Supplementary Information

Heteroleptic Iron(III) Spin Crossover Complexes; Ligand Substitution Effects

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Table S1. Crystallographic data and structure refinement at 100 K.

	1	**2**
Formula	$C_{26}H_{20}ClFeN_6O_2S$	$C_{24}H_{17}ClFeN_5O_2S$
Molecular weight / gmol^{-1}	571.84	530.79
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	12.280 (3)	12.280 (3)
b/Å	13.820 (3)	13.869 (3)
c/Å	16.800 (3)	16.607 (3)
α/°	103.12 (3)	103.40 (3)
β/°	98.99 (3)	99.34 (3)
γ/°	109.39 (3)	108.56 (3)
Cell volume/Å^3	2534.6 (9)	2521.3 (9)
Z	4	4
Absorption coefficient/mm^{-1}	0.820	0.817
Reflections collected	45115	55091
Independent reflections, R_{int}	11961, 0.0695	14121, 0.1028
Max. and min. transmission	0.9838 and 0.9679	0.998 and 0.9919
Restraints/parameters	0/669	0/613
Final R indices [I>2σ(I)]: R_1, wR_2	0.0431, 0.1150	0.0567, 0.1723

Table S2. Selected bond length and octahedral distortion for compound 1 and 2 at 100 K.

	1	**2**
Fe1-O1/Å	1.8807 (17)	1.8755 (19)
Fe1-O2/Å	1.902 (2)	1.912 (2)
Fe1-S1 /Å	2.2201 (14)	2.2200 (14)
Fe1-N1/Å	1.9336 (19)	1.932 (2)
Fe1-N2/Å	1.974 (2)	1.971 (2)
Fe1-N3/Å	1.9546 (19)	1.949 (2)
Fe2-O3/Å	1.9544 (19)	1.951 (2)
Fe2-O4/Å	1.912 (2)	1.917 (3)
Fe2-S2 /Å	2.4309 (15)	2.4421 (16)
Fe2-N6/Å	2.132 (2)	2.132 (2)
Fe2-N7/Å	2.162 (2)	2.180 (3)
Fe2-N9/Å	2.119 (2)	2.119 (2)
Σ, Fe1, Fe2	44, 75	40, 81
Θ, Fe1, Fe2	79, 229	77, 247

Table S3. Intermolecular interactions for compound 1 and 2 at 100 K.

Interaction/Å	1	2
In 1D along the c axis		
π-π	3.716	3.732
π-π	3.037	3.022
C33-H33···O2	2.3631(20)	2.3630(23)
N5-H5A···N8	2.0349(25)	2.0117(28)
N10-H10A···N4	2.4620(23)	2.3329(27)
Diagonal on b plane		
C20-H20···O1	2.6941(21)	2.8662(24)
π-π	3.611	3.790
C5-H5···S1	2.9491(12)	3.0682(13)
C7-H7···S1	2.6388(11)	2.6798(12)
C9-H9···S1	2.9888(10)	3.0435(12)
N5-H5B···O3	2.1981(19)	2.2686(23)
Along the a axis		
C11-H11···Cl2	2.9299(11)	2.9976(14)
C43-H43···Cl1	2.8885(11)	2.8017(13)
P4AE Fe1-Fe1		
C13-H13···π	3.070	3.086
π-π	3.154	3.167
P4AE Fe2-Fe2		
C37-H37···π	3.275	3.273
π-π	3.368	3.339
Interaction to solvent		
N10-H10B···N11	2.6360(37)	-
C18-H18···N11	2.5512(34)	-
C50-H50A···S2	2.9711(11)	-
C50-H50A···π	2.741	-
C50-H50B···N12	2.6882(70)	-
C39-H39···N12	2.6851(60)	-

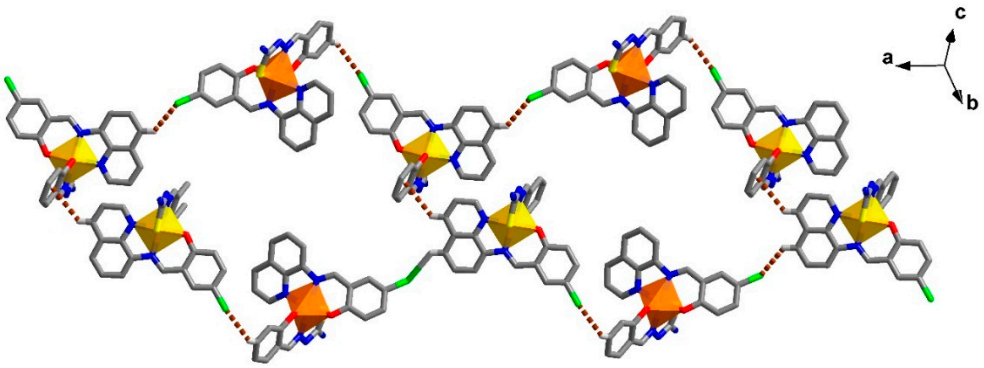


Figure S1. C-H···Cl and P4AE interactions along the *a* axis that forms a double helical-liked chain in compound 1.

