

SUPPORTING INFORMATION

Reduction of Iron Porphyrin Nitrate to the Iron Nitrosyl by H₂S/Thiol.

Studies in Sublimed Layers.

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Experimental details:

Materials: The parent six-coordinate $\text{Fe}(\text{TTP})(\text{B})_2$ complex (TTP^{2-} = tetratolylporphyrin dianion, B = piperidine) was synthesized according to published methods [1]. The NO_2 ($^{15}\text{NO}_2$), was obtained by oxidation of NO (^{15}NO) (preliminary dried over P_2O_5) with excess of pure O_2 in the glass tube fitted with a Schlenk valve. The ^{15}NO (98.5% isotopic enrichment) was purchased from the Institute of Isotopes, Republic of Georgia. The $\text{NO}_2/\text{N}^{18}\text{O}_2$ gas mixture with ~50% ^{18}O was obtained commercially from “ICON isotopes”. Ethanethiol (97%) was purchased from Sigma-Aldrich. The hydrogen sulfide was prepared by heating the mixture of elementary sulfur and paraffin wax [2] in the vacuum system fitted with mercury manometer and purified by multiple vacuum distillation before use. The IR spectra of the H_2S condensed on the low temperature substrate of cryostat and in the gas phase showed no impurities present [3].

Procedures: The $\text{Fe}(\text{TTP})(\text{B})_2$ samples were placed in a Knudsen cell of the optical cryostat and heated to about 470 K (2-3 hours) under high vacuum conditions to remove solvent traces and the protective base ligand. Subsequent rise of the temperature resulted in porphyrin sublimation onto the liquid N_2 cooled substrate (KBr or CaF_2) of the optical cryostat.

The advantages of this approach originates from the pioneering studies of Kazuo Nakamoto [4] who showed that metalloporphyrins could be sublimated in vacuum cryostat without degradation and that IR, Raman and UV-Vis spectra then measured avoid the interfering influence of the solvent. Low temperature sublimates of metalloporphyrins are sponge-like and allow the penetration of guest molecules into the entire volume of the layers. Sequential addition (and vacuum) of different coordinating ligands as vapors (or gases) allows one to construct the five- and/or six-coordinate complexes as monitored by IR and UV-Vis spectroscopy. In addition, using isotopic species allows unambiguous assignment of vibrations. Thus, biomimetic models with the corresponding spectrochemical properties can be generated.

The synthetic analogues obtained in this way can reproduce key aspects of structure, spectroscopy, and chemical reactivity of biological systems.

The Fe(TTP)(NO₃) species were obtained by interaction of Fe(II)(TTP) sublimates with NO₂ gas at 278 K and characterized by IR spectra according to procedures described elsewhere [5]. The cryostat was cooled to 77 K, and various quantities of the ethanethiol vapors and H₂S gas measured with mercury manometer were then introduced. FTIR / UV–visible spectra were then measured in the course of slow warming. The temperature was allowed to rise stepwise by ~ 5 K and kept constant by dropping liquid N₂ to the cryostat. The IR spectra were recorded continuously at each temperature point until no further changes were detected. In the case of H₂S, however keeping the temperature constant to accumulate an intermediate was complicated. Dropping of N₂ to the cryostat led to evolution of weakly bonding H₂S from a bulk of solid and condensation at the more cooled metal parts of substrate. Thus, the reaction with H₂S was monitored upon almost spontaneous warming of cryostat.

The FTIR spectra and UV-visible spectra were recorded using “Nexus” Nicolet and “Cary 60” of Agilent. Mass spectra were obtained by residual gas analyzer “RGA-200” of the Stanford Research Systems.

Density functional theory (DFT) calculations were performed for the complexes in vacuo at the unrestricted UTPSS-TPSS level of theory using the DGDZVP basis set without symmetry constraints using the Gaussian’16 package.

References:

1. L. Epstein, D. Straub, C. Maricondi, *Inorg. Chem.*, 1967, **6**, 1720
2. W. Jolly, *The Synthesis and Characterization of Inorganic Compounds*. Prentice Hall, N.Y., 1970. p.545
3. K. Fathe, J. Holt, S. Oxley, C. Pursell, *J. Phys. Chem. A*, 2006, **110**, 37, 10793
4. M. Kozuka, K. Nakamoto, *J. Am. Chem. Soc.* 1981, **103**, 2162-2168
5. T. S. Kurtikyan, P. C. Ford, *Coord. Chem. Rev.*, 2008, **252**, 1486.

