Electronic Supplementary Information for:

Redox Flexibility of Iron Complexes Supported by Sulfur-based tris(*o*-methylenethiophenolato)amine relative to its tripodal Oxygen-based congener

Alexander Mondragón,[†a] Paulina R. Martínez-Alanis,[b] Gabriel Aullón,[b] Simón Hernández-Ortega,[a] Elvis Robles-Marín,[a] Marcos Flores-Alamo,[c] Víctor M. Ugalde-Saldívar,[c] and Ivan Castillo*[a]

[a.] *Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, CU, México DF, 04510, México*
[b.] *Departament de Química Inorgànica and Institut de Química Teòrica i Computacional, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain*
[c.] *Facultad de Química, División de Estudios de Posgrado, Universidad Nacional Autónoma de México, Ciudad Universitaria, México DF, 04510, México*
†Present Address: A. Mondragón, e-mail: mondragon.alexander@correounivalle.edu.co; Departamento de Química, Facultad de Ciencias, Universidad del Valle, Ciudad Universitaria Meléndez, Calle 13 # 100-00, Cali, Colombia.
*E-mail: joseivan@unam.mx (I. Castillo). Fax: +5255 56162217

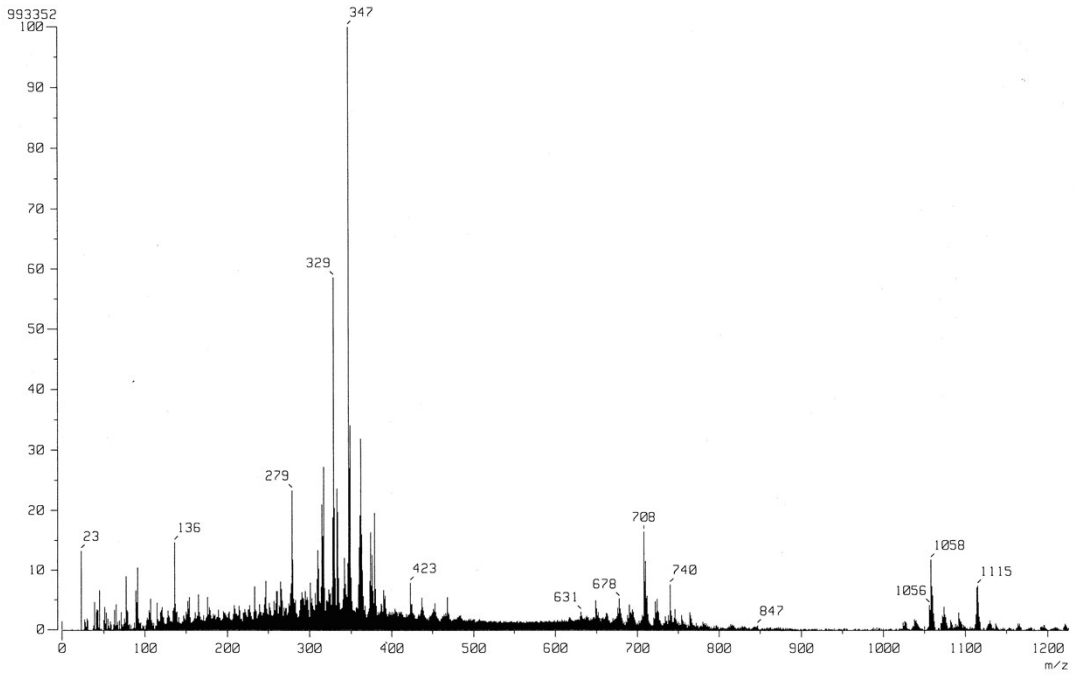

Figure S1. FAB$^+$ MS of **1^{THF}**

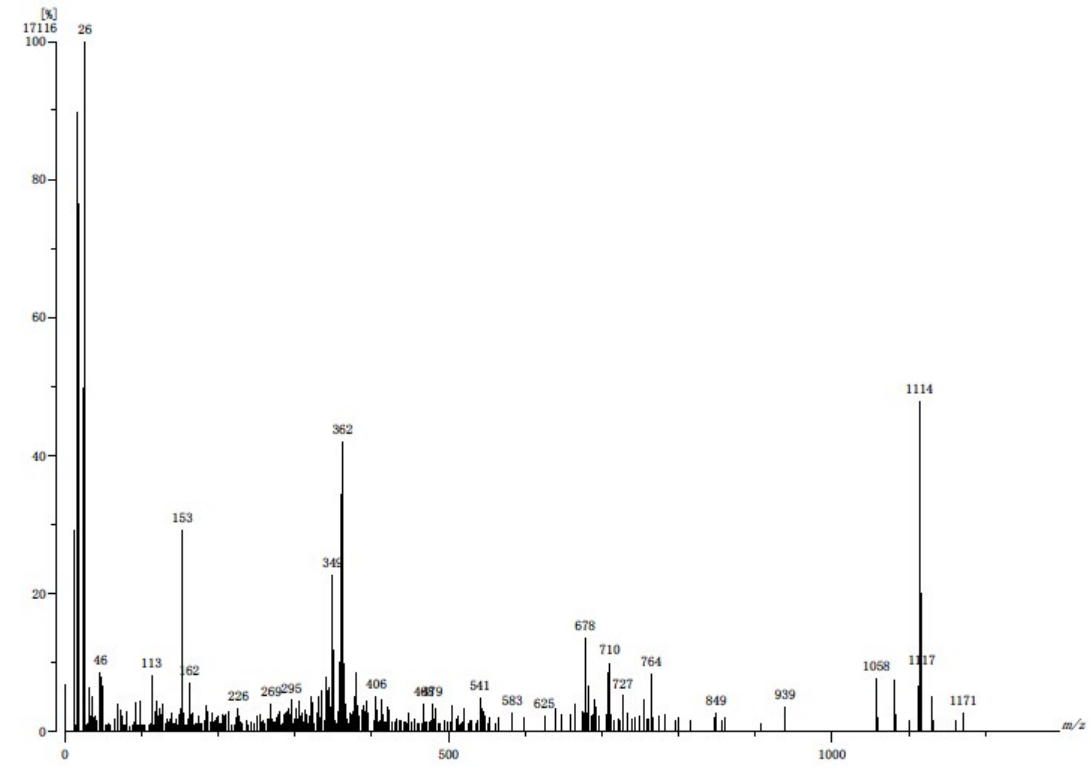

Figure S2. FAB$^-$ MS of **1^{THF}**.

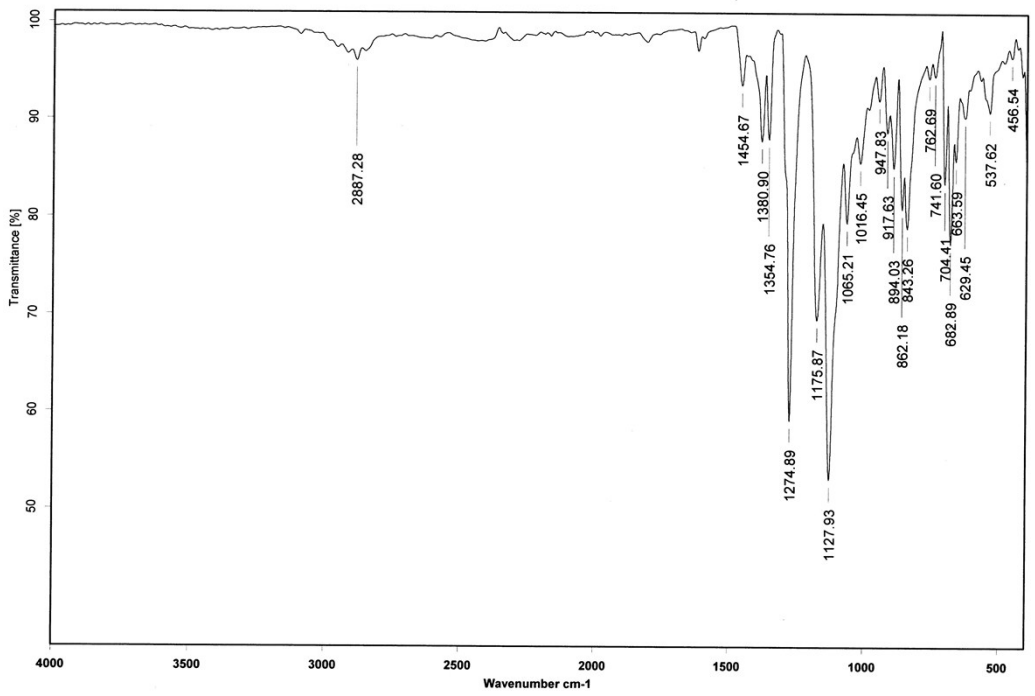

Figure S3. FT-IR of **1^{THF}**.

