Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information For:

Biomimetic O_2 Adsorption in an Iron Metal–Organic Framework for Air Separation

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Materials and Methods

All reagents were purchased from commercial vendors and used without further purification. Fe-BTTri ($Fe_3[(Fe_4Cl)_3(BTTri)_8]_2 \cdot 18CH_3OH$, H_3BTTri =1,3,5-tris(1*H*-1,2,3-triazol-5-yl)benzene)) was prepared according to a previously reported method.[1] All gases, including He, N_2, and O_2, were ultra-high purity grade (99.999%) sources. Isotopically labelled $^{18}O_2$ (99 atom % ^{18}O) was purchased from Sigma-Aldrich.

Gas adsorption measurements.

Gas adsorption isotherms for pressures in the range 0–1 bar were measured by a volumetric method using a Micromeritics ASAP2020 gas sorption analyzer. A typical sample of approximately 50 mg was transferred in an N_2 filled glovebox to a pre-weighed analysis tube, which was capped with a Micromeretics TranSeal and evacuated by heating at 160 °C with a ramp rate of 0.2 °C/min under dynamic vacuum until an outgas rate of less than 2 µbar/min was achieved, approximately 12 hours. The evacuated analysis tube containing the degassed sample was then carefully transferred to an electronic balance and weighed again to determine the mass of sample. The tube was then transferred back to the analysis port of the gas adsorption instrument. The outgas rate was again confirmed to be less than 2 µbar/min. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity); O_2 and N_2 isotherms were measured using UHP–grade gas sources. Gas adsorption isotherms of O_2 and N_2 measured between –78 and –49 °C were measured using a Julabo FT902 immersion cooler with silicone-based Julabo thermal bath fluid. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the evacuation process or of the feed gases during the isotherm measurements.

Adsorption isotherm fitting.

Adsorption isotherms were fit with a dual-site Langmuir–Freundlich equation (eq. 1), where n is the total amount adsorbed in mmol/g, P is the pressure in bar, and for site i, $n_{sat,i}$ is the saturation capacity in mmol/g, b_i is the Langmuir parameter in bar^{-1} defined in eq. 2, and v_i is the Freundlich parameter, for two sites 1 and 2.

$$n = \frac{n_{sat,1} b_1 P^{v_1}}{1+b_1 P^{v_1}} + \frac{n_{sat,2} b_2 P^{v_2}}{1+b_2 P^{v_2}} \tag{1}$$

$$b_i = e^{-S_i} e^{\frac{H_i}{RT}} \tag{2}$$

For eq. 2, for site i, S_i is the entropy of adsorption at saturation in units of R, and H_i is the enthalpy of adsorption in kJ/mol. The fitted parameters for all gases for can be found in Tables S1.

Isosteric heat of adsorption calculations.

Using the dual-site Langmuir-Freundlich fits, the isosteric heat of adsorption, $-Q_{st}$, was calculated for each compound as a function of the amount of gas adsorbed using the Clausius-Clapeyron relation (eq. 3), where R is the ideal gas constant, P is the pressure, and T is the temperature.

$$-Q_{st} = RT^2 \left(\frac{\partial \ln P}{\partial T}\right)_n \tag{3}$$

For multi-site Langmuir-Freundlich models, it is necessary to calculate the loading dependence of the isosteric heat of adsorption. As written, multi-site Langmuir-Freundlich equations specify the amount adsorbed as a function of pressure, while the pressure as a function of the amount adsorbed is needed to use the Clausius-Clapeyron relation. To calculate the isosteric heat of adsorption for evenly spaced loadings, each multi-site Langmuir equation was solved for the pressures that correspond to specific loadings of a given gas at –78 to –49 °C, and these calculated pressures were then used in eq. 3 to determine the isosteric heat of adsorption as a function of the total amount of gas adsorbed.

Ideal adsorbed solution theory calculations.