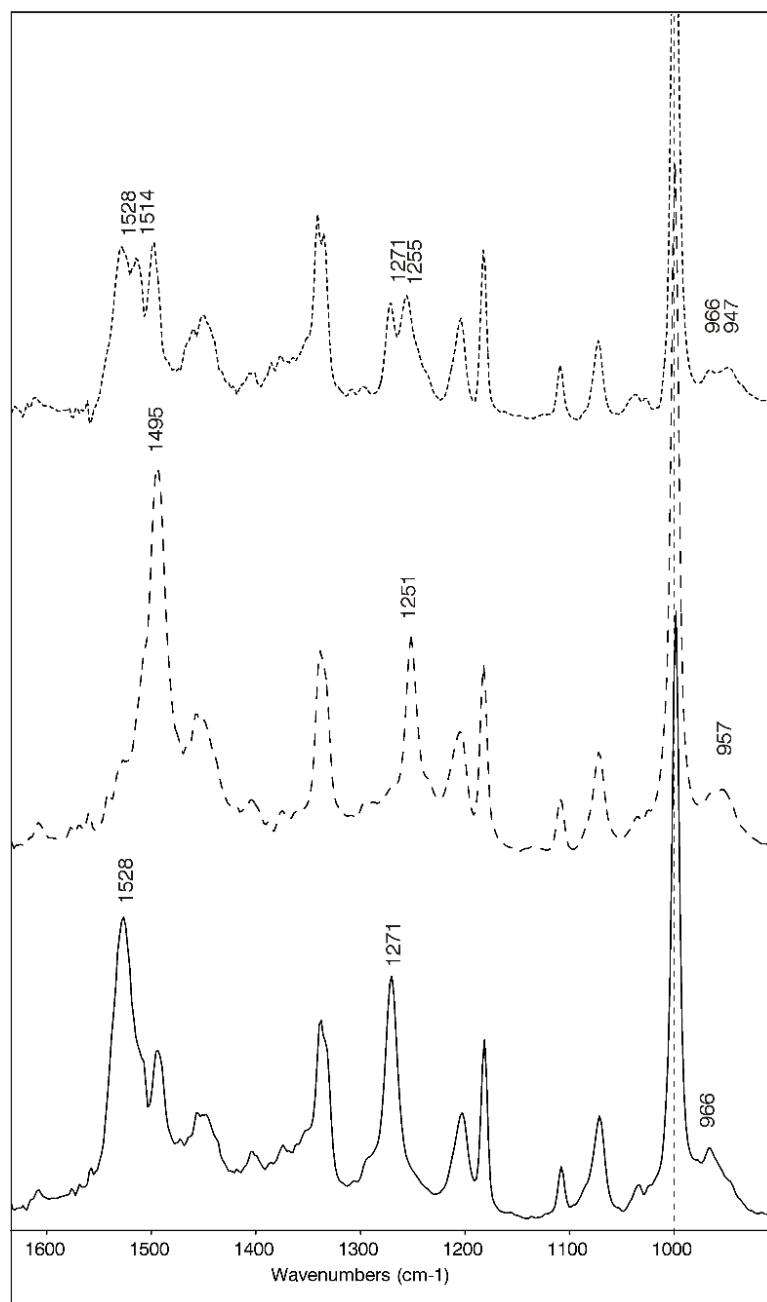


Figure S1. Room temperature IR spectra of the starting iron porphyrin nitrates used. solid line - $\text{Fe}(\text{TTP})(\text{NO}_3)$, dashed line - $\text{Fe}(\text{TTP})(^{15}\text{NO}_3)$, dotted line - $\text{Fe}(\text{TTP})(\text{NO}_3)/\text{Fe}(\text{TTP})(\text{N}^{18}\text{O}_3)$ mixture (~50% ^{18}O labelled). All spectra were recorded of complexes deposited as solids in sublimed layers.

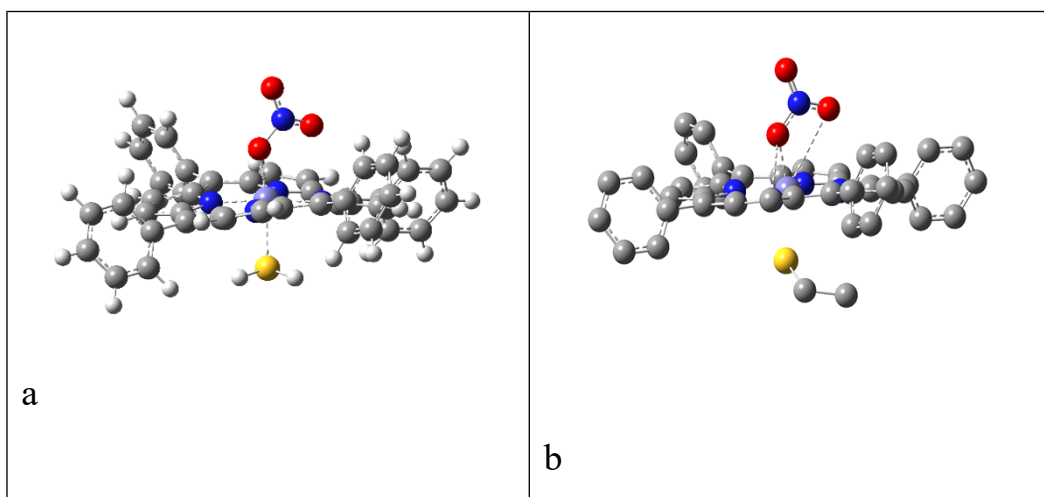


Figure S2. Computed structures for $\text{Fe}(\text{TTP})(\text{H}_2\text{S})(\text{NO}_3)$ (a) and $\text{Fe}(\text{TTP})(\text{EtSH})(\text{NO}_3)$ (b).

