Supporting information

Reversible Binding of Nitric Oxide to an Fe(III) Complex of a Tetra-amido Macrocycle

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Materials and Methods.

Reagents for synthetic procedures were purchased from Strem Chemicals or Aldrich Chemical Co. and used as received. Air-sensitive manipulations were performed using standard Schlenk techniques or in an N_2-filled glove box. Nitric oxide (Matheson, 99%) was purified as described in the literature.[1] The NO gas was passed through a 6-foot silica-filled coil cooled to −78 °C, and then through an Ascarite column (NaOH fused on silica gel). After collection, NO was stored in gas bulbs and transferred using gas-tight syringes. ^{15}NO was purchased from Aldrich and purified by the above method. Methanol and acetonitrile were dried by distillation over CaH_2 followed by successive freeze-pump-thaw cycles to remove dissolved gasses. Li_2[Fe(TAML)Cl], where TAML is the hexamethyl tetra-amide macrocycle (TAML) analog, was prepared as described in the literature.[2]

Physical Methods.

NMR spectra were recorded on a 400 MHz Bruker spectrometer and referenced to residual solvent peaks. Solid state IR spectra were measured on a ThermoNicolet Avatar 360 spectrophotometer equipped with OMNIC software. Solution state React-IR data were measured on a Mettler Toledo spectrometer in an air-tight cell with an N_2 inlet and a septum port for NO addition. UV-vis spectra were recorded on a Cary 50 spectrophotometer. UV-vis experiments were performed in septum-capped UV-vis cells (Starna). Low temperature UV-vis experiments were performed in a custom-built jacketed UV-vis cell. Zero field ^{57}Fe Mössbauer spectra were recorded on an MSI spectrometer (WEB Research Company) with a ^{57}Co source in a Rh matrix at 80 K. Isomer shift values (δ) are reported with respect to metallic iron that was used for velocity calibration. Mössbauer spectra were fit to Lorenztian lines using the WMOSS program. X-band EPR spectra were recorded on a Bruker EMX EPR spectrometer at 77 K.

Sample Preparation Procedures.

General conditions for UV-vis experiments: In a glove box, a concentrated stock solution of Li[Fe(TAML)] was prepared in MeOH and added to MeCN to attain the desired concentration. The volume ratio of MeOH:MeCN was held constant at 1:100. The resultant solution was transferred to a septum-capped UV-vis cell (3 mL solution volume) and removed from the glove box. Nitric oxide was added by gas-tight syringe. Purging of the solutions was achieved by bubbling dry N_2 through the cuvette.

General conditions for React-IR experiments: The gas-tight solution cell for React-IR experiments was flushed with N_2 for 30 min prior to introduction of the $[Fe(TAML)]^-$ solution. A higher MeOH content was used in the React-IR studies to maintain sufficient solubility to monitor the IR spectrum. MeOD was used instead of MeOH to provide a more clear spectral window for observation of the nitrosyl stretch. After rigorous flushing of the cell with N_2, the solution of $[Fe(TAML)]^-$ in 5:1 MeCN:MeOD prepared in a glove box was added by syringe. The solution was stirred and the React-IR spectrum was monitored to confirm stability. After stirring for 5 minutes, 5 equiv. of NO gas was added using a gas tight syringe. To remove the NO from the React-IR cell, a steady flow of N_2 was administered through the cell. We attribute the slower coordination and release of NO in the React-IR studies to the small solution-gas contact area in the React-IR cell and the higher concentrations required.

General conditions for EPR/NMR experiments: In a glove box, a stock solution of Li[Fe(TAML)] in either MeOH or *d*$_4$-MeOH was prepared. This solution was transferred to a septum-capped NMR or EPR tube. Nitric oxide was added to the NMR/EPR tubes by gas tight syringe.

Calculations

All calculations were performed by using the Gaussian 03 software package.[3] Geometry optimizations, and unscaled frequency calculations were carried out using the B3LYP/6-31+g(d,p) level of theory. Frequency calculations were performed on all converged structures and confirmed that they corresponded to local minima or transition states on their respective potential-energy surfaces. TDDFT calculations were performed at the PBE1PBE/6-311+g(d,p) level of theory on the optimized structures. UV-vis spectra were generated from the TDDFT output using GaussSum, with a FWHM of 3000 cm^{-1}.