Since binary gas adsorption isotherms cannot be measured in a straightforward manner, it is often necessary to use an adsorption model, such as ideal adsorbed solution theory (IAST), to predict mixed gas behavior from experimentally measured single–component isotherms.[2] The accuracy of the IAST procedure has already been established for adsorption of a wide variety of different gases in zeolites and metal−organic frameworks.[3] Here, IAST is used to estimate the selectivity of Fe-BTTri for mixtures of O_2 and N_2 at –78, –61, and –49 °C, with a total pressure of 1 bar for all calculations. The selectivity factor, S, is defined according to eq. 4, where n_i is the amount adsorbed of each component as determined from IAST and x_i is the mole fraction of each component in the gas phase at equilibrium.

$$S = \frac{n_{O_2}/n_{N_2}}{x_{O_2}/x_{N_2}} \tag{4}$$

Synchrotron powder X-ray diffraction.

Powder X-ray diffraction data for Fe-BTTri was collected on Beamline 17-BM-B at the Advanced Photon Source at Argonne National Laboratory. Approximately 3 mg of fully desolvated framework was loaded into a 1.0 mm borosilicate capillary inside a N_2-filled glovebox. The capillary was then attached to a custom designed gas-dosing cell equipped with a gas valve and transferred to the goniometer head. All adsorbed N_2 was removed by evacuating *in situ* using a turbomolecular pump. An Oxford Cryosystems Cryostream 800 was used to maintain the temperature of the sample. Scattered intensity was measured by a PerkinElmer a-Si flat panel detector, and the average wavelength of measurement was 0.45241 Å.

Diffraction data was collected for desolvated Fe-BTTri under vacuum at – 80 °C, after which 7 mbar of O_2 gas was dosed using a custom-built gas dosing manifold. The gas was equilibrated on the sample for half an hour, until no further change was observed in both the pressure above the sample and in the resulting diffraction patterns. The temperature was then raised to –30 °C at 3 ºC/min, equilibrated for five minutes, cooled back down to –80 °C, equilibrated for five minutes, then raised to –30 °C and then subsequently to 27 °C. Precise unit cell parameters were obtained by Pawley refinement as implemented in TOPAS-Academic 4.1,[4] and were found to be consistent with the $Pm\bar{3}m$ space group for all patterns (Table S2), as previously found in an analogous framework.[5]

Infrared Spectroscopy.

Infrared spectra were collected using a Bruker Vertex 70 spectrometer equipped with a glowbar source, KBr beamsplitter, and a liquid nitrogen cooled mercury-cadmium-telluride detector. A custom-built diffuse reflectance system with a IR-accessible gas dosing cell was used for all measurements. Sample temperature was controlled by an Oxford Instruments OptistatDry TLEX cryostat, and sample atmosphere was controlled by a Micromeritics ASAP 2020Plus gas sorption analyzer. Prior to measurement, activated Fe-BTTri (~10 wt%) was dispersed in dry KBr in an argon-filled glovebox and evacuated at room temperature overnight. Spectra were collected *in situ* under UHP-grade O_2 or $^{18}O_2$ (99 atom % ^{18}O, Sigma-Aldrich) at 4 cm^{-1} resolution continually until equilibrium was observed.

Mössbauer Spectroscopy.

The Mössbauer spectra of O_2-dosed Fe-BTTri were measured at various temperatures with a constant acceleration spectrometer which utilized a rhodium matrix cobalt-57 source. Isomer shifts were reported relative to 27 μm α-iron foil at 295 K. The absorber contained 40 mg/cm^2 of activated Fe-BTTri and was prepared in an N_2-filled glovebox. The sample was placed in a Schlenk flask and placed under vacuum, chilled to –78 °C, and dosed with 210 mbar of O_2 for 10 minutes. The sample was then quickly transferred to a pre-cooled cryostat under dry helium. The Mössbauer spectra were fit with a sum of symmetric Lorentzian doublets. In some cases, some spectral parameters were constrained and they are reported without error bars in Table S3.

