

## Supplementary Information

**Mononitrosyl Tris(Thiolate) Iron Complex  $[\text{Fe}(\text{NO})(\text{SPh})_3]^-$  and Dinitrosyl Iron Complex  $[(\text{EtS})_2\text{Fe}(\text{NO})_2]^-$ : Formation Pathway of Dinitrosyl Iron Complexes (DNICs) from Nitrosylation of Biomimetic Rubredoxin  $[\text{Fe}(\text{SR})_4]^{2-/\text{l}-}$  ( $\text{R} = \text{Ph}, \text{Et}$ )**

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Fig. S1. X-band EPR spectrum of complex **1** frozen in  $\text{CH}_2\text{Cl}_2$ -tolune measured at 4 K  
(The “\*” indicates the signal ( $g = 2.028$ ) of  $[(\text{PhS})_2\text{Fe}(\text{NO})_2]$ ).

Fig. S2. Plots of effective magnetic moment vs temperature for complex **1** in a 0.5 T applied field.

Fig. S3. X-band EPR spectra of complex **5** frozen in THF measured at (a) 298 K and (b) 77 K.

Fig. S4. Plots of effective magnetic moment vs temperature for complex **5** in a (a) 0.5 and (b) 1 T applied field.

Table. S1. Crystallographic data and refinement parameters for complex **1**.

Table S2. Crystallographic data and refinement parameters for complex **5**.

