambridge Isotope). Solvothermal syntheses were conducted in 100-mL Duran Schott bottles unless otherwise stated. Sample purity was verified by powder X-Ray diffraction (PXRD) with a Bruker D2 Phaser benchtop diffractometer. Photoirradiations were carried out using a mercury arc lamp. H NMR spectra were recorded at 600 MHz, d1 = 30 s, on a Bruker Advance-III-HD NMR spectrometer.

MIL-125 Synthesis

Following a procedure adapted from Dan-Hardi et. al,[3] terephthalic acid (0.748 g, 4.50 mmol), *N,N*-dimethylformamide (DMF, 9 mL) and methanol (1 mL) were added to a Pyrex jar and sonicated for ca. 5 min to ensure complete dissolution. Under an N_2 environment, titanium (IV) ethoxide (0.684 g, 3 mmol) was added to the mixture. The reaction mixture was sealed under N_2 and heated at 150 ºC for 18 hr. The contents were isolated by sequential centrifugation and decanting the mother liquor. To clean the product, the material was soaked in fresh DMF (10 mL x 3), methanol (10 mL x 3), and acetone (10 mL x 3). The product was dried using Schlenk line technique under dynamic vacuum at 180 ºC and transferred into a N_2 glovebox for analysis.

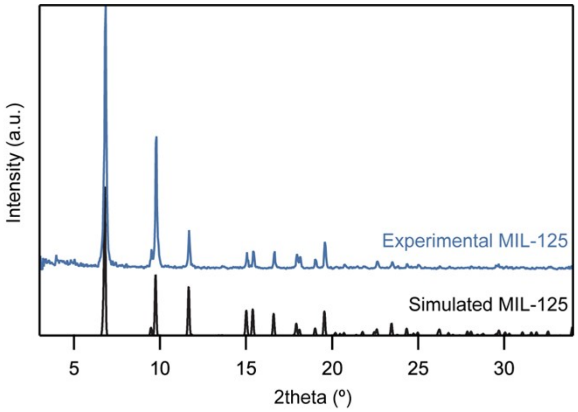

Figure S6: Experimentally determined powder X-ray diffraction pattern versus the simulated pattern for MIL-125.

q-^{1}H NMR Photodoping In an N_2 glove box, MIL-125 (10 mg) was placed in an air-free quartz cuvette with a small stir bar, DMSO-d6, and an amount of BnOH (added either neat, or dilute in DMSO-d6). The cuvette was sealed and irradiated with a mercury arc lamp while stirring. The solution was then centrifuged after irradiation, the liquid is decanted, and the standard (1,3,5-trimethoxybenzene, 10 mg) was added for quantitative analysis. After dissolution, an aliquot was taken for ^{1}H NMR and mixed with additional deuterated solvent.

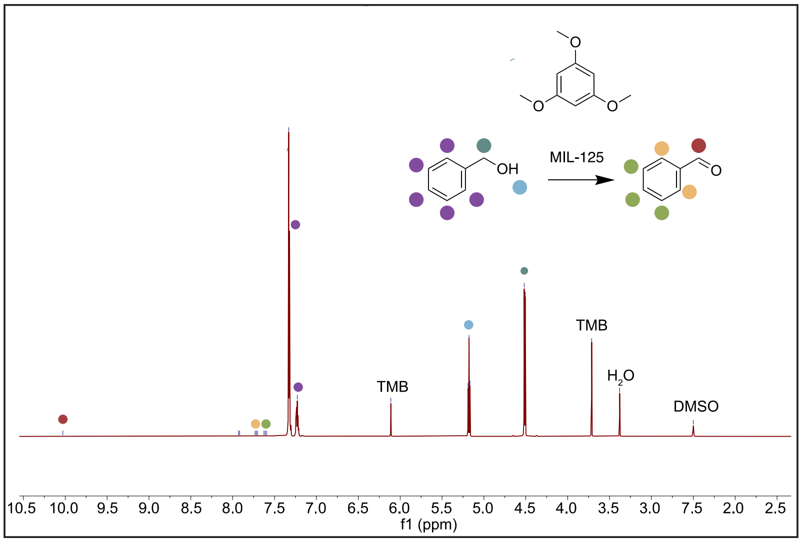

Figure S7: 1H NMR spectra for an excess amount of BnOH. A large amount of BnOH is still present in solution, marked by difference in relative peak integrations, with the small emergence of expected shifts corresponding to benzaldehyde around 10 ppm.