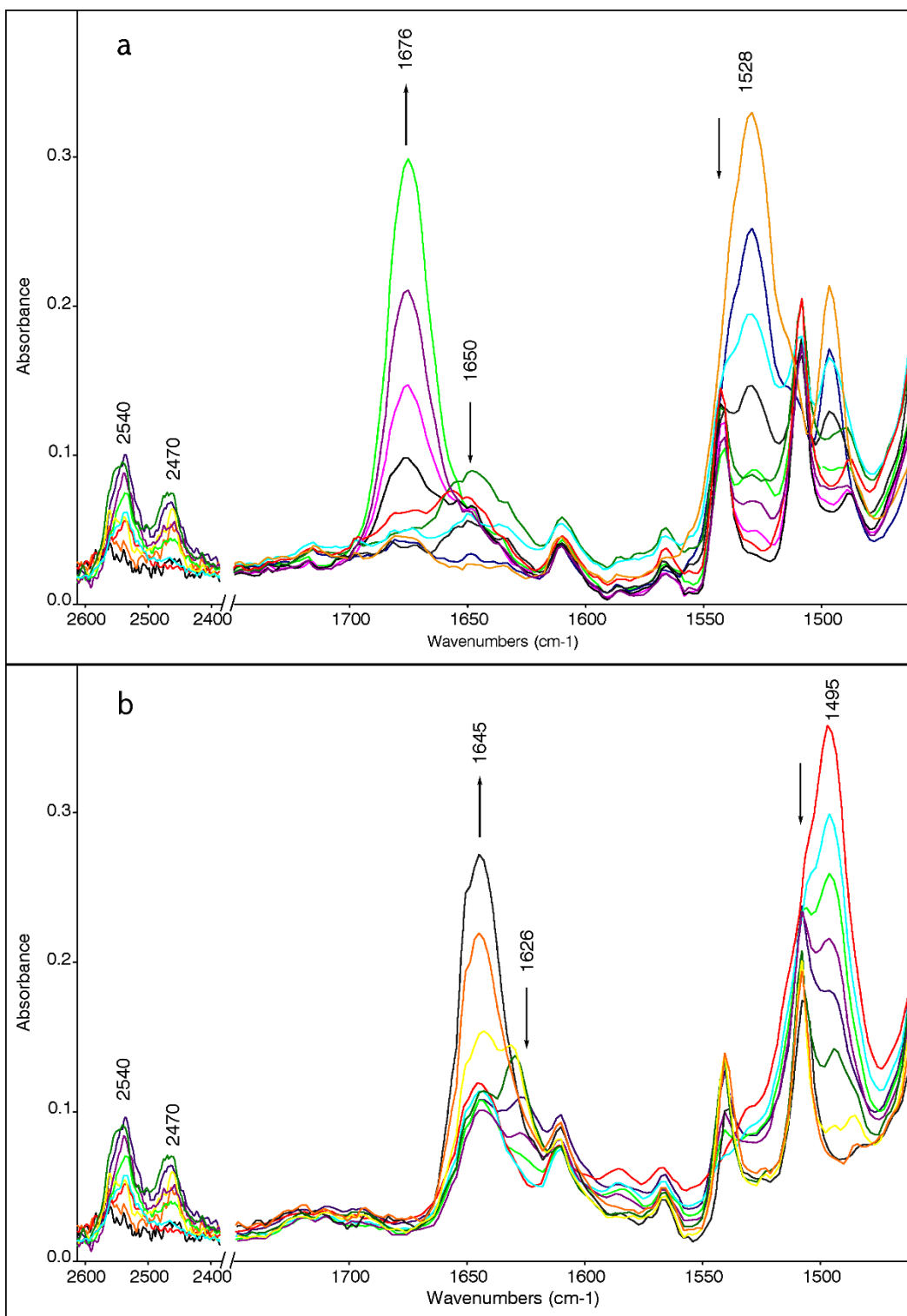


Figure S3. (a) The IR spectral changes observed after addition of EtSH (~ 4 torr) to the cryostat containing Fe(TTP)(NO₃) at 77 K and warming from 130 K to 150 K showing initial formation of the band at 1650 cm⁻¹, which gradual transforms to the band at 1676 cm⁻¹ (assigned to Fe(TTP)(NO)) upon farther warming. (b) The IR changes observed with starting Fe(TTP)(¹⁵NO₃) (contains a small band of nitrosyl impurity formed upon nitrate preparation), showing initial formation of the band at 1626 cm⁻¹, which transforms to the band at 1645 cm⁻¹, assigned to Fe(TTP)(¹⁵NO), upon warm up. Note: The corresponding decrease of the nitrate band at 1528 cm⁻¹ (1495 cm⁻¹) is also apparent.