Supporting Discussion

Mössbauer spectroscopy. The Mössbauer spectra collected at –78 °C shows a small amount of sites that we attribute to a high-spin Fe(III) species that accounts for 15.2(7)% of the total absorption area. This likely comes from an irreversible oxidation upon exposure to O_2 at temperatures greater than –15 °C. This could be due to incomplete cooling or some warming during the dosing or sample transferring process. The relative amount of this site is relatively consistent between both spectra measured at different temperatures.

There also exists two different high-spin Fe(II) species after O_2 dosing at –78 °C. A small amount, approximately 11%, are attributed to charge-balancing extra framework cations, which have been demonstrated to not participate in gas binding.[1] Additionally, due to incomplete saturation of the iron sites at this pressure as determined through the gas adsorption isotherm (Figure S1), there remains some residual high-spin Fe(II) of the activated framework at –78 °C. Accounting for the presence of the charge-balancing extra framework cations, the total amount of Fe(III) species corresponds to the O_2 loading observed in the gas adsorption isotherms at these temperatures and pressures. The O_2 loading calculated from the Mössbauer data is approximately 2.9 mmol/g, while the actual uptake from the gas adsorption isotherm is 3.3 mmol/g, which likely includes a small amount of physisorbed O_2 at these low temperatures.

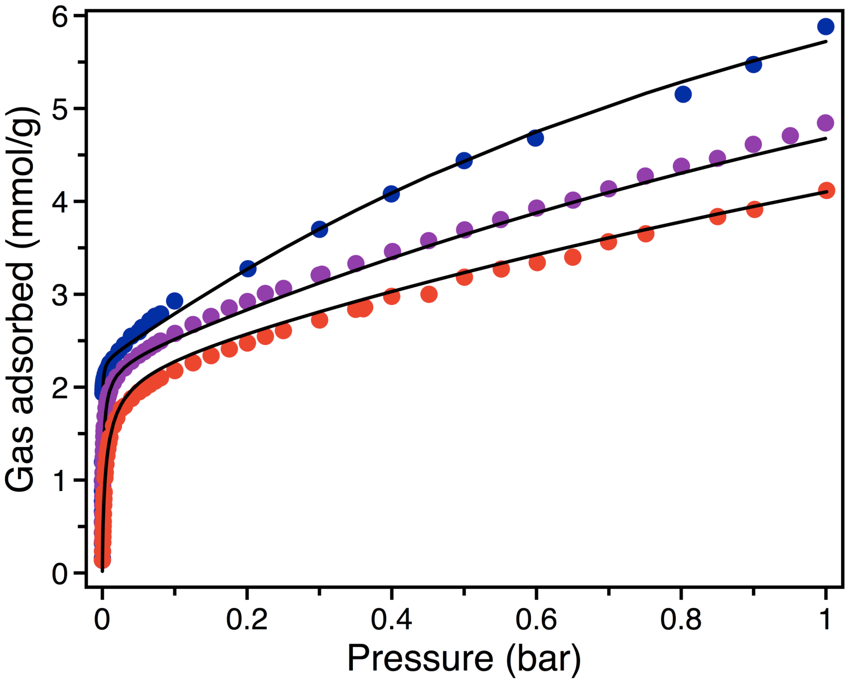

Figure S1. Adsorption isotherms of O_2 for Fe-BTTri collected at –78 °C (blue), –61 °C (purple), and –49 °C (red), with fits to the Langmuir-Freundlich equation shown in black.