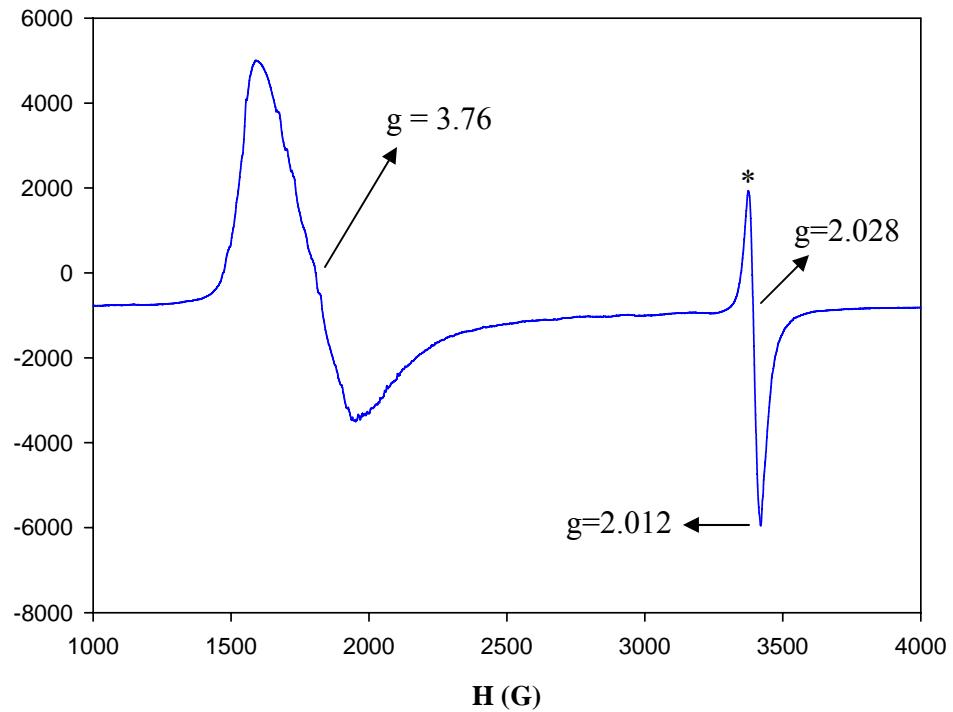


Fig. S1

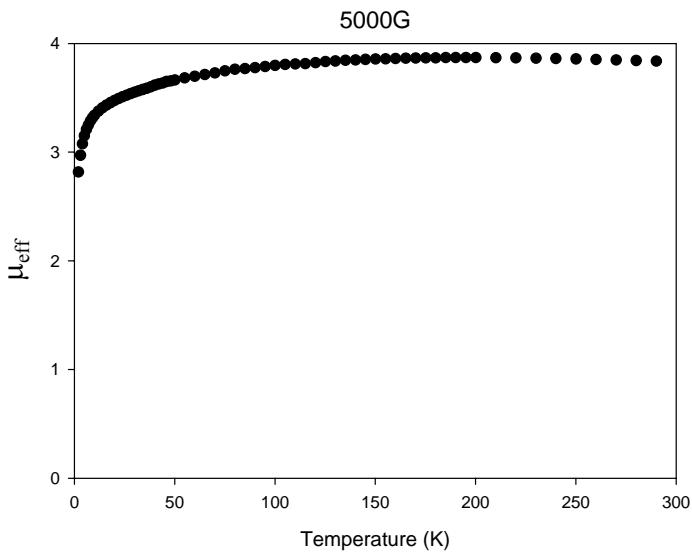


Fig. S2

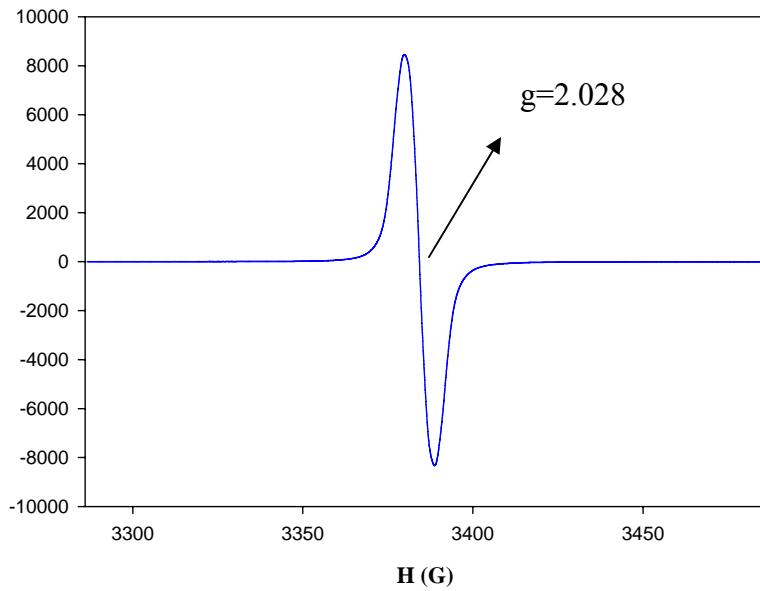


Fig S3 (a)

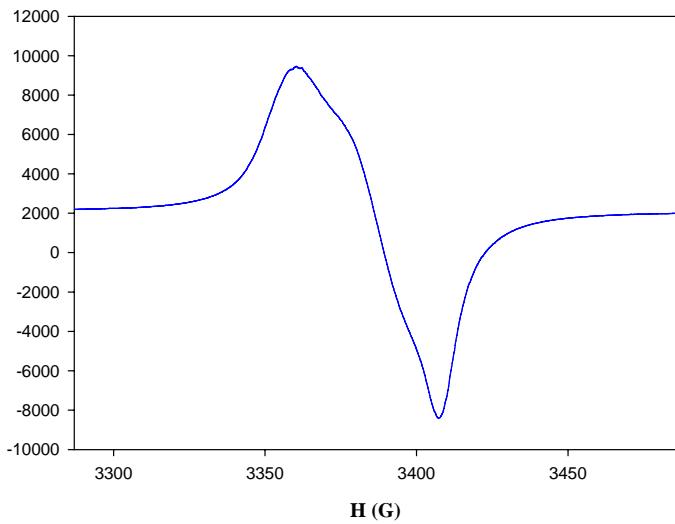


Fig S3 (b)

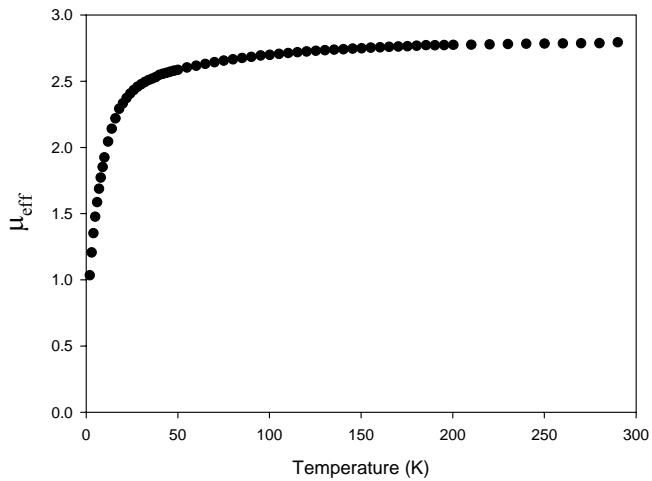


Fig S4 (a)