H_2O titration of [Fe(TAML)-NO]$^-$

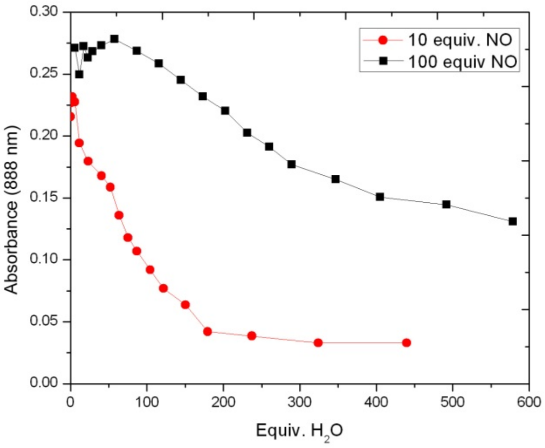

Figure S1. Addition of H_2O to a solution of 80 μM [Fe(TAML)]$^-$ in 99:1 CD_3CN:CH_3OH containing 10 equiv of NO (red) or 100 equiv of NO (black) results in NO displacement.

EPR Spectra

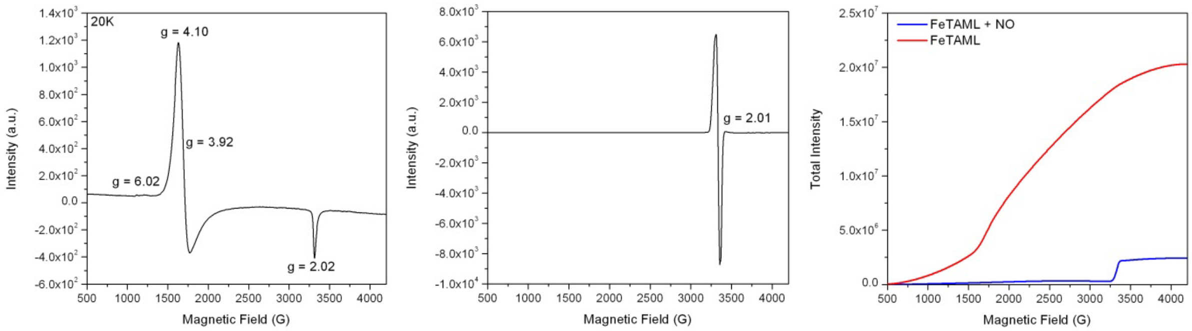

Figure S2. Left: EPR Spectrum of [Fe(TAML)]$^-$ at 20 K. Middle: EPR spectrum of [Fe(TAML)]$^-$ after reaction with NO. Right: Comparison of the spin integration of [Fe(TAML)]$^-$ before and after reaction with NO. Conditions: 10 mM [Fe(TAML)]$^-$ in MeOH, 10 equiv of NO.

NMR Spectra

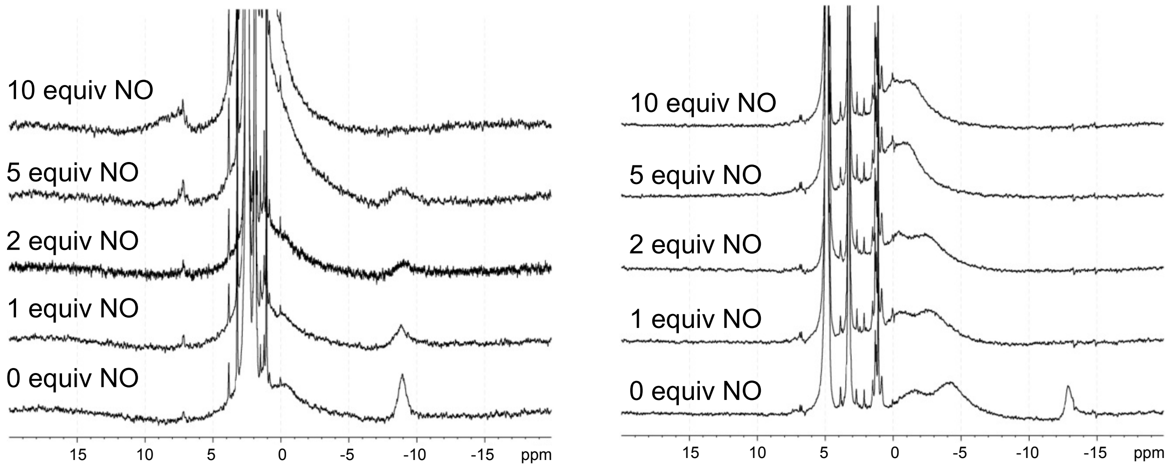

Figure S3. Left: Addition of NO to a 10 mM solution of $[Fe(TAML)]^-$ in 9:1 CD_3CN:CD_3OD. Right: Addition of NO to a 10 mM solution of $[Fe(TAML)]^-$ in CD_3OD.