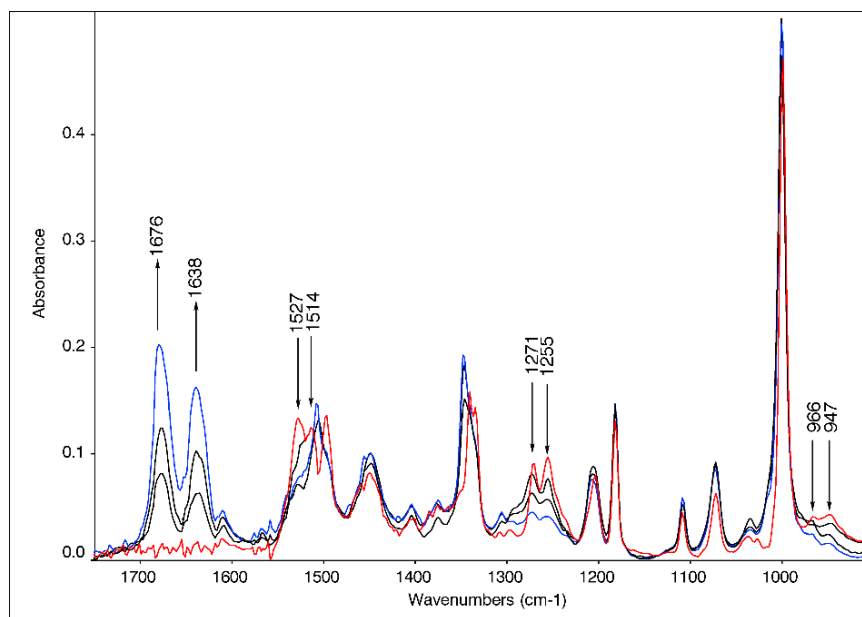


Figure S4. The IR spectral changes observed after addition of EtSH (~10 torr) to the cryostat containing nearly equal Fe(TTP)(NO₃)/Fe(TTP)(N¹⁸O₃) at room temperature and stored overnight. Disappearance of bands characteristic of the nitrate complexes and appearance of bands characteristic of the respective nitrosyls Fe(TTP)(NO) and Fe(TTP)(N¹⁸O) are apparent.

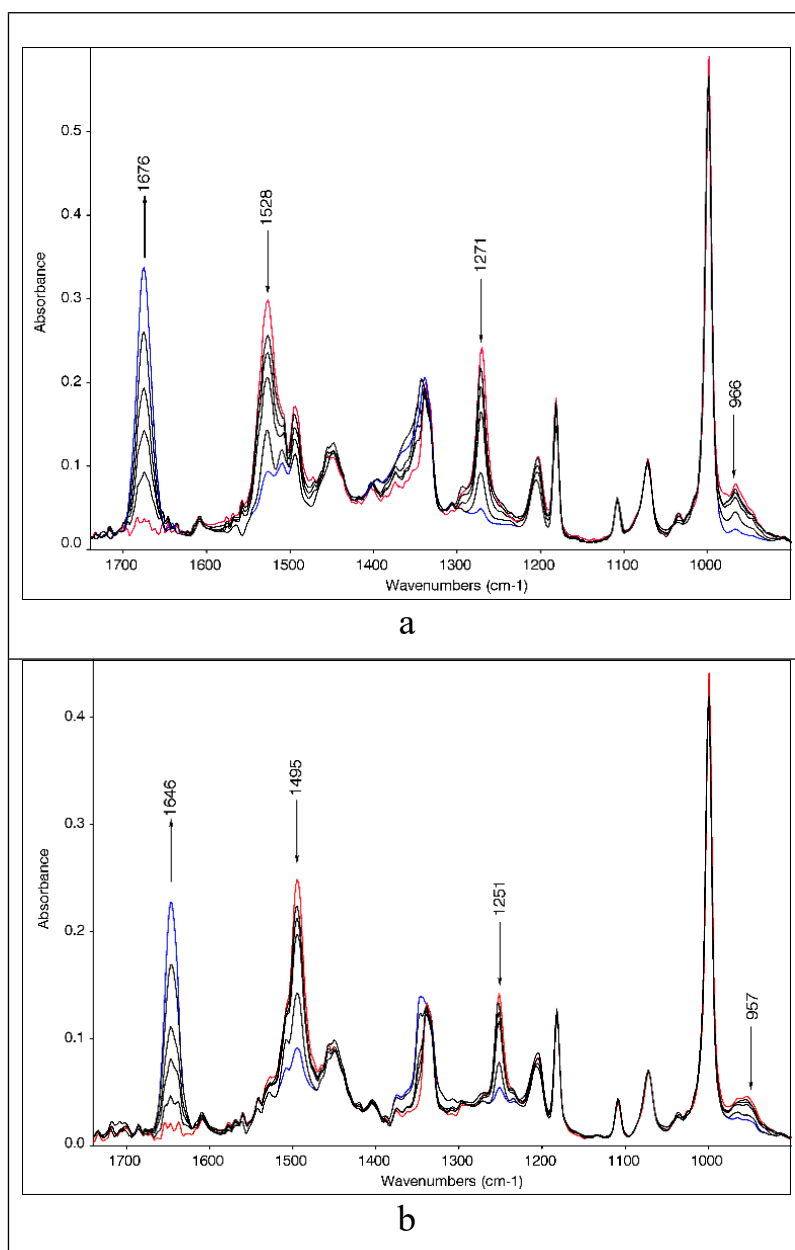


Figure S5. (a) The IR spectral changes observed after addition of H₂S (~ 8 torr) to the cryostat containing Fe(TTP)(NO₃) (the bands at 1528 and 1271 cm⁻¹) at 77 K, followed by warming to room temperature and storing overnight. Formation of Fe(TTP)(NO) is evident by emergence of the band at 1676 cm⁻¹, while bands of nitrate disappeared. (b) the same experiment beginning with Fe(TTP)(¹⁵NO₃) (1495 and 1251 cm⁻¹) lead to the formation of Fe(TTP)(¹⁵NO).

