Supporting Information

To the paper

Influence of supramolecular bonding contacts on the spin-crossover behaviour of iron(II) complexes from 2,2'-dipyridylamino/*s*-triazine ligands

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Table S1. Crystal data and structure refinement for complex **1** at three different temperatures.

Empirical formula		$C_{52}H_{36}FeN_{14}O_4S_2$, $2CH_2Cl_2$	
F_w (g mol^{-1})		1210.77	
CCDC number	921061	921062	921063
Temperature (K)	100(2)	240(2)	300(2)
Crystal system	triclinic	triclinic	triclinic
Space group	*P*–1	*P*–1	*P*–1
Crystal size (mm^3)	0.08 × 0.06 × 0.04	0.08 × 0.06 × 0.04	0.08 × 0.06 × 0.04
a (Å)	10.1377(7)	10.2386(8)	10.3010(14)
b (Å)	10.8050(7)	10.9671(8)	11.0444(15)
c (Å)	13.0202(9)	13.2109(10)	13.2848(18)
α (°)	83.376(2)	85.375(2)	86.033(2)
β (°)	78.242(2)	79.889(2)	80.447(2)
γ (°)	70.723(2)	69.869(2)	69.556(2)
V (Å^3)	1316.21(15)	1370.84(18)	1396.5(3)
Z	1	1	1
ρ_{calcd}	1.528	1.467	1.440
μ (mm^{-1})	0.794	0.763	0.749
F(000)	620	620	620
ϑ for data collection (°)	2.86–33.60	2.87–33.62	2.86–28.97
Reflections collected / unique	18860 / 7887	39494 / 8326	11351 / 5637
Completeness to theta	99.2	99.5	98.4
Data / restraints / parameters	7887 / 0 / 358	8326 / 37 / 358	5637 / 52 / 358
Goodness-of-fit on F^2	1.076	1.075	1.051
Final R indices [$I>2\sigma(I)$]	R1 = 0.0591, wR2 = 0.1770	R1 = 0.0678, wR2 = 0.1984	R1 = 0.0918, wR2 = 0.2586
R indices (all data)	R1 = 0.0641, wR2 = 0.1837	R1 = 0.0769, wR2 = 0.2088	R1 = 0.1071, wR2 = 0.2813
largest diff. peak and hole (*e* Å^3)	1.191 and –0.831	1.239 and –0.959	1.304 and –0.711

Figure S1. Intramolecular lone pair···π interactions taking place between the thiocyanate sulfur atoms and the triazine rings of the two **L1** ligands [Cg5···S1 = 3.459(1) Å].

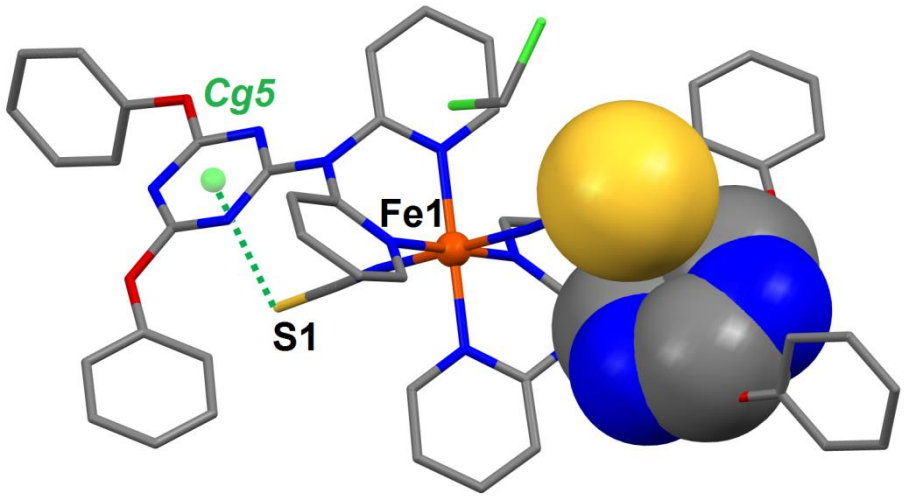

Table S2. Crystal data and structure refinement for complex **2** (LS) at 100 K.

Empirical formula	$C_{52}H_{36}FeN_{14}O_4Se_2$, $4CH_2Cl_2$, $4CH_3OH$
F_w (g mol^{-1})	1602.59
CCDC number	921064
Temperature (K)	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
Crystal size (mm^3)	0.06 × 0.10 × 0.18
a (Å)	8.642(2)
b (Å)	32.287(6)
c (Å)	13.175(2)
β (°)	111.243(12)
V (Å^3)	3426.4(12)
Z	2
ρ_{calcd}	1.553
μ (mm^{-1})	1.657
F(000)	1624
ϑ for data collection (°)	2.08–25.35
Reflections collected / unique	23597 / 6249
Completeness to theta	99.7
Data / restraints / parameters	6249 / 94 / 483
Goodness-of-fit on F^2	1.065
Final R indices [$I>2\sigma(I)$]	R1 = 0.0657, wR2 = 0.1882
R indices (all data)	R1 = 0.0790, wR2 = 0.1978
largest diff. peak and hole (e Å^3)	1.837 and –0.945

Figure S2. Views of the crystal packing of **2** along the 3 different crystallographic axes showing the numerous methanol and dichloromethane molecules (in space-filling mode) surrounding an iron(II) complex. A) along the *c* axis; B) along the *b* axis; C) along the *a* axis.