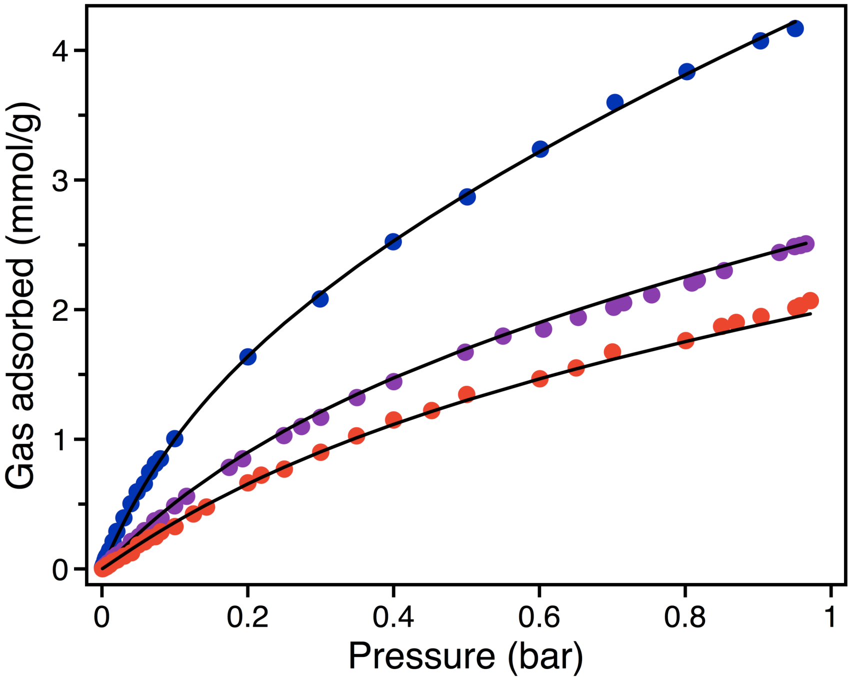

Figure S2. Adsorption isotherms of N_2 for Fe-BTTri collected at –78 °C (blue), –61 °C (purple), and –49 °C (red), with fits to the Langmuir-Freundlich equation shown in black.

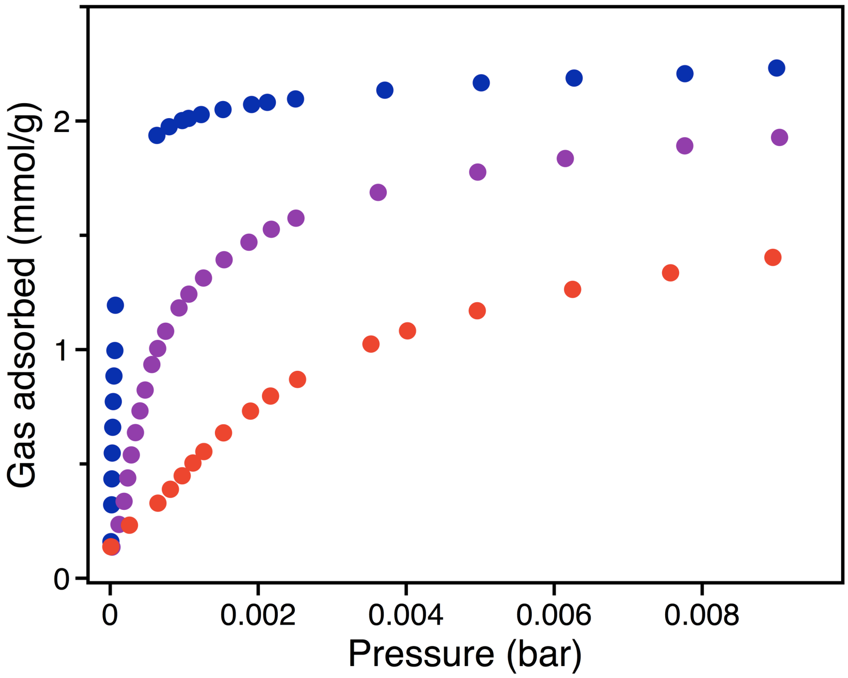

Figure S3. Adsorption isotherms of O_2 for Fe-BTTri collected at –78 °C (blue), –61 °C (purple), and –49 °C (red), highlighting the low-pressure region.

Table S1. Dual-site Langmuir-Freundlich parameters for O_2 and N_2 adsorption isotherms in Fe-BTTri, with variable defined in eq. 1 and eq. 2.