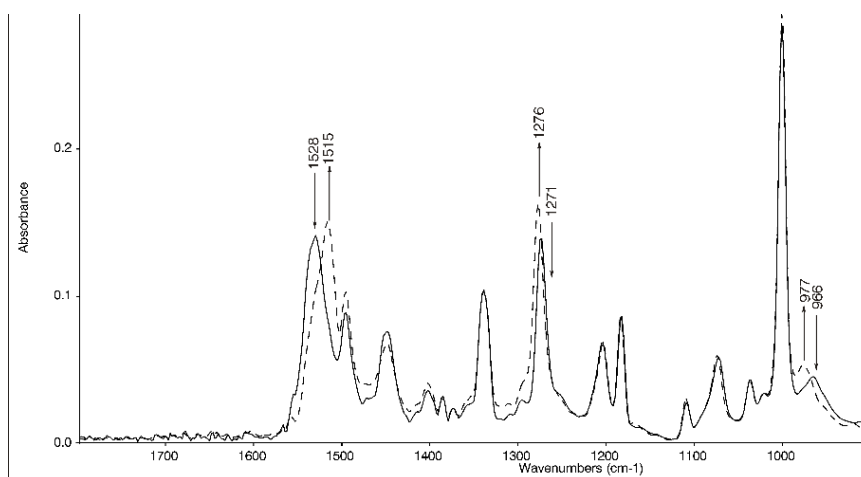


Figure S6. The IR spectral changes observed after addition of H_2S (~ 8 torr) to the cryostat containing $\text{Fe}(\text{TTP})(\text{NO}_3)$ at 77 K and warming to 140 K. The shifts of all three bands of the nitrate complex due to formation the $6\text{C Fe}(\text{TTP})(\text{H}_2\text{S})(\text{NO}_3)$ are clearly seen.

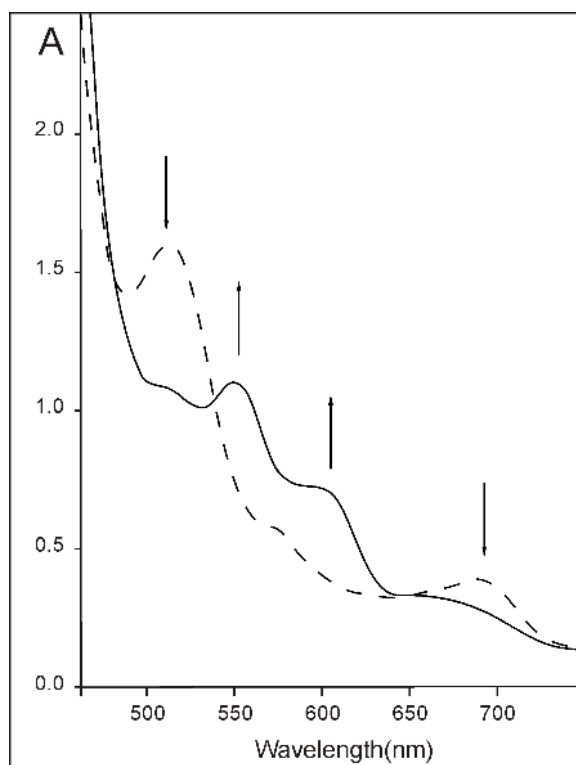


Figure S7. The visible spectra observed after addition of ca. ~ 6 torr of H_2S to the cryostat containing solid $\text{Fe}(\text{TTP})(\text{NO}_3)$ at 77 K (dashed line) followed by warming to room temperature and storing overnight (solid line).