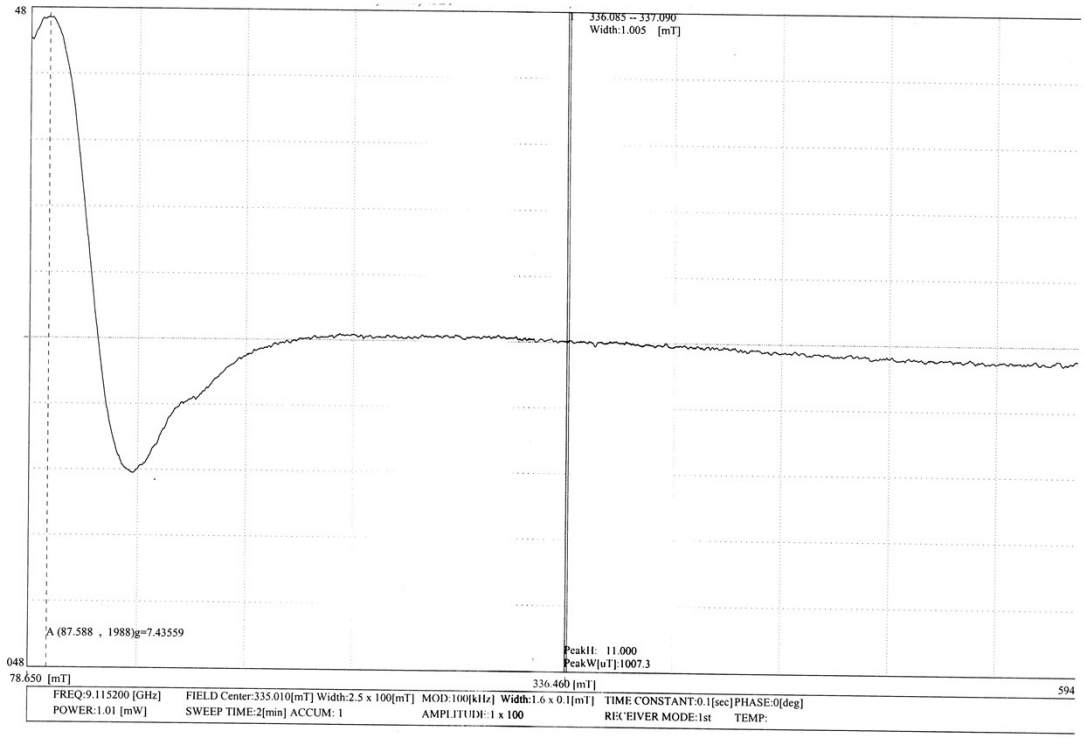

Figure S4. Experimental X-band EPR spectrum (77 K, ν = 9.115200 [GHz], power = 1.01 [mW], modulation = 100[KHz], amplitude = 1 x 100) of **1**^{THF} in the solid state; g = 7.43.