	O_2	N_2
$n_{sat,1}$ (mmol/g)	2.32	19.0
H_1 (kJ/mol)	38.0	17.0
S_1 (R)	16.5	12.5
v_1	0.748	1.03
$n_{sat,2}$ (mmol/g)	7.29	2.06
H_2 (kJ/mol)	12.1	13.9
S_2 (R)	7.57	7.00
v_2	1.09	1.03

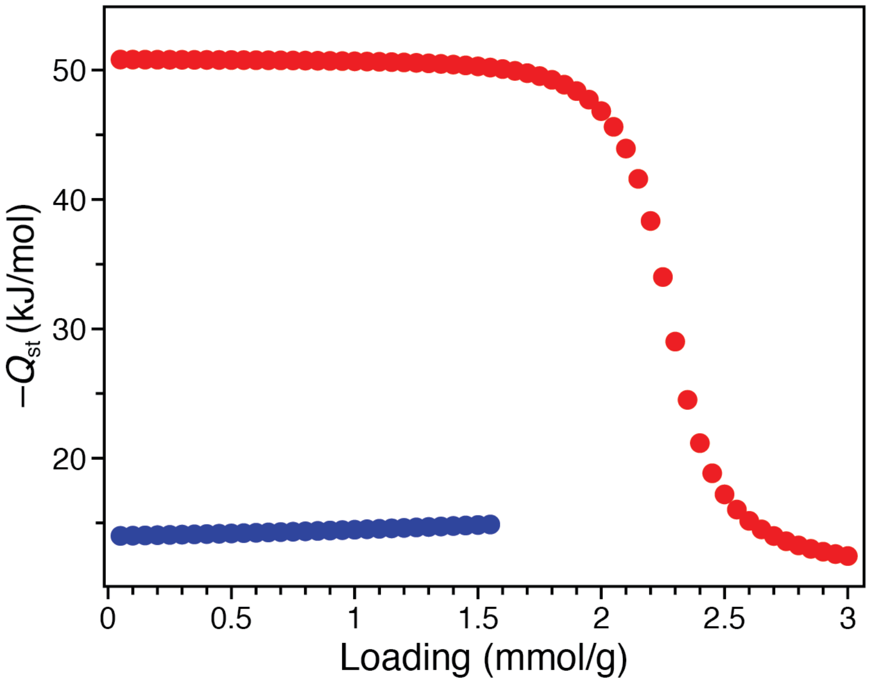

Figure S4. Isosteric heat of adsorption for O_2 (red) and N_2 (blue) as a function of loading for Fe-BTTri, calculated from isotherms collected at –78, –61, and –49 °C. Error bars (not shown) are within the symbols.