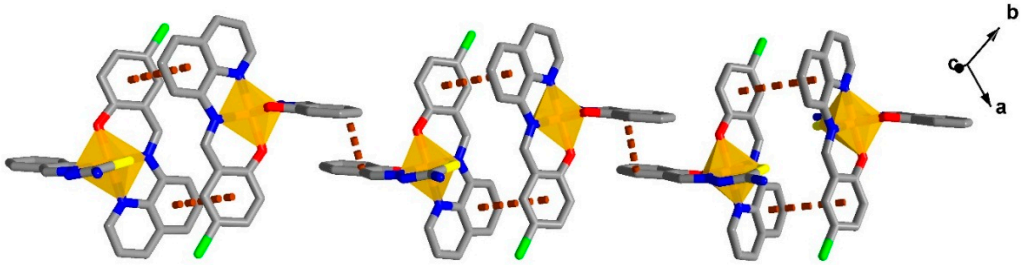
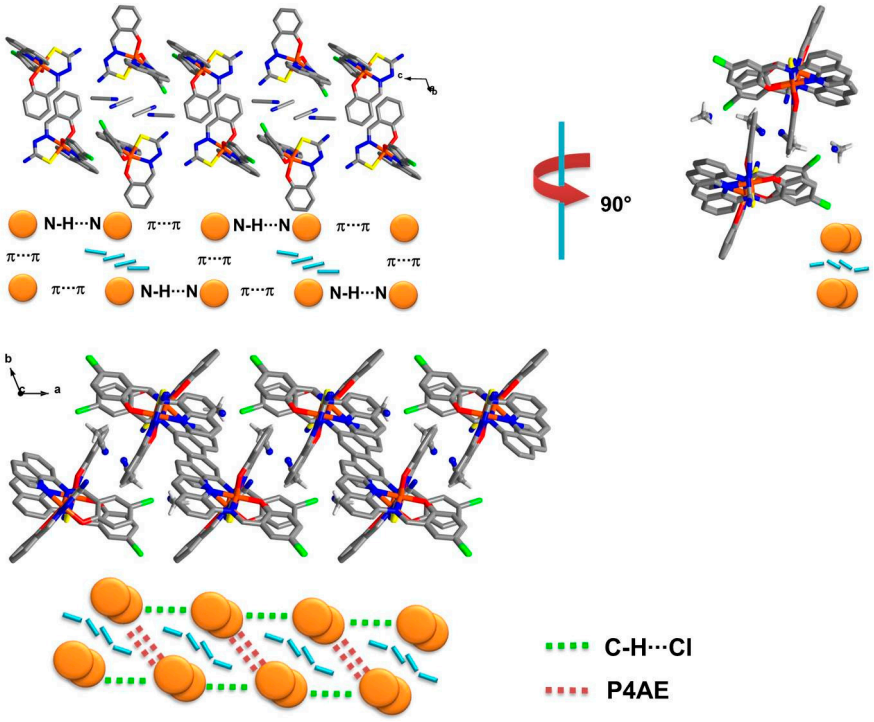
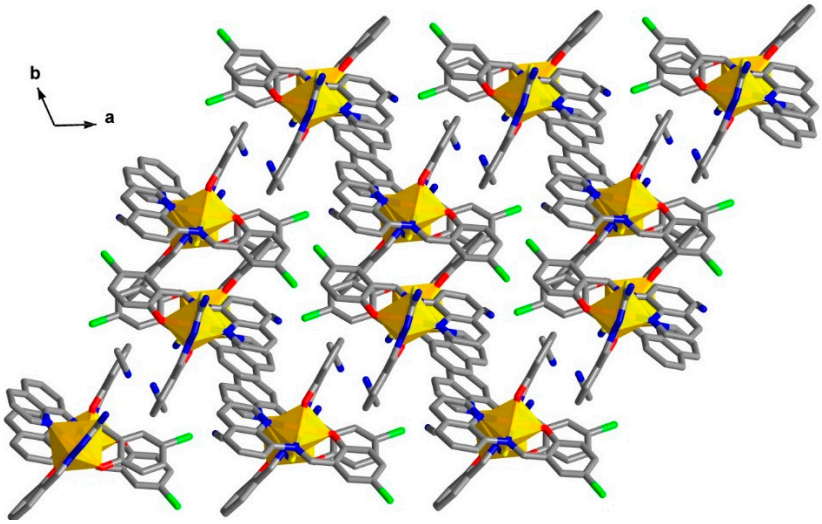


Figure S2. π-π interactions of qsal-qsal and thsa-thsa along diagonal *ab* axes connecting Fe1-Fe1 in a chain.

