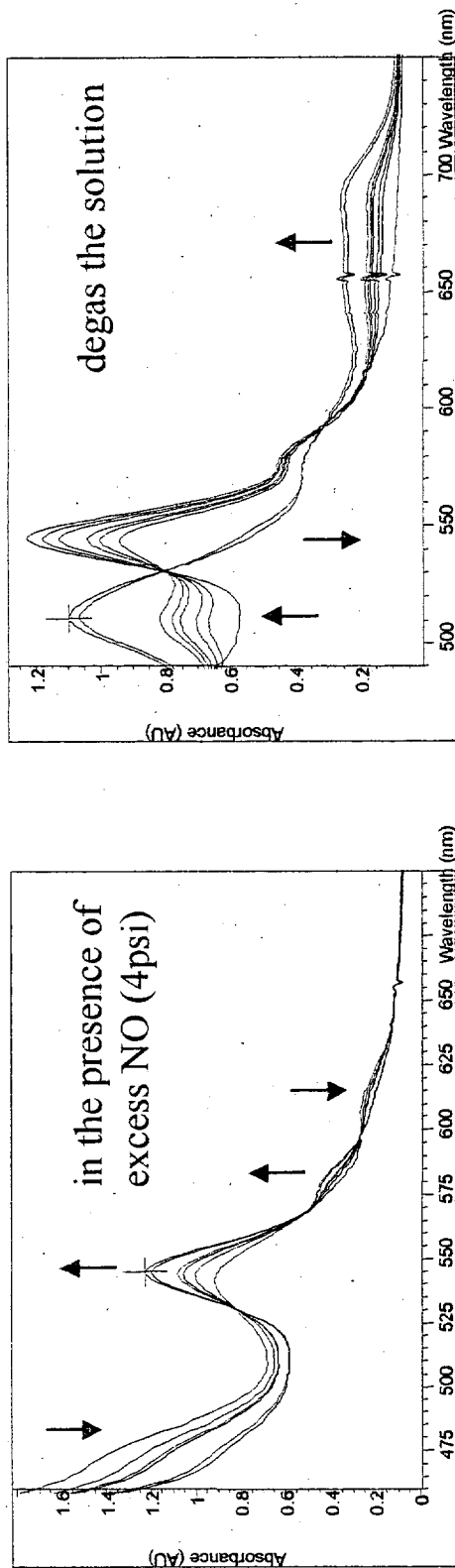


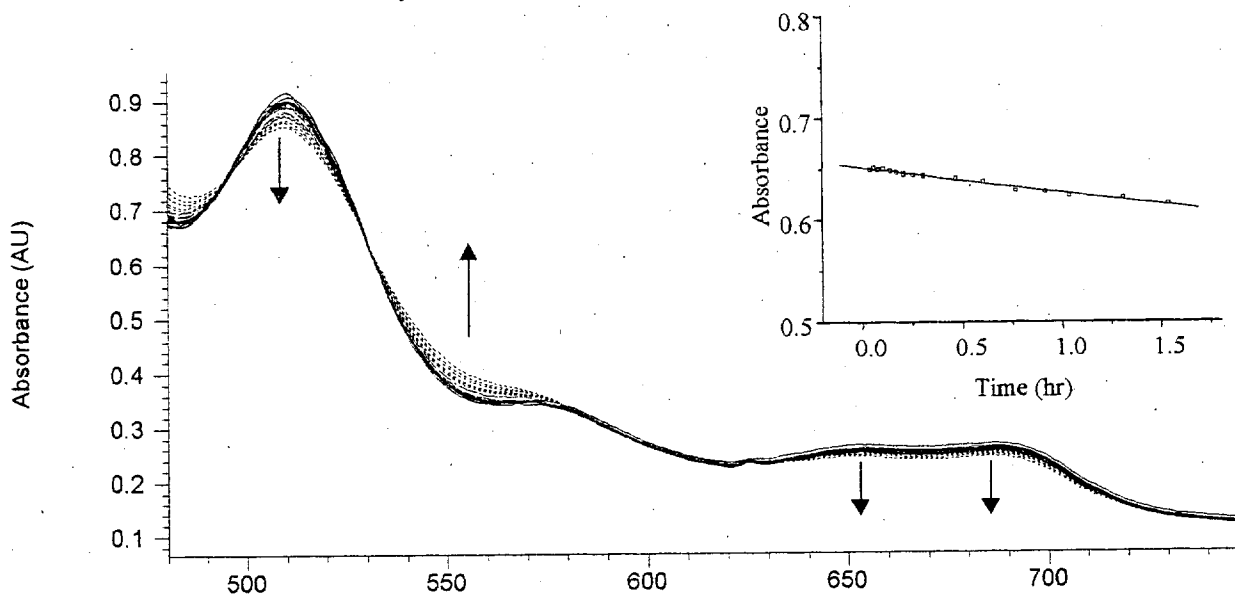
S1. Absorbance characterization of the reaction of Fe(TPP)(NO) with excess NO