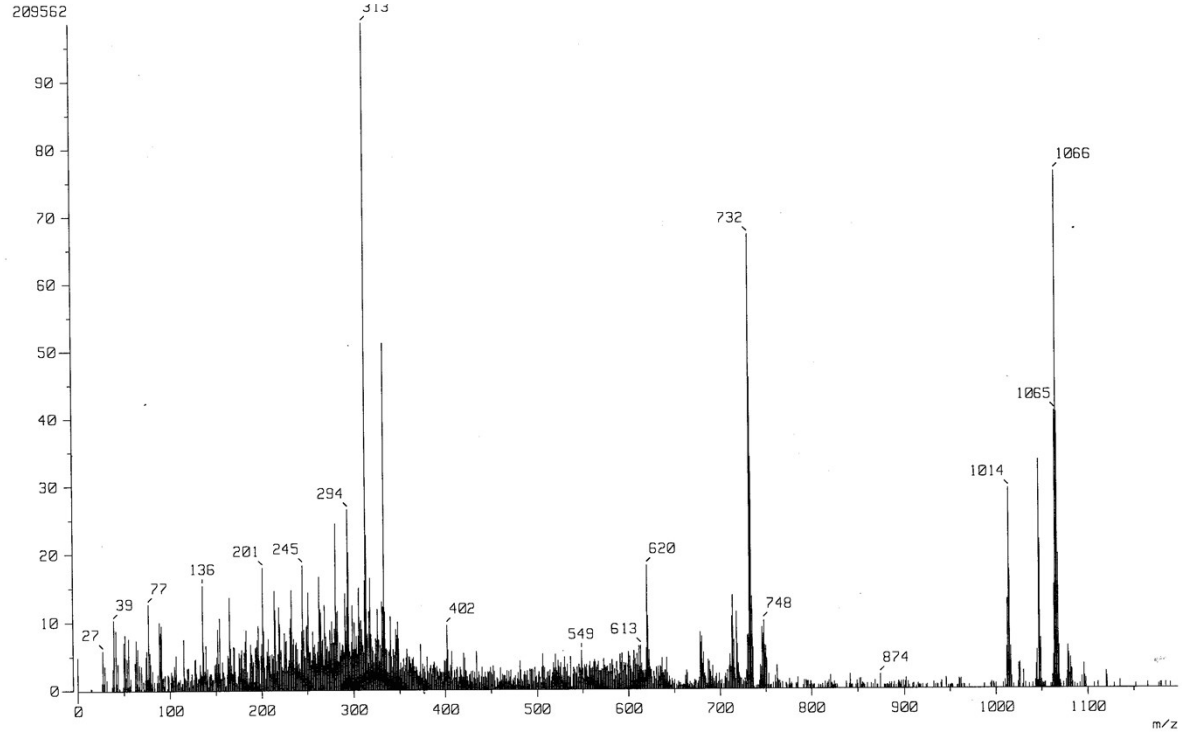

Figure S5. FAB$^+$ MS of **2**^{H2O}**.**

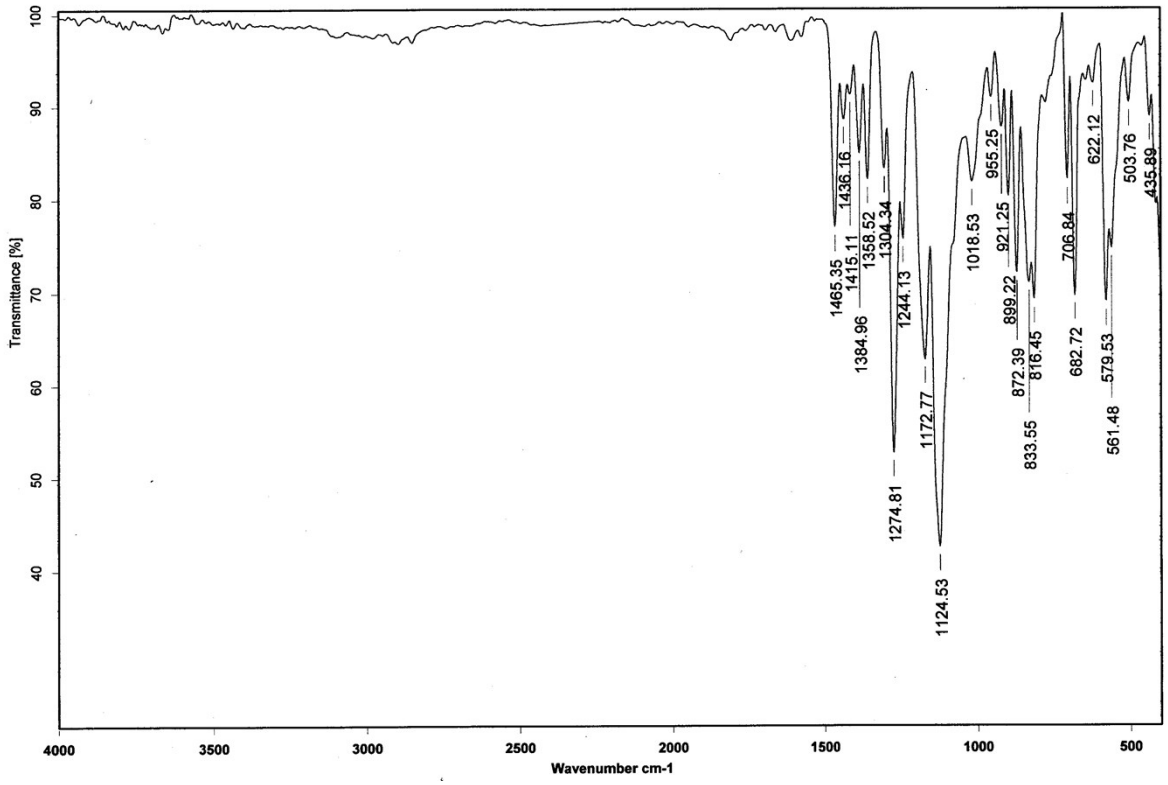

Figure S6. FT-IR of $\mathbf{2}^{H2O}$.

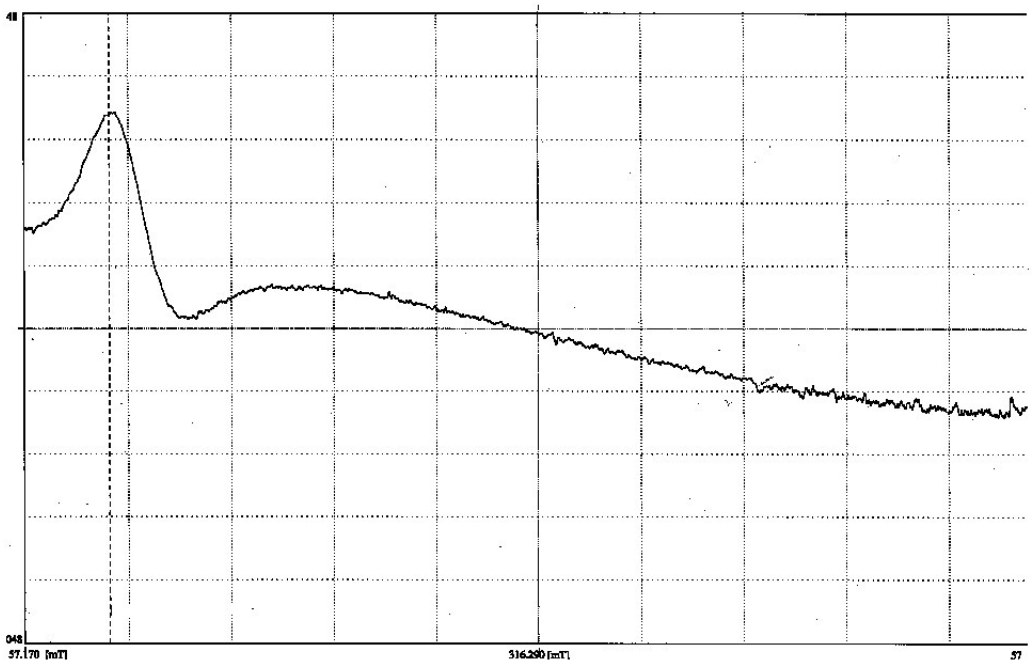

Figure S7. Experimental X-band EPR spectrum (77 K, ν = 9.113320 [GHz], power = 1.01 [mW], modulation = 100[KHz], amplitude = 1 x 100) of $\mathbf{2}^{H2O}$ in the solid state; g = 6.56.