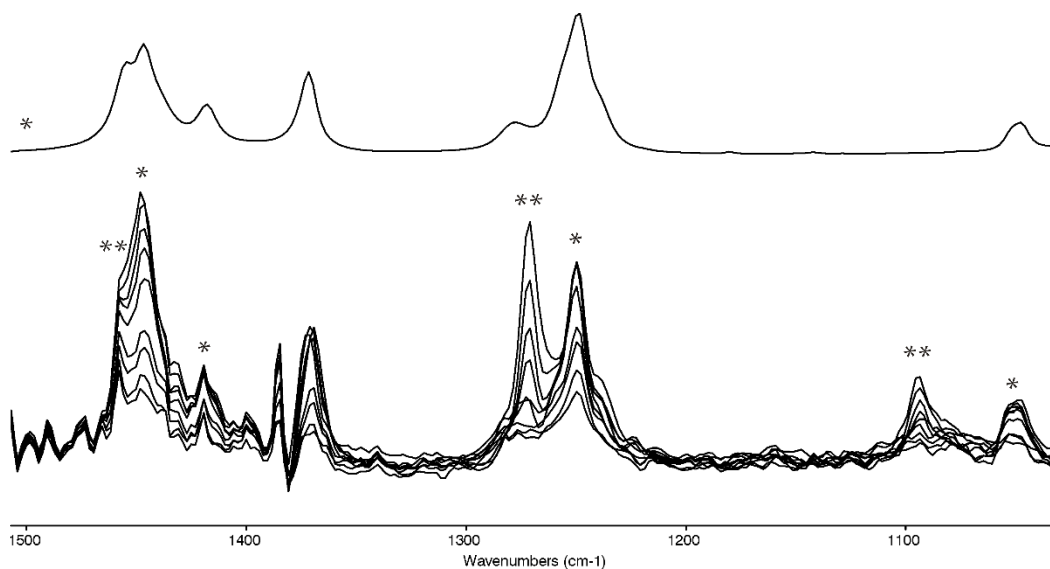


Figure S 8. Bottom: The IR spectral changes observed after condensation of volatile products (next day after the reaction of $\text{Fe}(\text{TTP})(\text{NO}_3)$ with EtSH) to the substrate of another clean cryostat at 77K and farther warming. * - FTIR spectra of ethanethiol 97% (neat) used in experiments, ** - these IR bands match the bands of ethyl disulfide (EtSSEt), 99% - from HR Aldrich Condensed Phase Library Aldrich Catalog No: E2622-3

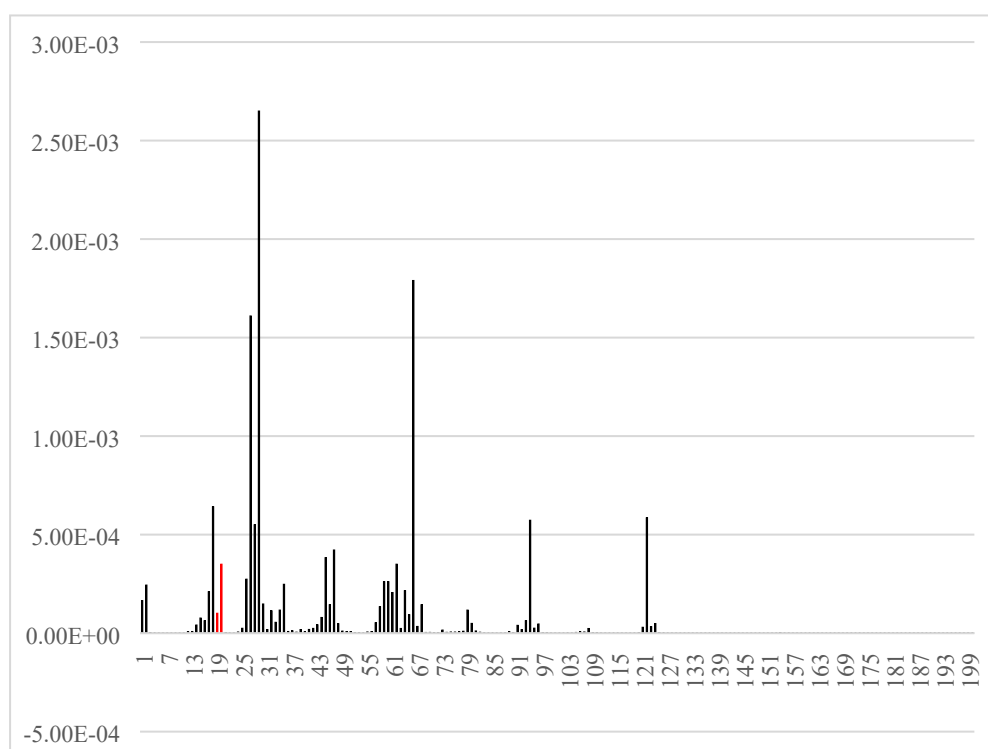


Figure S10. MS of the volatile reactions products obtained after the reaction of $\text{Fe}(\text{TTP})(\text{N}^{18}\text{O}_3)$ ($\sim 50\%$ ^{18}O) with EtSH. Red lines peaks at m/z 19 and 20 a.u attributed to the formation of H_2O^{18}