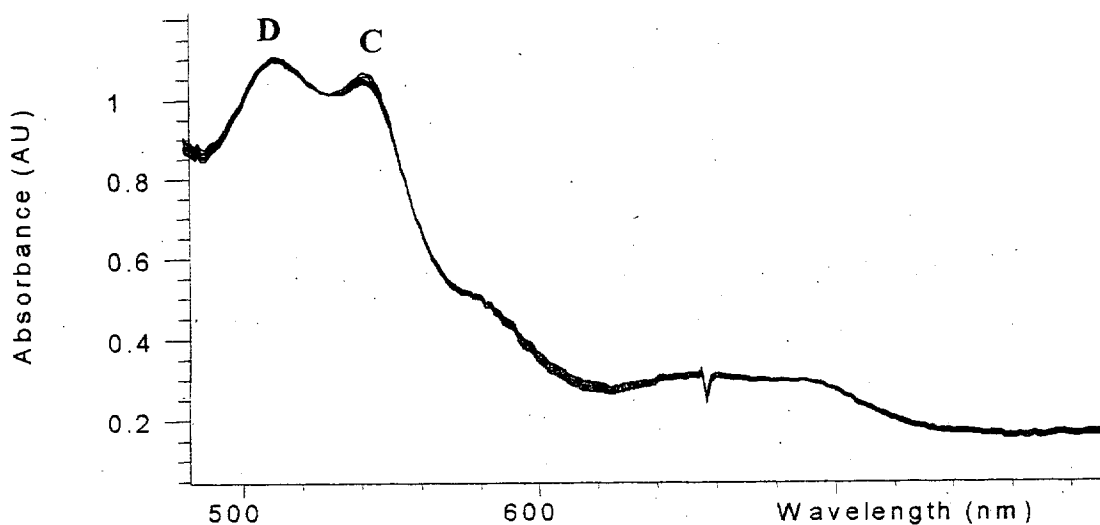
Under 4 psi NO pressure, the spectrum of NO-Fe(TPP) changes gradually with the peak positions shifted to 545 and 580 nm, assigned as Fe(TPP)(NO<sub>2</sub>)(NO) or **C** in the text. As the NO headgas is evacuated, the spectrum changes to a new species, assigned as Fe(TPP)(NO<sub>2</sub>) or **D**, with peak positions at 508, 576, 653 and 686 nm. Repeating the same pressure cycle, we can only see the interchange between compounds **C** and **D**.



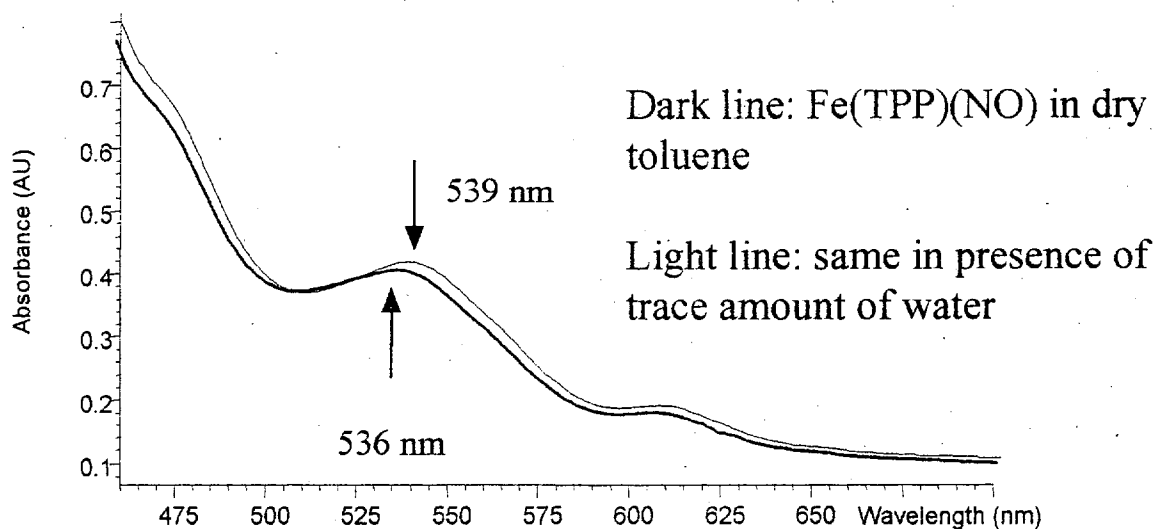
Supplemental Page 2: The reactions of  $(\text{NO})(\text{NO}_2)\text{Fe}(\text{TPP})$  and  $(\text{NO}_2)\text{Fe}(\text{TPP})$  with  $\text{PPh}_3$  as followed by absorbance.



**S2:** Above: Changes in the absorbance spectra during the reaction between compound **D**,  $(\text{NO}_2)\text{Fe}(\text{TPP})$ , (0.05 mM) and  $\text{PPh}_3$  (0.5 mM) to form compound **A**,  $(\text{NO})\text{Fe}(\text{TPP})$  over 90 minutes. Time course of the absorbance change at 511nm. The slow transformation suggested a negligible effect of this side reaction to the reactions described in the text. Below, same mixture under an NO atmosphere where both Compounds **C** and **D** are present, there is no compound **A** formation after 2 hours.