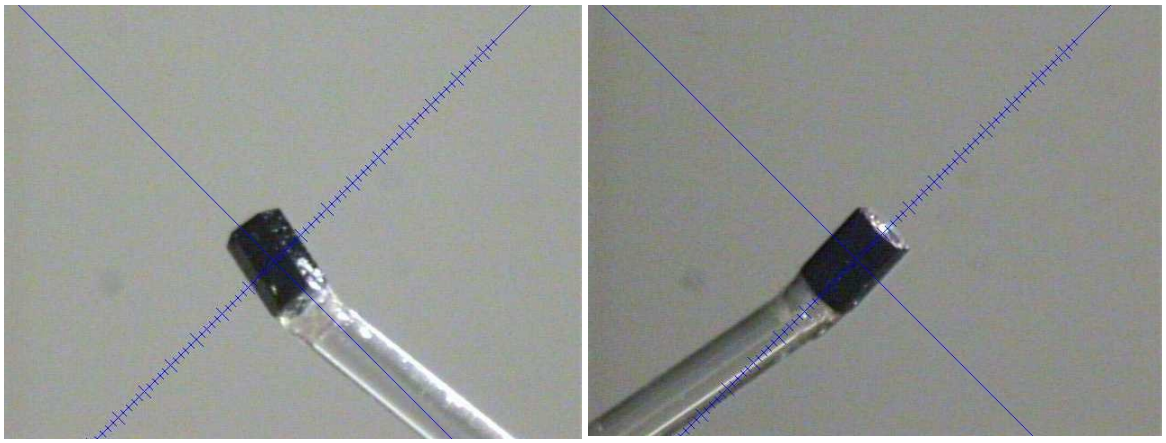

Figure S8. Crystalline form of **1**^{DMSO}

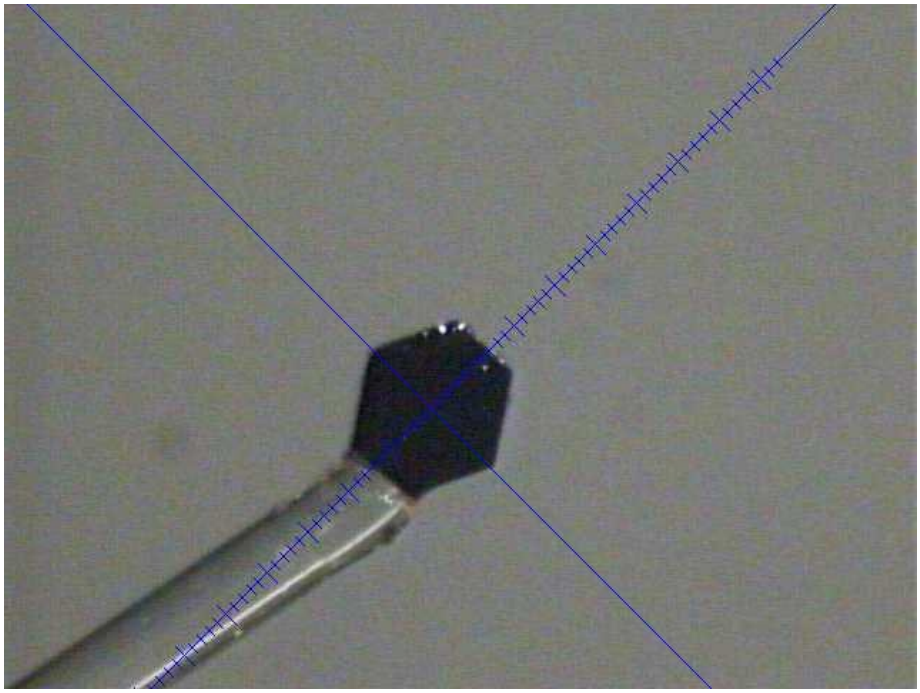

Figure S9. Crystalline form of the **1**^{THF}

Table S1. Formation enthalpies of [Fe{*N*($CH_2ArS)_3$}(THF)] **1^{THF}**, [Fe{$N(CH_2ArS)_3$}(H_2O)] **1^{H2O}** and [Fe{$N(CH_2ArO)_3$}(H_2O)] **2^{H2O}**.

Compound	ΔH_f [kcal/mol]	
	Fe(II)	*Fe(III)*
[Fe{$N(CH_2ArS)_3$}(THF)]	-15.2	-12.8
[Fe{$N(CH_2ArS)_3$}(H_2O)]	-13.6	-18.4
[Fe{$N(CH_2ArO)_3$}(H_2O)]	-20.4	-26.6

Table S2. Mulliken charges and spin densities calculated for [Fe{$N(CH_2ArS)_3$}(H_2O)] **1^{H2O}**, [Fe{$N(CH_2ArS)_3$}(THF)] **1^{THF}**, and [Fe{$N(CH_2ArO)_3$}(H_2O)] **2^{H2O}**.