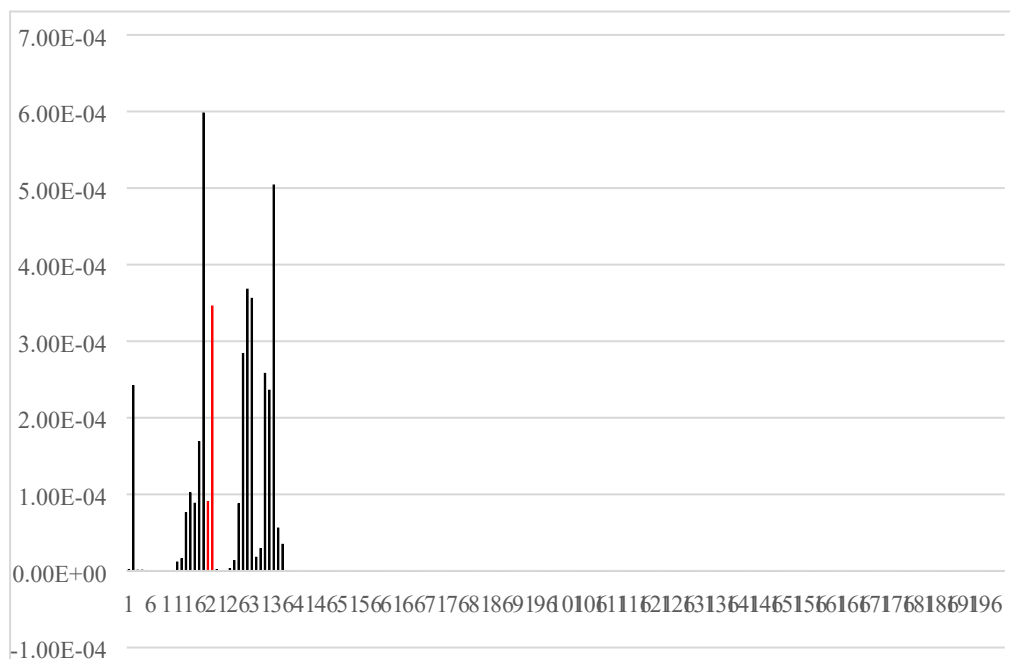


Figure S11. MS of the volatile reactions products obtained after the reaction of $\text{Fe}(\text{TTP})(\text{N}^{18}\text{O}_3)$ ($\sim 50\%$ ^{18}O) with H_2S . Peaks at m/z 19 and 20 a.u attributed to the formation of H_2O^{18}

Table S1. Coordinates of DFT calculated $\text{Fe}(\text{TTP})(\text{NO}_3)(\text{H}_2\text{S})$

N	-1.368000	-1.502000	-0.222000
N	1.355000	1.410000	-0.389000
N	-1.452000	1.321000	-0.347000
N	1.448000	-1.412000	-0.218000
C	2.808000	-1.189000	-0.371000
C	1.321000	-2.767000	0.059000
C	-1.140000	-2.861000	-0.062000
C	-2.727000	-1.379000	-0.476000
C	-2.813000	1.086000	-0.461000
C	-1.322000	2.696000	-0.182000
C	1.133000	2.780000	-0.327000
C	2.715000	1.263000	-0.618000
C	3.339000	2.559000	-0.750000
C	3.419000	0.049000	-0.632000
C	3.542000	-2.412000	-0.148000
C	0.109000	-3.469000	0.159000
C	2.365000	3.497000	-0.541000
C	-0.111000	3.403000	-0.147000
C	-2.623000	3.317000	-0.134000
C	-2.369000	-3.598000	-0.227000
C	-3.429000	-0.170000	-0.602000

C	-3.545000	2.325000	-0.334000
C	2.624000	-3.383000	0.145000
C	-3.346000	-2.683000	-0.511000
H	4.622000	-2.501000	-0.185000
H	2.806000	-4.424000	0.390000
H	-2.458000	-4.677000	-0.174000
H	-4.391000	-2.869000	-0.732000
H	-4.625000	2.412000	-0.364000
H	-2.802000	4.374000	0.023000
H	2.457000	4.577000	-0.565000
H	4.387000	2.723000	-0.975000
Fe	-0.003000	-0.039000	-0.370000
S	0.056000	0.053000	2.072000
C	0.143000	-4.946000	0.407000
C	0.185000	-7.737000	0.874000
C	0.666000	-5.831000	-0.559000
C	-0.366000	-5.484000	1.607000
C	-0.342000	-6.867000	1.841000
C	0.686000	-7.213000	-0.327000
H	1.044000	-5.429000	-1.498000
H	-0.775000	-4.813000	2.362000
H	-0.733000	-7.263000	2.778000
H	1.088000	-7.881000	-1.089000
H	0.201000	-8.811000	1.054000
C	4.896000	0.067000	-0.881000
C	7.681000	0.078000	-1.372000
C	5.791000	0.611000	0.063000
C	5.418000	-0.474000	-2.074000
C	6.799000	-0.466000	-2.318000
C	7.172000	0.615000	-0.180000
H	5.401000	1.020000	0.995000
H	4.735000	-0.891000	-2.813000
H	7.184000	-0.881000	-3.249000
H	7.850000	1.033000	0.564000
H	8.753000	0.082000	-1.562000
C	-0.146000	4.895000	-0.022000
C	-0.193000	7.713000	0.204000
C	0.328000	5.531000	1.143000
C	-0.638000	5.692000	-1.077000
C	-0.660000	7.090000	-0.964000
C	0.302000	6.928000	1.257000
H	0.712000	4.924000	1.963000
H	-0.987000	5.210000	-1.989000
H	-1.036000	7.691000	-1.791000
H	0.666000	7.403000	2.168000
H	-0.211000	8.798000	0.291000
C	-4.905000	-0.207000	-0.851000
C	-7.690000	-0.252000	-1.348000
C	-5.427000	0.270000	-2.072000
C	-5.802000	-0.703000	0.118000
C	-7.182000	-0.724000	-0.127000

