Heterometal incorporation in NH₂-MIL-125(Ti) and its participation in the photoinduced charge separated excited state

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Supplemental Information

Experimental Methods:

Materials:

Dry methanol, dry dimethylformamide (DMF), and anhydrous iron (III) chloride dissolved in dried solvents, were further dried over molecular sieves prior to use. Titanium (IV) tert-butoxide (Ti(OC₄H₉)₄), 2-aminoterephthalic acid (NH₂-BDC), and cetyltrimethylammoniumbromide, (CTMAB) were used without further purification.

Synthesis:

 NH_2 -MIL-125(Ti) was synthesized according to literature precedent with a slight modification¹. 0.26 mL of Ti(OC₄H₉)₄ was measured into a Schlenk flask in a glove box. To the Schlenk flask, outside the glove box, 0.504 g of NH₂-BDC, 12.1 mL DMF and 1.4 mL methanol were added to the Schlenk flask under the flow of N₂. The solution was sonicated for 30 minutes and then a spatula tip full of CTMAB was added. The reaction mixture was then transferred to a

Teflon-lined autoclave and heated to 150°C for 24 hours. The MOF was then centrifuged and resuspended with DMF and methanol 3 times. The supernatant was decanted after each washing.

NH₂-MIL-125(Ti,Fe) was synthesized using a similar procedure to the parent all Ti(IV) MOF, however, anhydrous iron (III) chloride was combined with the linker and the solvents. Similarly, 0.26 mL of Ti(OC₄H₉)₄ was measured into a Schlenk flask in a glove box. To the Schlenk flask, outside the glove box, a stoichiometric amount of anhydrous FeCl₃ dissolved in 12.1 mL DMF and 1.4 mL methanol was added, as well as 0.504 g of NH₂-BDC, under the flow of N₂. The solution was sonicated for 30 minutes and then a spatula tip full of CTMAB was added. The reaction mixture was then transferred to a Teflon-lined autoclave and heated to 150°C for 24 hours. The MOF was then centrifuged and resuspended with DMF and methanol 3 times. The supernatant was decanted after each washing.

Synthesis of NH₂-MIL-125(Ti,Fe) via a transmetallation was attempted by first activating the as-synthesized NH₂-MIL-125(Ti) under vacuum at 160°C for 24 hours. The activated framework was transferred, under N₂ gas, to a scintillation vial. Dry methanol was saturated with anhydrous FeCl₃ and added to the vial and stirred for 20 minutes. After soaking in the undisturbed vial for 7 days, the sample was isolated by centrifugation and washed three times with methanol and DMF to remove excess salt.

Characterization:

Powder XRD patterns were recorded using a Bruker D8 ADVANCE ECO Diffractometer. Steady-state electronic absorption spectra were collected using a Cary Varian UV-visible-nearinfrared (NIR) spectrophotometer. Solid-state powder samples were ground thoroughly and measured undiluted using a diffuse reflectance (DR) accessory (Harrick Scientific). Solution and liquid samples were measured in a 2 mm cuvette. Samples were suspended in DMF and centrifuged at 2.5 krpm for 20 minutes. This washing procedure was repeated 4 times to ensure complete removal of residual linker.

Atomic Absorption Spectroscopy

Iron content in NH₂-MIL-125(Ti,Fe) was evaluated using atomic absorption spectroscopy (Thermo Scientific iCE 3500 with Fe hollow cathode lamp). The MOF was first activated under vacuum at 200°C for 6 hours then digested by adding 30 mL 10% v/v H₂SO₄ to 7.5 mg NH₂-MIL-125(Ti,Fe) and stirred overnight. After diluting to 50 mL total volume, the concentration measured by AA was 5.565 (+/- 0.148) ppm. Given the theoretical concentration based on this volume and using stoichiometry of 1 Fe site per MOF cluster, the experimentally derived concentration translates to an average Fe doping level of about 1.1 per MOF cluster.

Steady State X-ray Absorption Spectroscopy:

X-ray absorption data were collected at the Fe K-edge (7112 eV) at Beamline 8-ID (ISS) at the National Synchrotron Light Source II at Brookhaven National Laboratory using a damping wiggler source and Si(111) double crystal monochromator. The monochromatic beam spot size was 1 mm. A Fe metal foil was used as the reference for energy calibration. Powder MOF sample was measured undiluted in fluorescence mode using a PIPS detector with Mn Z-1 filtering. All data were collected at room temperature. Thirty continuous-scan spectra were collected, each with 1 min. total acquisition time, and averaged. No more than 10 scans were collected on one spot to minimize x-ray damage. Negligible X-ray damage was observed with sequential scans within 10 scans per spot.