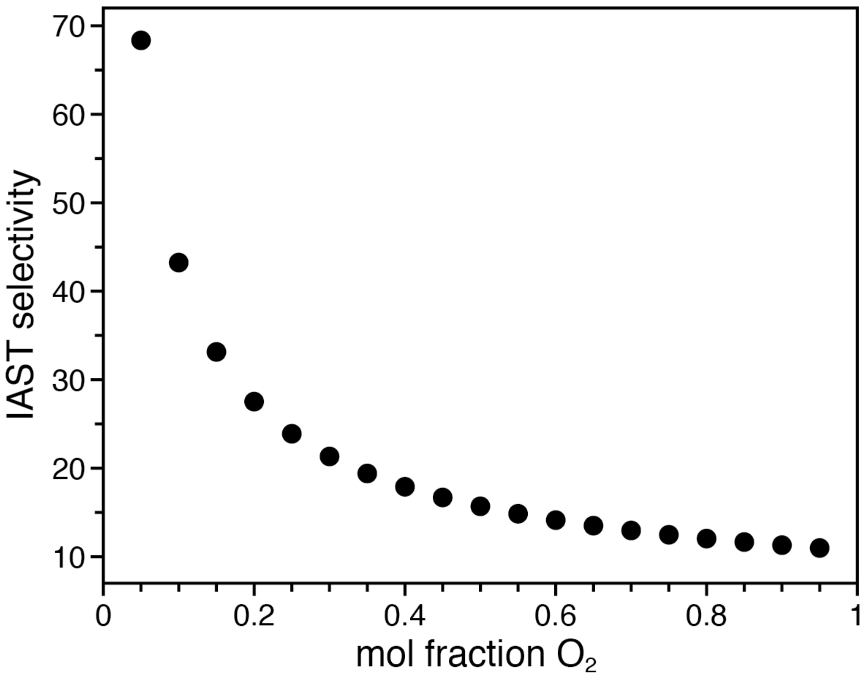

Figure S5. Ideal adsorbed solution theory (IAST) values collected for varying O_2:N_2 ratios in Fe-BTTri at –78 °C and a total pressure of 1 bar.

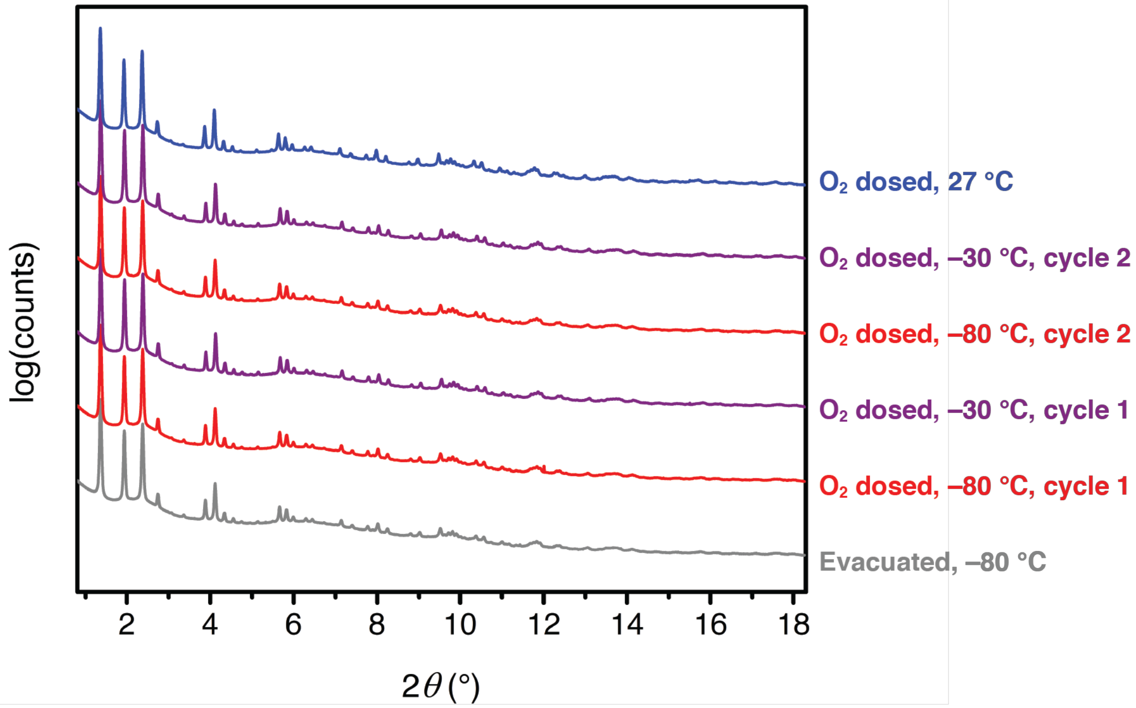

Figure S6. Variable temperature powder X-ray diffraction data of Fe-BTTri collected with a synchrotron source (λ = 0.45241 Å) either under vacuum (grey) or a 7 mbar atmosphere of O_2 (red, purple, and blue). For the O_2-dosed framework, consecutive heating and cooling cycles between –80 °C (red) and –30 °C (purple) are performed, with each cycle labelled as cycle 1 or cycle 2. The spectra are offset for clarity.