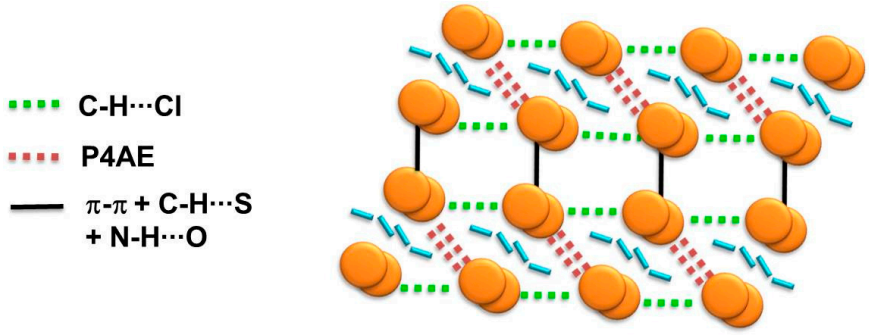


(**a**)



(**b**)

Figure S3. *Cont.*



(**c**)

Figure S3. (**a**) and (**c**) Representation of simplified packing in 1, (**b**) pseudo-3D packing in 1.

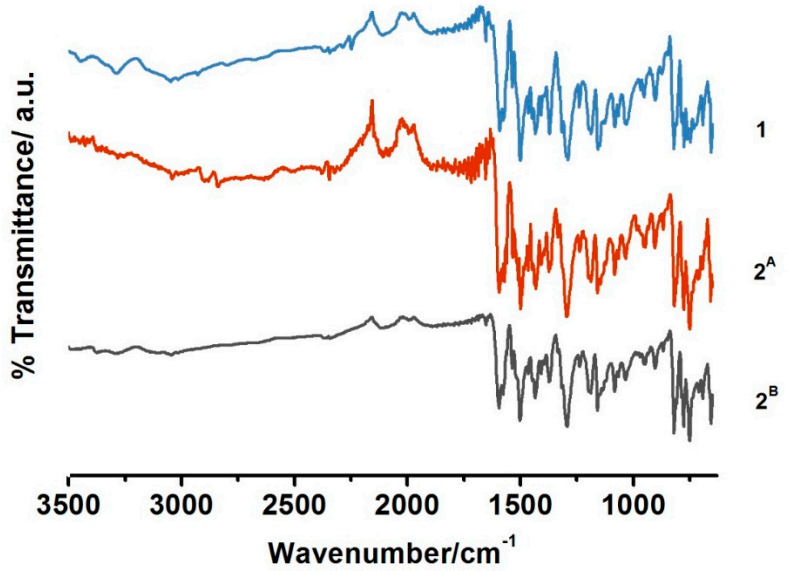


Figure S4. FT-IR spectra of the compounds showing similar pattern between solvate and de-solvate compounds. Free MeCN is observed at 2249 cm^{-1} for fresh compound 1.

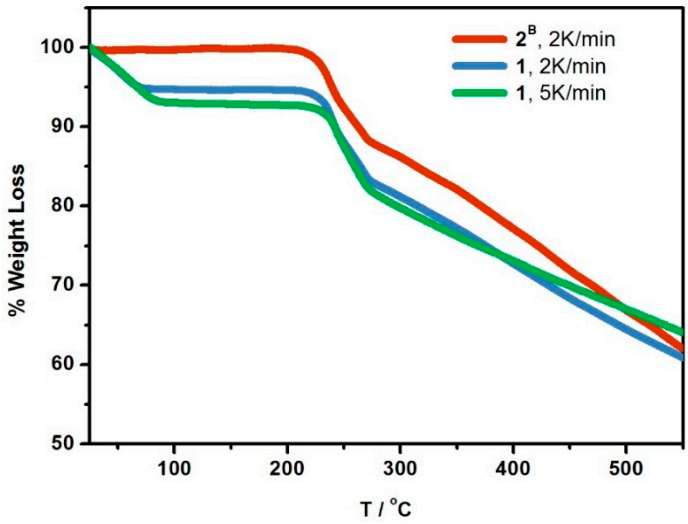


Figure S5. TGA data of compound 2^B and 1 at different heating rates.