Optical Transient Absorption Spectroscopy

Optical transient absorption spectra were measured using Light Conversion Inc. ultrafast spectroscopy system. The system consists of a *Harpia* pump-probe spectrometer, an adjustable repetition rate "one box" *Pharos-SP* laser with Yb:KGW pumped design and an Orpheus-F hybrid optical parametric amplifier used to generate the pump pulse and also the probe pulse through white light continuum generation from the idler. Measurements were conducted using a 400 nm pump pulse wavelength and white light probe at 10 kHz repetition rate. Liquid samples were prepared by suspending 250 mg of MOF in dimethylformamide (DMF) and centrifuging at 2.5 krpm for 20 minutes. The supernatant containing the smallest suspended MOF nanoparticles was measured in a 2mm cuvette with concentration adjusted to achieve optical density of ~0.3-0.5. The UV/VIS of the suspensions were measured before and after OTA measurements.

X-Ray Transient Absorption Spectroscopy

The X-ray transient absorption (XTA) measurements were performed at 11-ID-D of the Advanced Photon Source (APS), at Argonne National Lab. The laser pump source was the second-harmonic output of a fs Ti:Sapphire regenerative amplified laser: 400 nm, 1.6 ps full width-half-maximum (fwhm) and 10 kHz repetition rate. The X-ray was Hybrid Fill RHB (Singlet) mode, where an intense X-ray pulse with 16% of the total average photon flux was separated in time from other weak X-ray pulses. The intense X-ray pulse with 118 ps FWHM and 271.5 kHz repetition rate was used as the probe. A mechanical chopper was used to reduce the number of probe pulses on the sample by ~50% to minimize the effect of X-ray damage.

Samples were prepared in acetonitrile. 250 mg of sample was suspended in acetonitrile and sonicated for 30 minutes. Samples were left undisturbed for at least 2 hours to allow unsuspended

larger particles to settle and the supernatant was used for measurement. To minimize photodamage, the suspended sample was purged with acetonitrile-saturated nitrogen and circulated in a closed-loop jet flow assembly during data collection. The complete experimental setup has been described elsewhere². In brief, the laser pump and X-ray probe beams were spatially and temporally overlapped at the 600 µm diameter sample stream. The laser fluence used in the measurements is ~40 μ J/mm². The X-ray fluorescence signal was detected by two avalanche photodiodes (APDs) positioned at 90° angle on both sides of the incident X-ray beam. A third APD detector, collecting upstream X-ray scattering, was used for the normalization. A Z-1 (Mn) filter/soller slit filter combination, which was custom-designed for the specific sample chamber configuration and the distance between the sample and the detector, was inserted between the sample fluid jet and the APD detectors to reduce the scattering background. Twenty-eight X-ray absorption spectra were collected and averaged at 100 ps (nominal time zero) delay time between the laser pulse and synchronized X-ray bunch to generate the "laser-on" spectrum. Spectra obtained using several X-ray bunches prior to the synchronized bunch were used to generate an average pre-time zero or "laser off" XTA spectrum. Spectra were also collected in the absence of laser light for comparison. "Laser on" – "laser off" difference spectra (Figure 4a) were generated in both the presence and absence of laser light irradiation of the sample. Time scans were collected by monitoring the signal at 7.123 keV as a function of delay time ranging from -0.2 ns to 36 ns between the laser pulse and synchronized x-ray bunch. The XTA signal derived from the next two subsequent x-ray bunches separated by 3.68 microseconds from one another, were collected simultaneously, as well.



Figure S1. Powder X-ray diffraction of MIL-125 simulated³ (black), TiO₂ anatase (red), TiO₂ rutile (blue), Fe₃O₄ (pink), Fe₂O₃ (green) and FeCl₃ soaked NH₂-MIL-125 (lime green)



Figure S2. Powder X-ray diffraction of MIL-125 simulated³ (black), NH₂-MIL-125(Ti,Fe) before XTA (purple), and NH₂-MIL-125(Ti,Fe) after XTA (light blue)



Figure S3. Model used for EXAFS fitting derived from local coordination environment of NH₂-MIL-125(Ti,) with one Ti site substituted with Fe.

EXAFS data were processed and analyzed using the Demeter program package.⁴ Fourier Transform spectra were obtained using k² weighting and a $\chi(k)$ range from 2.5 to 11 Å⁻¹. Fitting was performed in R space over the range of 1 to 3.8 Å using a fitting model derived from the reported crystal structure for NH₂-MIL-125(Ti)⁵ with 1 Ti site substituted with Fe Figure S3. Theoretical scattering paths derived from this model and associated EXAFS fitting parameters are summarized in Table S1 along with the best fit values.