Table S2. Experimental, unit cell, and refinement parameters obtained by Pawley refinement using synchrotron X-ray powder diffraction patterns of Fe-BTTri under vacuum at –80 °C, and after being dosed with 7 mbar of O_2 at different temperatures.

	Evacuated Fe-BTTri	7 mbar O_2, Cycle 1	7 mbar O_2, Cycle 1 up	7 mbar O_2, Cycle 2 down	7 mbar O_2, Cycle 2 up	7 mbar O_2, RT
λ (Å)	0.45241	0.45241	0.45241	0.45241	0.45241	0.45241
Temperature	–80 °C	–80 °C	–30 °C	–80 °C	–30 °C	27 °C
Space Group	$Pm\bar{3}m$	$Pm\bar{3}m$	$Pm\bar{3}m$	$Pm\bar{3}m$	$Pm\bar{3}m$	$Pm\bar{3}m$
a (Å)	18.9829(8)	18.8497(8)	18.8912(8)	18.8428(8)	18.8871(8)	18.8967(8)
Vol. (Å^3)	6840.5(8)	6697.5(8)	6741.9(8)	6690.1(9)	6737.5(8)	6747.7(9)
R_{wp} (%)	2.20	2.28	2.17	2.25	2.18	2.15
R_{exp} (%)	2.16	2.14	2.17	2.16	2.18	2.19
R_p (%)	1.59	1.73	1.60	1.72	1.60	1.59

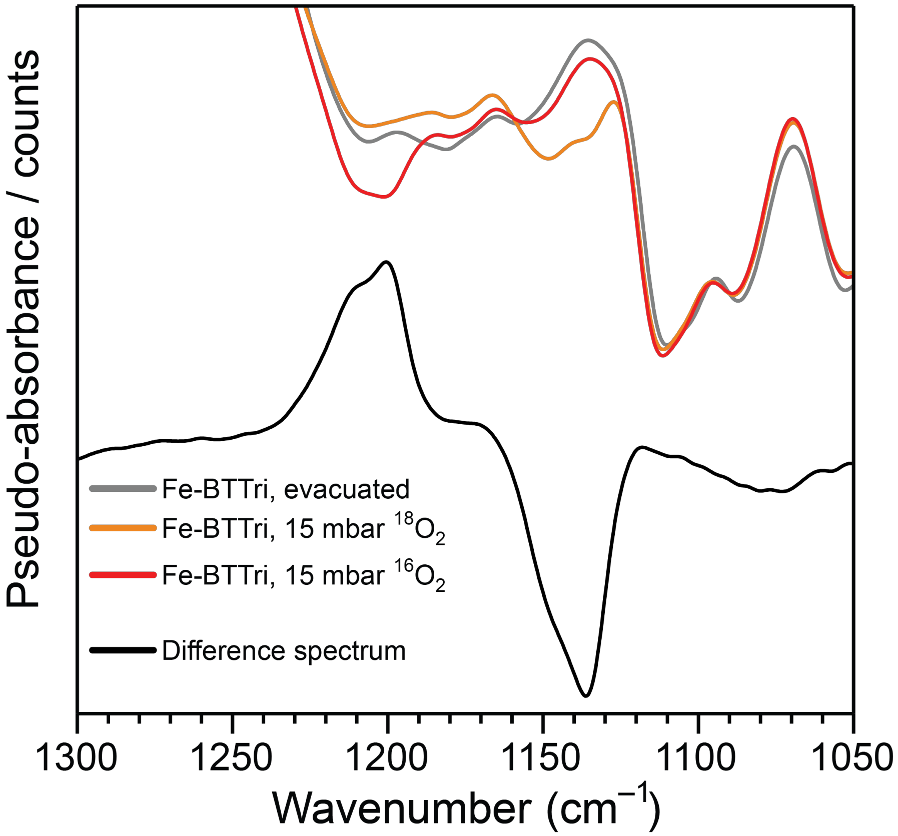

Figure S7. Raw *in-situ* DRIFTS spectra of activated Fe-BTTri (grey), Fe-BTTri dosed with 15 mbar of $^{16}O_2$ (red), and Fe-BTTri dosed with 15 mbar of $^{18}O_2$ (orange). Difference spectra between $^{16}O_2$- and $^{18}O_2$-dosed framework (black) allows unambiguous assignation of υ(O–O) peaks distinct from framework vibrations (positive peak for $^{16}O_2$ and negative for $^{18}O_2$) which fall in the expected region for superoxide species.[6]