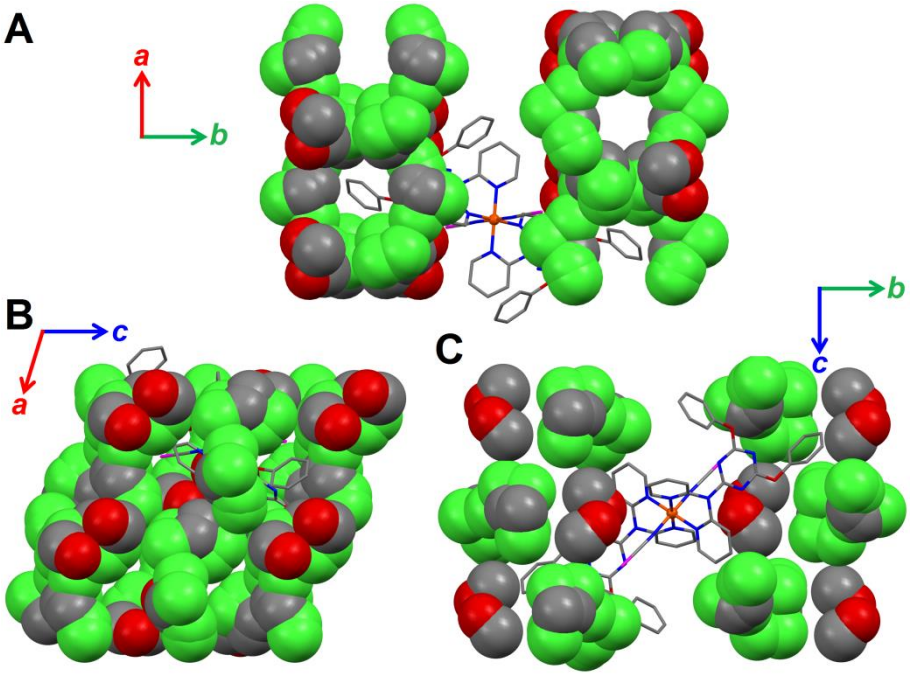

Figure S3. Intramolecular lone pair···π interactions taking place between the selenocyanate selenium atoms and the triazine rings of the two **L1** ligands [Cg5···Se1 = 3.501(2) Å].

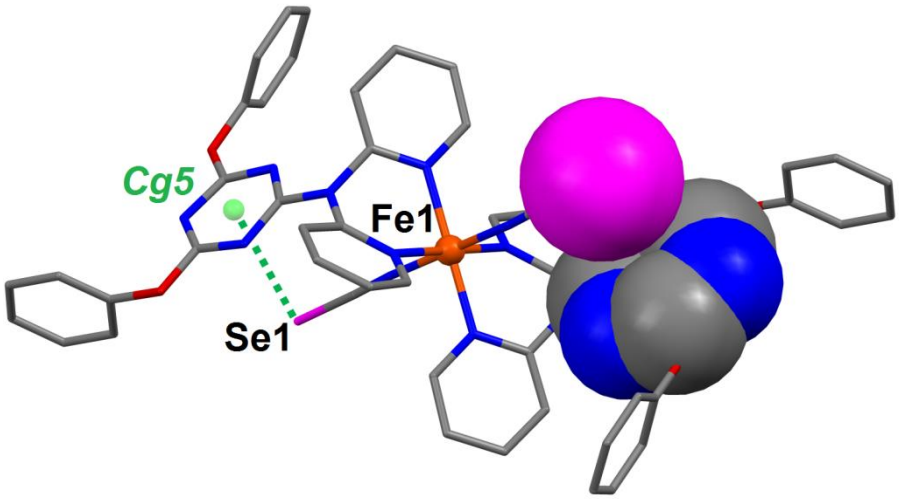

Table S3. Crystal data and structure refinement for complex **3** at three different temperatures.