Preparation and Reduction of [FeCp$^*{}_2$][BF$_4$] In an N_2 glovebox, FeCp$^*{}_2$ was weighed into a Schlenk flask and dissolved in ca 5 mL hexanes. In air, benzoquinone was dissolved in ca 5 mL of ethyl ether, and HBF_4 was added. The FeCp$^*{}_2$ and benzoquinone solutions were combined by cannula transfer, creating a cloudy dark-green mixture. This solution was left to stir for one hour, and let stand for 30 minutes, yielding a green precipitate. The flask was transferred to a benchtop N_2 glovebox, where it was vacuum filtered and washed with dry hexanes (~40 mL). Once transferred into an N_2 glovebox, the powder was dissolved in dry MeCN. The concentration of the solution was tested via UV vis by way of a dilution of 100 µL in 3 mL MeCN in an air-free quartz cuvette with pathlength 1 cm, and the concentration was determined to be 25.09 mM by the 30 min irr. abs value at 778 nm for an absorptivity coefficient of 488 L mol^{-1} cm^{-1}. 1 mg of MUV-10 (Ca) was added to a mixture of 250 µL of stock [FeCp$^*{}_2$]$^+$, 200 µL dry ethanol (excess), and 3 mL dry MeCN for a total ratio of 1Ti:1.25 FeCp$^*{}_2{}^+$. The cuvette was irradiated with a mercury arc lamp, and the UV-vis spectra were recorded after allowing the powder to settle. After 23 hr of irradiation with a mercury arc photolysis lamp, the vibrant green solution had reached a steady yellow color, indicative of FeCp$^*{}_2$ formation. Using the initial absorbance values at t=0 hr and 23 hr, a relative concentration of FeCp$^*{}_2{}^+$ to FeCp$^*{}_2$ can be calculated, and thus, a solution state Fermi level can be calculated using the Nernst equation displayed in **Figure 5.**

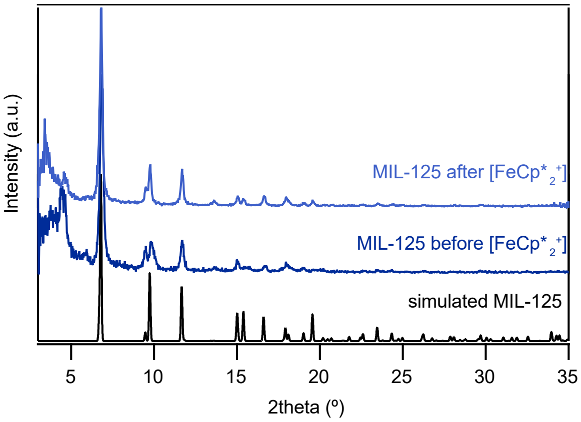

Figure S8: PXRD of MIL-125 before and after treatment with FeCp$^*{}_2{}^+$, displaying a full retention of its crystalline lattice and Bragg reflections.

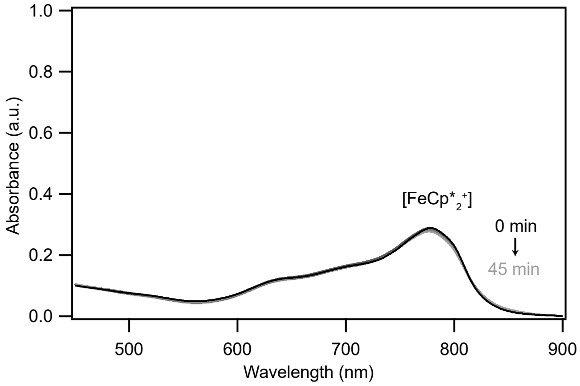

Figure S9: Solution state UV-vis of a mixture of neat FeCp$^*{}_2{}^+$ and ethanol, showing no reduction in absorbance after 45 min irradiation.

References

1. C. T. Saouma, C-C. Tsou, S. Richard, R. Ameloot, F. Vermoortele, S. Smolders, B. Bueken, A. G. DiPasquale, W. Kaminsky, C. N. Valdez, D. E. De Vos, J. M. Mayer, *Chem. Sci.* **2019**, *10*, 1322-1331.
2. K. T. Butler, C. H. Hendon, A. Walsh, *J. Am. Chem. Soc.* **2014**, *136*, 2703-2706.
3. M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez, G. Férey*, J. Am. Chem. Soc.* **2009**, *131*, 10857-10859