C	-6.807000	0.245000	-2.319000
H	-4.743000	0.649000	-2.831000
H	-5.414000	-1.061000	1.071000
H	-7.860000	-1.104000	0.636000
H	-7.190000	0.609000	-3.271000
H	-8.762000	-0.270000	-1.539000
H	-1.249000	0.307000	2.305000
H	-0.087000	-1.270000	2.301000
O	-0.161000	1.810000	-2.904000
N	-0.089000	0.611000	-3.203000
O	0.008000	-0.354000	-2.209000
O	-0.089000	0.129000	-4.344000

Table S2. Coordinates of DFT calculated Fe(TTP)(NO₃)(C₂H₅SH)

N	-1.425000	-1.459000	-0.205000
N	1.340000	1.418000	-0.399000
N	-1.497000	1.349000	-0.411000
N	1.440000	-1.388000	-0.243000
C	2.805000	-1.177000	-0.342000
C	1.288000	-2.755000	-0.068000
C	-1.185000	-2.823000	-0.111000
C	-2.796000	-1.335000	-0.385000
C	-2.868000	1.126000	-0.512000
C	-1.352000	2.728000	-0.381000
C	1.113000	2.789000	-0.402000
C	2.722000	1.275000	-0.526000
C	3.350000	2.567000	-0.636000
C	3.432000	0.068000	-0.514000
C	3.521000	-2.422000	-0.192000
C	0.068000	-3.447000	0.007000
C	2.357000	3.503000	-0.539000
C	-0.136000	3.425000	-0.350000
C	-2.644000	3.372000	-0.429000
C	-2.424000	-3.555000	-0.217000
C	-3.498000	-0.127000	-0.533000
C	-3.582000	2.380000	-0.527000
C	2.582000	-3.398000	-0.003000
C	-3.420000	-2.633000	-0.402000
H	4.601000	-2.522000	-0.204000
H	2.741000	-4.457000	0.162000
H	-2.508000	-4.635000	-0.198000
H	-4.478000	-2.812000	-0.556000
H	-4.660000	2.481000	-0.578000
H	-2.804000	4.443000	-0.394000
H	2.446000	4.582000	-0.594000
H	4.412000	2.730000	-0.781000
Fe	-0.037000	-0.005000	-0.356000
S	0.140000	0.046000	2.029000
C	0.104000	-4.940000	0.139000
C	0.164000	-7.757000	0.376000

C	0.547000	-5.742000	-0.932000
C	-0.313000	-5.571000	1.329000
C	-0.281000	-6.968000	1.448000
C	0.575000	-7.140000	-0.815000
H	0.857000	-5.266000	-1.861000
H	-0.657000	-4.962000	2.164000
H	-0.600000	-7.439000	2.377000
H	0.914000	-7.744000	-1.656000
H	0.187000	-8.842000	0.467000
C	4.923000	0.099000	-0.665000
C	7.734000	0.139000	-0.962000
C	5.748000	0.587000	0.368000
C	5.527000	-0.371000	-1.849000
C	6.921000	-0.349000	-1.997000
C	7.142000	0.606000	0.221000
H	5.292000	0.943000	1.291000
H	4.898000	-0.743000	-2.657000
H	7.370000	-0.708000	-2.922000
H	7.765000	0.982000	1.032000
H	8.817000	0.156000	-1.077000
C	-0.169000	4.924000	-0.356000
C	-0.223000	7.749000	-0.386000
C	0.129000	5.660000	0.808000
C	-0.491000	5.622000	-1.538000
C	-0.517000	7.025000	-1.552000
C	0.100000	7.063000	0.794000
H	0.379000	5.129000	1.726000
H	-0.708000	5.060000	-2.445000
H	-0.762000	7.550000	-2.474000
H	0.329000	7.617000	1.704000
H	-0.244000	8.838000	-0.398000
C	-4.984000	-0.174000	-0.714000
C	-7.788000	-0.253000	-1.075000
C	-5.561000	0.184000	-1.950000
C	-5.835000	-0.573000	0.337000
C	-7.225000	-0.611000	0.159000
C	-6.951000	0.144000	-2.129000
H	-4.913000	0.484000	-2.773000
H	-5.403000	-0.846000	1.300000
H	-7.867000	-0.917000	0.985000
H	-7.378000	0.418000	-3.093000
H	-8.868000	-0.284000	-1.215000
H	0.509000	-1.244000	2.184000
O	-0.079000	1.651000	-3.038000
N	-0.043000	0.431000	-3.274000
O	-0.062000	-0.457000	-2.243000
O	0.009000	-0.092000	-4.399000
C	-1.500000	-0.086000	2.885000
C	-2.085000	1.319000	3.053000
H	-1.318000	-0.572000	3.850000
H	-2.141000	-0.724000	2.269000

H	-3.099000	1.253000	3.467000
H	-1.474000	1.927000	3.730000
H	-2.136000	1.810000	2.079000