The six Fe-O single scattering paths, as defined and illustrated in the figure, were parameterized using a universal expansion/contraction multiplier variable and a single Debye-Waller factor (σ^2) to account for changes in the average first coordination sphere bond length and disorder during the fit. The two carbon single scattering paths (Fe-C₁ and Fe-C₄) were treated similarly to the oxygen paths, assigning one σ^2 variable and one expansion/contraction variable to both paths. The two single scattering paths involving the adjacent Ti sites (Ti₁ and Ti₂ in the model) as well as two distal oxygen scatterers (O_{1,2}) and (O_{3,2}) were each parameterized using separate distance and σ^2 variables. Four multiple scattering paths were included in the fit as defined in Table 5.1 and Figure 5.7. Using the assumption that the C-O distance of the carboxylate moiety is fixed and defined by the crystal structure, the multiple scattering paths were varied using expansion/contraction terms based on the triangular scattering geometry involved and therefore only depended on the independent variables associated with the corresponding Fe-O and Fe-C single scattering path distances.

Table S1 EXAFS Fitting Parameters for NH₂-MIL-125(Ti, Fe) and comparison with crystallographic data for NH₂-MIL-125(Ti)

Path	CN	R _{cryst} (Å) ^a	R _{fit} (Å)	σ²
Fe-O₃	2	(Ti-O ₃) 1.89(9)	1.94(6) ± 0.017(4)	0.006 ± 0.001
Fe-O ₁	1	(Ti-O ₁) 1.94(6)	1.99(4) ± 0.017(8)	0.006 ± 0.001
Fe-O ₂	2	(Ti-O ₂) 1.98(7)	2.03(6) ± 0.018(2)	0.006 ± 0.001
Fe-O ₄	1	(Ti-O ₄) 1.98(7)	2.03(6) ± 0.018(2)	0.006 ± 0.001
Fe-Ti ₁	1	(Ti-Ti ₁) 2.76(8)	2.93(3) ± 0.04(8)	0.004 ± 0.009
Fe-Ti ₂	1	(Ti-Ti ₂) 3.55(2)	3.35(4) ± 0.01(7)	0.004 ± 0.009
Fe-C ₁	1	(Ti-C ₁) 2.87(6)	3.02(8) ± 0.22(4)	0.003 ± 0.002
Fe-C ₄	1	(Ti-C ₄) 3.00(1)	3.16(0) ± 0.23(4)	0.003 ± 0.002
Fe-O _{1_2}	1	(Ti-O _{1_2}) 3.12(9)	2.98(2) ± 0.25(8)	0.003 ± 0.003
Fe-O _{3_2}	2	(Ti-O _{3_2}) 3.35(9)	3.53(1) ± 0.11(6)	0.003 ± 0.003
Fe-O ₃ O ₂	4	(Ti-O ₃ O ₂) 3.88(5)	3.93(3) ± 0.01 ^b	0.008 ± 0.002
$Fe-O_1 O_4$	2	(Ti-O ₁ O ₄) 3.92(7)	3.97(6) ± 0.01 ^b	0.008 ± 0.002
Fe-C ₄ O ₃	4	(Ti-C ₄ O ₃) 2.98(4)	3.08(4) ± 0.11 ^c	0.008 ± 0.002
$Fe- C_1 O_1$	2	(Ti- C ₁ O ₁) 3.13(0)	3.23(4) ± 0.11 ^c	0.008 ± 0.002

^a Ti-X Distances obtained from crystal structure of NH₂-MIL-125(Ti) reported in ref 5,

^{*b*} defined parameter dependent on corresponding Fe-O single scattering path distance variables ^{*c*} defined parameter dependent on corresponding Fe-O and Fe-C single scattering path distance variables $S_0^2 = 1.00$ and $E^0 = 1.65$ eV for all paths

R = 0.003

	NH ₂ -BDC	NH ₂ -MIL-125(Ti)	NH ₂ -MIL-125(Ti,Fe)
A_1	0.18 ± 0.03	0.49 ± 0.07	0.21 ± 0.01
$ au_1$	$2119 \pm 448 \text{ ps}$	2 ± 0.4 ps	7 ± 1 ps
A ₂		0.48 ± 0.02	0.29 ± 0.01
τ_2		116 ± 17 ps	$135 \pm 12 \text{ ps}$
y _s	0.79 ± 0.03	0.05 ± 0.02	0.49 ± 0.07

Table S2. Fitting Results of Optical Transient Absorption kinetics monitored at 585 nm for NH₂-BDC, MIL-125-NH₂, and MIL-125-NH₂(Ti,Fe).^a

^{*a*} fits obtained using a multiexponential decay function with a post-time zero offset term, y_s . The function was convoluted with a Gaussian IRF (FWHM = 250 fs).

X-Ray Transient Absorption Fitting Results

Table S3. Multiexponential decay fitting parameters for the XTA kinetics monitored at 7.123 keV for NH₂-MIL-125(T,Fe)

Parameter	Value
A1	0.023 ± 0.001
$ au_1$	2 ± 0.2 ns
A2	0.009 ± 0.001
$ au_2$	70 ± 20 ns
A ₃	0.02 ± 0.0004
τ ₃	$16 \pm 1.1 \mu s$

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