Mulliken charge	**1^{H2O}**	**1^{THF}**	**2^{H2O}**
Fe	-0.100	0.420	0.950
Solv.	0.150	-1.190	0.120
N	-0.400	-0.418	-0.460
S1(O1)	-0.069	-0.081	-0.705
S2(O2)	-0.036	-0.091	-0.702
S3(O3)	-0.048	-0.071	-0.701
CH_2Ar [a]	0.200	0.100	0.480
Spin density			
Fe	3.740	3.751	3.963
N	0.092	0.100	0.130
O(solv.)	0.039	0.052	0.040
S1(O1)	0.298	0.322	0.226
S2(O2)	0.350	0.302	0.237
S3(O3)	0.322	0.318	0.242

[a] Average charge

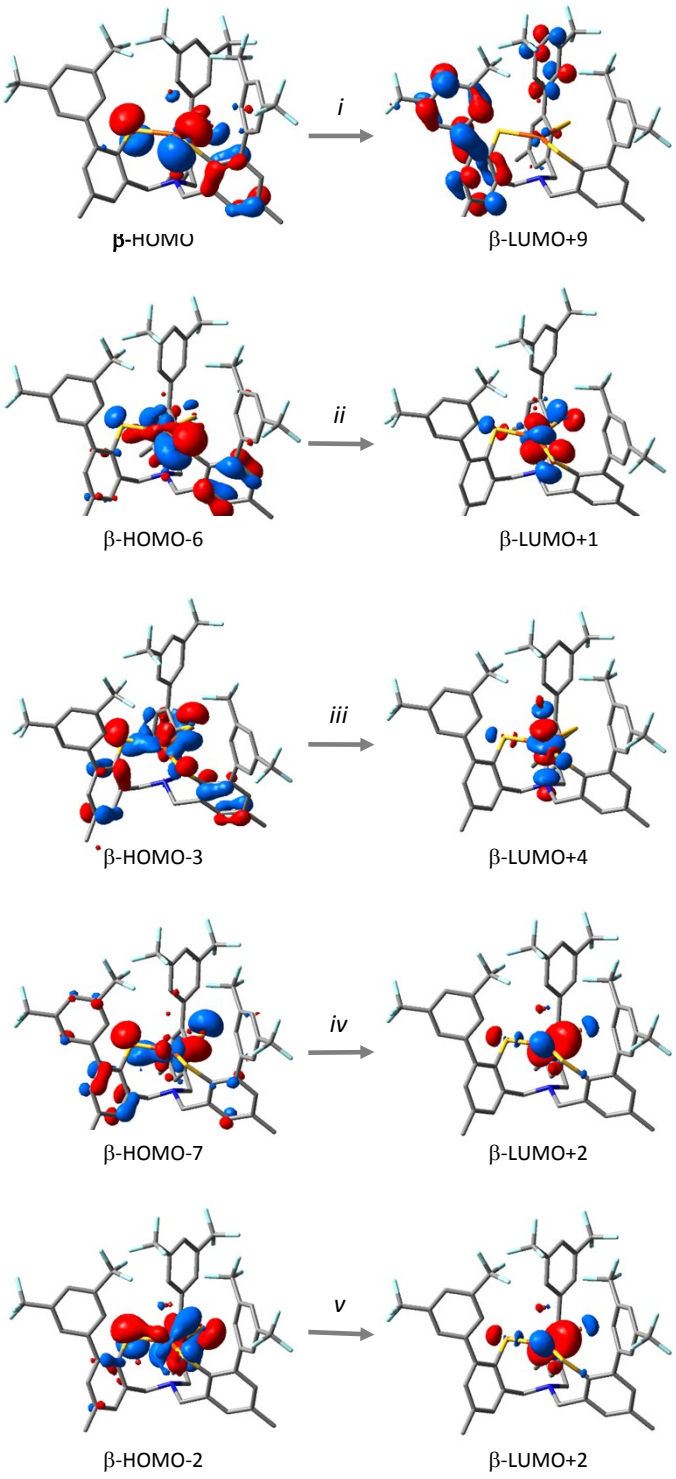

Figure S10. The molecular orbitals involved in the main electronic transitions for $\mathbf{1}^{H2O}$

Table S3 Representative electronic transitions in the UV-vis of $\mathbf{1^{H2O}}$ using THF as solvent.