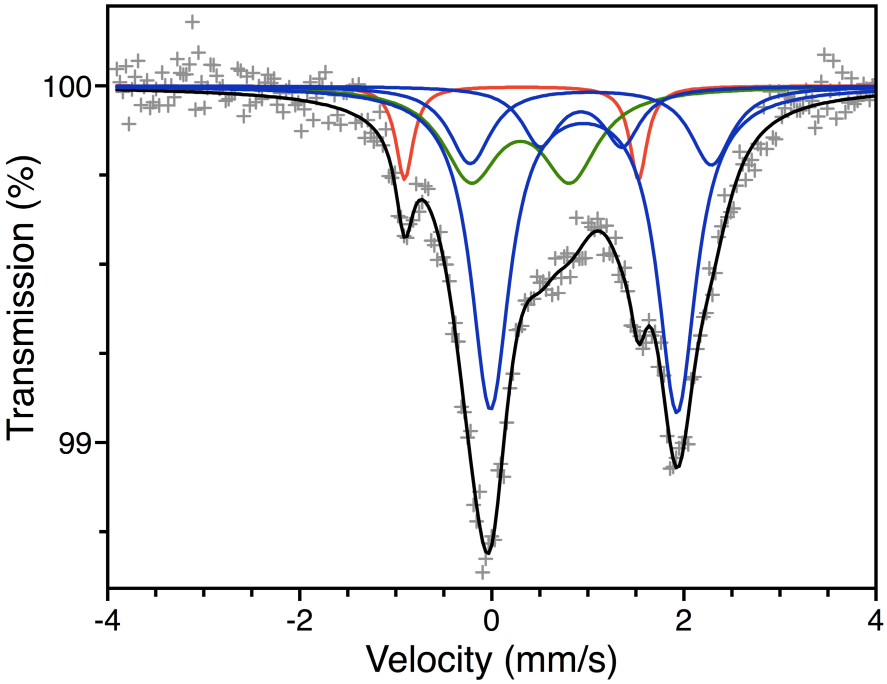

Figure S8. Mössbauer spectrum of Fe-BTTri collected at –28 °C under an atmosphere of 210 mbar of O_2, with the experimental data in grey plusses and the total fit in black. The red component is assigned to low-spin Fe(III), the green component is assigned to high-spin Fe(III), and the blue components are assigned to high-spin Fe(II). The parameters for all components are listed in table S3.

Table S3. Mössbauer parameters. [a]LS = low-spin, HS = high-spin

Temperature	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	Area (%)	Assignment[a]
–78 °C	0.309(2)	2.370(3)	0.362(6)	50.8(9)	Fe(III) (LS)
	0.351(40)	1.04(9)	0.70	15.2(7)	Fe(III) (HS)
	1.036(18)	2.08(8)	0.61(8)	20(6)	Fe(II) (HS)
	1.032(20)	2.64(6)	0.48(7)	14(5)	Fe(II) (HS)
–28 °C	0.309(11)	2.44(2)	0.22(4)	7(1)	Fe(III) (LS)
	0.30(5)	1.04(10)	0.70	20(3)	Fe(III) (HS)
	0.93(4)	0.85(9)	0.46(14)	9(3)	Fe(II) (HS)
	0.96(1)	1.94(3)	0.49(7)	51(11)	Fe(II) (HS)
	1.03(4)	2.51(4)	0.53(12)	13(6)	Fe(II) (HS)

References

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