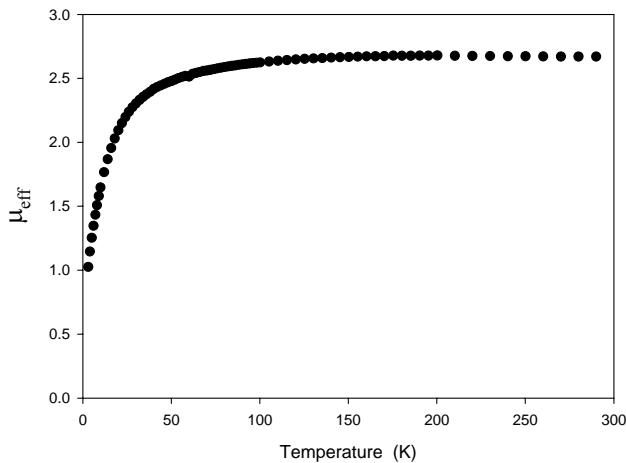


Fig. S4 (b)

Table S1. Crystal data and structure refinement for complex **1**.

Identification code	sp30m
Empirical formula	C54 H45 Fe N2 O P2 S3
Formula weight	951.89
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)
Unit cell dimensions	a = 10.1411(6) Å b = 24.009(1) Å c = 11.1545(6) Å
Volume	2651.9(3) Å <sup>3</sup>
Z	2
Density (calculated)	1.192 Mg/m <sup>3</sup>
Absorption coefficient	0.500 mm <sup>-1</sup>
F(000)	990
Crystal size	0.5 x 0.5 x 0.5 mm <sup>3</sup>
Theta range for data collection	1.70 to 28.31°
Index ranges	-13 ≤ h ≤ 10, -32 ≤ k ≤ 30, -12 ≤ l ≤ 14
Reflections collected	19716
Independent reflections	12821 [R(int) = 0.0399]
Completeness to theta = 28.31°	99.9 %
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	12821 / 1 / 569
Goodness-of-fit on F <sup>2</sup>	0.969
Final R indices [I>3sigma(I)]	R1 = 0.0563, wR2 = 0.1614
R indices (all data)	R1 = 0.0815, wR2 = 0.1607
Extinction coefficient	0.0361(19)
Largest diff. peak and hole	0.854 and -0.325 e. Å <sup>-3</sup>

Table S2. Crystal data and structure refinement for complex **5**.

Identification code	06fe28m	
Empirical formula	C <sub>80</sub> H <sub>80</sub> Fe <sub>2</sub> N <sub>6</sub> O <sub>4</sub> P <sub>4</sub> S <sub>4</sub>	
Formula weight	1553.32	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pca2</i> <sub>1</sub>	
Unit cell dimensions	a = 26.3429(9) Å	= 90°.
	b = 9.8941(3) Å	= 90°.
	c = 29.1480(10) Å	= 90°.
Volume	7597.1(4) Å <sup>3</sup>	
Z	8	
Density (calculated)	2.716 Mg/m <sup>3</sup>	
Absorption coefficient	1.260 mm <sup>-1</sup>	
F(000)	6480	
Crystal size	0.3 x 0.2 x 0.1mm <sup>3</sup>	
Theta range for data collection	1.40 to 28.33°.	
Index ranges	-35 ≤ h ≤ 34, -11 ≤ k ≤ 13, -30 ≤ l ≤ 38	
Reflections collected	54508	
Independent reflections	17046 [R(int) = 0.1254]	
Completeness to theta = 28.33°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.94673 and 0.89273	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	17046 / 1 / 902	
Goodness-of-fit on F <sup>2</sup>	0.892	
Final R indices [I>3sigma(I)]	R1 = 0.0526, wR2 = 0.1421	
R indices (all data)	R1 = 0.1251, wR2 = 0.1412	
Absolute structure parameter	0.00	
Extinction coefficient	0.00000(6)	
Largest diff. peak and hole	0.686 and -0.544 e .Å <sup>-3</sup>	