λ (f)	Assignment	% Participation
650 (0.03)	π, Ar-S → yz, Fe	9 [0.31]
	π, 4-CH_3-C_6H_2-S → β-LUMO	5 [0.23]
	π, 4-CH_3-C_6H_2-S → x^2-y^2, Fe	4 [0.21]
	π, 4-CH_3-C_6H_2-S → yz, Fe	14 [0.38]
	π, 4-CH_3-C_6H_2-S → z^2, Fe	12 [0.35]
527 (0.04)	π, Ar-S →yz, Fe	12 [0.36]
	π, Ar-S →yx, Fe	5 [0.24]
	π, Ar-S → z^2, Fe	6 [0.26]
	π, 4-CH_3-C_6H_2-S →yx, Fe	4 [0.20]
	π, 4-CH_3-C_6H_2-S → z^2, Fe	4 [0.21]
525 (0.04)	π, Ar-S →yx, Fe	9 [0.30]
	π, 4-CH_3-C_6H_2-S→ z^2, Fe	29 [0.54]
470 (0.03)	π, Ar-S →β-LUMO	4 [0.22]
	π, Ar-S → x^2-y^2, Fe	16 [0.40]
	π, 4-CH_3-C_6H_2-S→yx, Fe	5 [0.23]
467 (0.05)	π, Ar-S →β-LUMO	4 [0.20]
	π, Ar-S →yx, Fe	6 [0.26]
	π, Ar-S → x^2-y^2, Fe	18 [0.43]

Table S4. Representative electronic transitions of **1**^{THF}.

λ (f)	Assignment	% Participation
567 (0.02)	π, 4-CH_3-C_6H_2-S → z^2, Fe π, 4-CH_3-C_6H_2-S → xz, Fe	36 [0.60] 6 [0.26]
536 (0.02)	π, 4-CH_3-C_6H_2-S; xy, Fe → LUMO π, 4-CH_3-C_6H_2-S; xy, Fe → xz, Fe π, 4-CH_3-C_6H_2-S → LUMO π, 4-CH_3-C_6H_2-S → xy, Fe π, 4-CH_3-C_6H_2-S → z^2, Fe	25 [0.50] 12 [0.35] 8 [0.29] 5 [0.24] 5 [0.24]
519 (0.02)	π, Ar-S → xy, Fe π, Ar-S → yz, Fe π, 4-CH_3-C_6H_2-S → yz, Fe π, 4-CH_3-C_6H_2-S → z^2, Fe	24 [0.49] 10 [0.32] 6 [0.25] 4 [0.22]
516 (0.03)	π, Ar-S → yz, Fe	11 [0.34]
461 (0.08)	π, 4-CH_3-C_6H_2-S; xy, Fe → yz, Fe	53 [0.73]
451 (0.10)	π, 4-CH_3-C_6H_2-S → xy, Fe π, Ar-S → LUMO π, 4-CH_3-C_6H_2-S → yz, Fe	49 [0.70] 11 [0.34] 5 [0.24]
418 (0.03)	π, Ar-S → z^2, Fe π, 4-CH_3-C_6H_2-S → z^2, Fe	31 [0.56] 6 [0.26]

Table S5. Representative electronic transitions in the UV-vis of **2**^{H2O} using THF as solvent.

λ (f)	Assignation	% Participation
519 (0.04)	π, Ar-S; yz, Fe → β-LUMO	9 [0.30]
	π, $(CF_3)_2$-C_6H_3; σ, S; xz, Fe → β-LUMO	15 [0.39]
	π, Ar-S; x^2-y^2,Fe → z^2, Fe	33 [0.58]
	π, Ar-S, x^2-y^2,Fe → yz, Fe	14 [0.38]
426 (0.02)	π, $(CF_3)_2$-C_6H_3; σ, S; xz, Fe → xy, Fe	7 [0.27]
	π, Ar-S; σ, N → xy, Fe	26 [0.51]
	π, Ar-S → xy, Fe	50 [0.71]
342 (0.03)	π, 4-CH_3-C_6H_2-S → π*, Ar-S	8 [0.29]
	π, Ar-S → z^2, Fe	4 [0.21]
	β-HOMO → π*, Ar-S	16 [0.41]
340 (0.04)	π, Ar-S; yz, Fe → Fe x^2-y^2	14 [0.38]
	π, Ar-S; σ, N → Fe z^2	3 [0.19]
339 (0.06)	π, 4-CH_3-C_6H_2-S → π*, Ar-S	18 [0.43]
	π, Ar-S; yz, Fe → Fe x^2-y^2	6 [0.26]
	β-HOMO -> π*,$(CF_3)_2$-C_6H_3	25 [0.50]