DFT Calculations

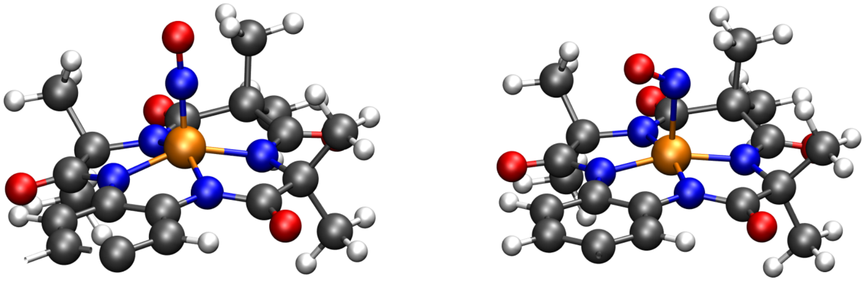

Figure S4. Optimized geometries of S=0 [Fe(TAML)NO]$^-$ (left) and S=1 [Fe(TAML)NO]$^-$ (right).

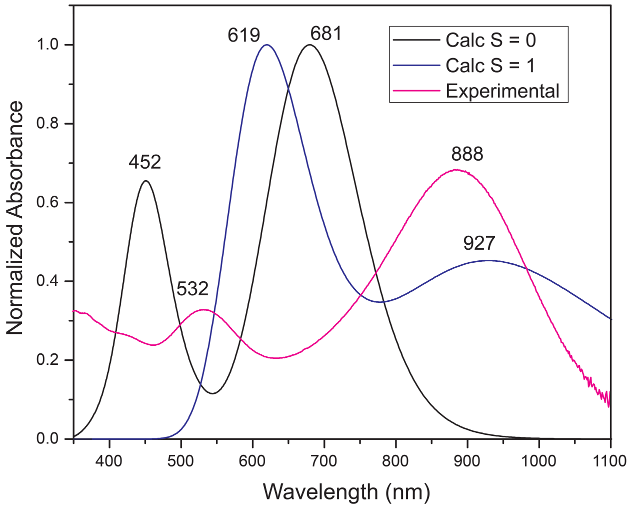

Figure S5. Calculated UV-vis spectra of S=0 [Fe(TAML)NO]$^-$ and S=1 [Fe(TAML)NO]$^-$ compared to the experimental spectrum.

XYZ coordinates of the optimized structures

X,Y,Z Coordinates for Optimized Geometry of S=0 $[Fe(TAML)NO]^{-}$

Fe	-0.00060700	-0.04261300	-0.01069600
O	0.00120800	-0.00000400	3.97703200
O	4.00563200	0.02614800	0.72127300
O	2.01915000	1.11995800	-3.35075500
O	-2.95924400	1.63807800	-2.08990200
N	-0.62530300	0.14895400	1.76014600
N	1.72679600	0.08505800	0.79807400
N	0.52226600	0.74768500	-1.67075800
N	-1.67847600	0.72885100	-0.39827200
C	-2.00340300	0.34105100	1.88353000
C	0.27394000	0.02335900	2.78099000
C	1.73173300	-0.04402700	2.27975100
C	2.91235200	0.07548700	0.14204100
C	2.93492500	0.06585400	-1.41309800
C	1.76399700	0.70673100	-2.21176700
C	-0.60260900	1.24769100	-2.50483800
C	-1.89072100	1.21973700	-1.65552300
C	-2.60915000	0.67482300	0.64207000
C	-3.98626100	0.92373800	0.57616600
H	-4.42955000	1.18683400	-0.37244100
C	-4.74566100	0.83767100	1.74118600
H	-5.81259800	1.02994800	1.69431000
C	-4.15003200	0.50929300	2.96213600
H	-4.75609700	0.44725800	3.86012500
C	-2.78171300	0.25980100	3.04563300
H	-2.30569100	0.01596100	3.98348700
C	2.46770400	1.13867300	2.95005700
H	3.53045000	1.09547100	2.72241900
H	2.30677400	1.08815400	4.02891200
H	2.06504600	2.08722200	2.58375200
C	2.32104100	-1.39286800	2.74471400
H	3.37637900	-1.44761400	2.48157600
H	1.79356000	-2.22673400	2.27137100
H	2.20217700	-1.48397300	3.82678000
C	4.23936100	0.75798100	-1.86442900
H	4.23739300	1.81376000	-1.58038400
H	4.32878200	0.70129100	-2.94815300
H	5.09243700	0.28156900	-1.38394900
C	3.01019400	-1.42508900	-1.84778800
H	2.12245200	-1.98785700	-1.55438700
H	3.88238100	-1.89543200	-1.38650500
H	3.11177400	-1.48420500	-2.93449000
C	-0.84675500	0.36295100	-3.74588900
H	0.00463000	0.42498400	-4.42212800
H	-1.75209700	0.69984900	-4.25583600
H	-0.98832100	-0.68110300	-3.45012600
C	-0.39394100	2.72441900	-2.91161300