Supplemental Page 3: Electronic absorbance spectra of ca. .2 mM NO-Fe(TPP) in 10 ml toluene, before and after addition of 1 uL water. Similar shift in the absorbance maxima was seen between wet and dry chloroform solutions of NO-Fe(TPP).



Supplemental Page 4: a table of the ion abundances obtained from mixed label  $\text{N}_2\text{O}$  with explanation of the data analysis.

Percentage ion abundances from mixed label  $\text{N}_2\text{O}$  ionization in GC/MS

Expt #	m/z 30	m/z 31	m/z 45	m/z 46
1	18	.75	8.6	1
2	19	.78	8.4	1
3	19	.77	8.6	1
4	24	.88	8.1	0.7
5	20	.84	8.9	1

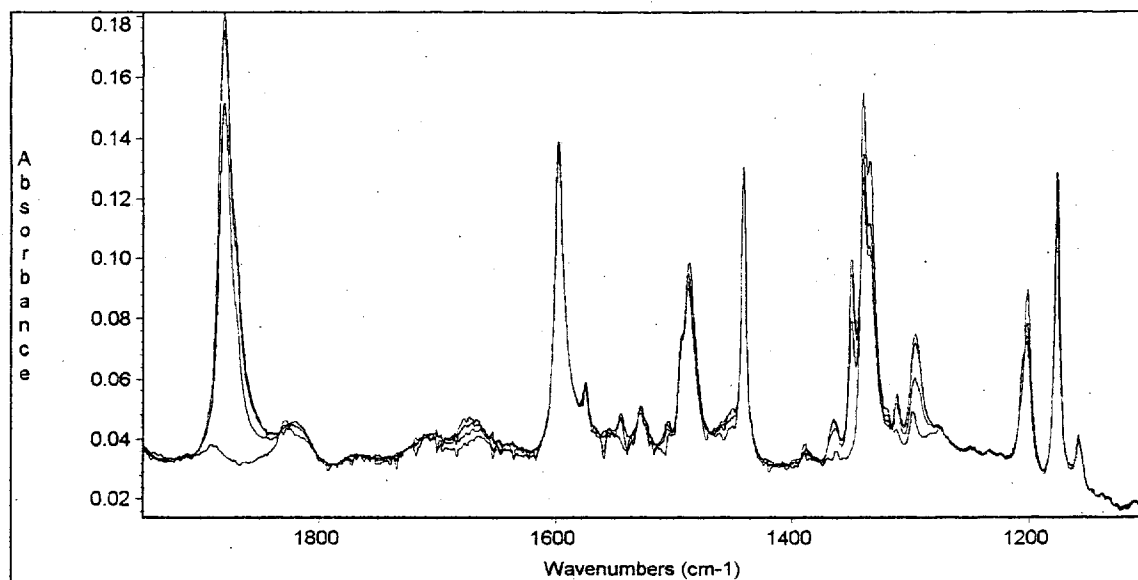
Abundances relative to  $^{14,14}\text{N}_2\text{O}$  (m/z 44), and are were corrected for natural abundance  $^{15}\text{N}$ . Experimental conditions described in text.

Comparison of Ratios

Expt #	30/44	31/45	Ratio
1	.18	.095	0.53
2	.19	.10	0.53
3	.19	.10	0.53
4	.24	.12	0.50
5	.20	.10	0.50
		Average	0.52

S4. The experimental ratios between  $^{14}\text{NO}^+$  (m/z 30) to  $^{14,14}\text{N}_2\text{O}^+$  (m/z 44) and between  $^{15}\text{NO}^+$  (m/z 31) to  $^{14,15}\text{N}_2\text{O}^+$  (m/z 45). The last ratio was a measure of label in  $\text{NO}^+$  fragments, since only  $^{14}\text{N}^{15}\text{NO}$  isomer could produce  $^{15}\text{NO}$  fragment.<sup>19</sup>

Supplemental Page 5: ATR-IR spectra of the reaction of NO(g) with an Fe(TPP)Cl film



**S5:** Changes in the ATR-IR spectra of ferric Fe(TPP)Cl upon exposure to purified NO gas stream, spectra taken within one minute. Peak at 1882 cm<sup>-1</sup> is assignable to the known compound, NO-Fe(TPP)Cl. Note that under same conditions as the reaction of gaseous NO with ferrous NO-Fe(TPP), no new peaks at 1900 and 1858 cm<sup>-1</sup> are seen.

Supplemental Page 6: Sequential spectra (left) and difference ATR-IR spectra (right) obtained from experiments run under  $^{14}\text{NO}$ ,  $^{15}\text{NO}$ , and  $^{14}\text{NO}/^{15}\text{NO}$  mixtures. The difference spectra were generated by subtraction of the final product spectra from the first intermediate spectra, calibrated by zeroing the second product peak (e.g.  $1298\text{ cm}^{-1}$  for  $^{14}\text{N}$ -label) in the subtraction. Spectra were smoothed and baseline corrected prior to subtraction.