H	0.44884800	2.80940200	-3.59391400
H	-0.19531900	3.33330900	-2.02511600
H	-1.30629500	3.09206800	-3.38575700
N	-0.19024700	-1.58945800	-0.33296800
O	-0.40142200	-2.71540700	-0.53318000

Energy: -2651.41262456 hartree
Lowest Freq: 30.78 cm^{-1}
v(NO): 1870 cm^{-1}

X,Y,Z Coordinates for Optimized Geometry of S=1 [Fe(TAML)NO]$^{-}$

Fe	-0.01105400	-0.04206000	-0.00664200
O	-0.00553700	0.02599600	3.97057400
O	3.98488600	-0.03876200	0.63121800
O	1.96474900	0.75113200	-3.45814300
O	-3.10830700	0.96929400	-2.29209000
N	-0.65740800	0.09952900	1.75154700
N	1.70115600	-0.08979600	0.76572500
N	0.44103800	0.37841600	-1.78999900
N	-1.77538400	0.40767100	-0.48667500
C	-2.05090600	0.24279100	1.84949000
C	0.24819200	0.02624700	2.76926600
C	1.71829300	-0.03151600	2.25946400
C	2.87988300	-0.08930500	0.08335700
C	2.85055200	-0.26496600	-1.47106800
C	1.69402900	0.37343300	-2.31332100
C	-0.71013300	0.78782700	-2.64774400
C	-2.01336200	0.72032900	-1.80013700
C	-2.68506400	0.41364800	0.58113300
C	-4.07353500	0.57139200	0.50770800
H	-4.53469000	0.70602400	-0.45993900
C	-4.82589700	0.56580000	1.68263400
H	-5.90229300	0.69026500	1.62569500
C	-4.20644900	0.40179000	2.92212500
H	-4.80256600	0.39822500	3.82899800
C	-2.82298100	0.23988600	3.01553700
H	-2.33009700	0.11664500	3.96887700
C	2.40287200	1.25235000	2.77876000
H	3.46309000	1.23927100	2.53291100
H	2.27017600	1.31533600	3.86105700
H	1.94617000	2.13593800	2.32303500
C	2.37846000	-1.28362200	2.86839400
H	3.43767300	-1.30803800	2.61520000
H	1.90273800	-2.19165700	2.48541600
H	2.25555600	-1.26483800	3.95337600
C	4.18840100	0.25655900	-2.02901300
H	4.29003900	1.33135000	-1.85965800
H	4.23223500	0.08135500	-3.10296600

H	5.01782600	-0.24103000	-1.52808300
C	2.77947900	-1.79588800	-1.73586600
H	1.84187200	-2.22861600	-1.38157700
H	3.60814200	-2.29811200	-1.22874900
H	2.86086900	-1.98803200	-2.80929200
C	-0.88591400	-0.15874700	-3.85174000
H	-0.03298800	-0.07039000	-4.52364500
H	-1.80476500	0.09726200	-4.38389100
H	-0.96196100	-1.19630800	-3.51319600
C	-0.58526600	2.25427400	-3.11849500
H	0.26936700	2.35866500	-3.78438300
H	-0.44424200	2.91608700	-2.25878000
H	-1.50200200	2.54847700	-3.63445500
N	-0.63397700	-2.05617500	-0.31030000
O	-1.21207300	-2.64600800	0.49553800

Energy: -2651.41896644 hartree
Lowest Freq: 25.47 cm^{-1}
v(NO): 1833 cm^{-1}

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