Empirical formula		$C_{52}H_{16}F_{20}FeN_{14}O_4S_2$, $2(C_2H_3N)$	
F_w (g mol^{-1})		1482.87	
CCDC number	921065	921066	921067
Temperature (K)	100(2)	190(2)	280(2)
Crystal system	triclinic	triclinic	triclinic
Space group	*P*–1	*P*–1	*P*–1
Crystal size (mm^3)	0.19 × 0.04 × 0.02	0.19 × 0.04 × 0.02	0.08 × 0.06 × 0.04
a (Å)	8.3499(8)	8.4120(7)	8.643(2)
b (Å)	11.3580(10)	11.4159(9)	11.494(2)
c (Å)	15.689(2)	15.757(2)	15.844(3)
α (°)	92.9740(10)	93.2930(10)	94.851(2)
β (°)	102.6160(10)	102.2240(10)	100.035(2)
γ (°)	99.2570(10)	99.4470(10)	100.981(2)
V (Å^3)	1427.2(3)	1452.1(2)	1510.2(5)
Z	1	1	1
ρ_{calcd}	1.725	1.696	1.630
μ (mm^{-1})	0.586	0.576	0.554
F(000)	740	740	740
ϑ for data collection (°)	2.82–33.62	3.38–33.62	3.64–30.43
Reflections collected / unique	20057 / 8387	20212 / 8576	17781 / 7059
Completeness to theta	97.2	97.3	98.0
Data / restraints / parameters	8387 / 0 / 449	8576 / 0 / 449	7059 / 6 / 450
Goodness-of-fit on F^2	1.047	1.035	0.969
Final R indices [$I>2\sigma(I)$]	R1 = 0.0429, wR2 = 0.1192	R1 = 0.0548, wR2 = 0.1556	R1 = 0.0689, wR2 = 0.1839
R indices (all data)	R1 = 0.0506, wR2 = 0.1264	R1 = 0.0656, wR2 = 0.1681	R1 = 0.0880, wR2 = 0.2027
largest diff. peak and hole (*e* Å^3)	0.496 and –0.588	0.439 and –0.650	0.390 and –0.434

Figure S4. Intramolecular lone pair···π interactions taking place between the thiocyanate sulfur atoms and the triazine rings of the two **L1^{F}** ligands [Cg5···S1 = 3.457(1) Å].

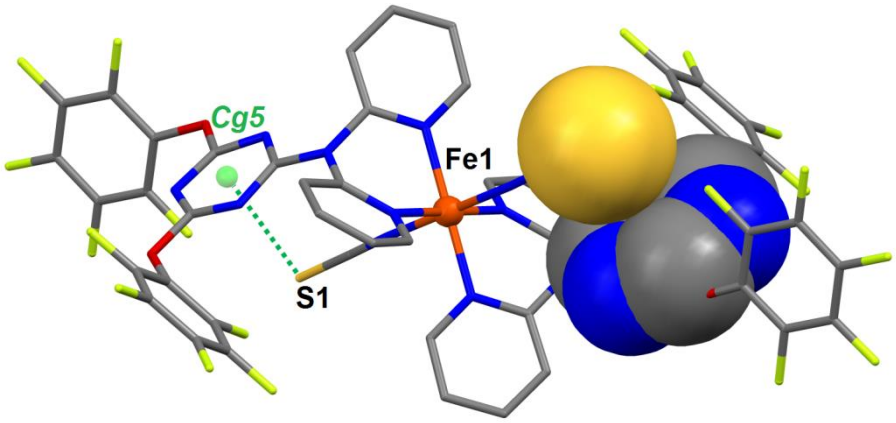

Figure S5. Excess enthalpy (left) and entropy (right) involved in the process of SCO in compound **3**, as derived from integration of ΔC_p data in the warming mode vs. respectively *T* and Ln*T*.

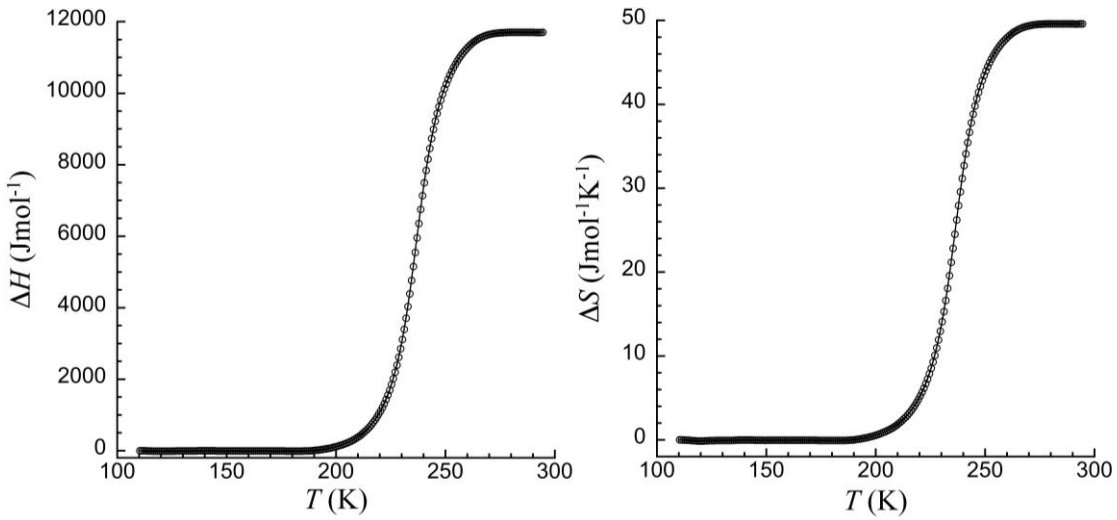

Figure S5. Derivative of χT with respect to T after full LIESST on **1'**, used to extract the value of T(LIESST).

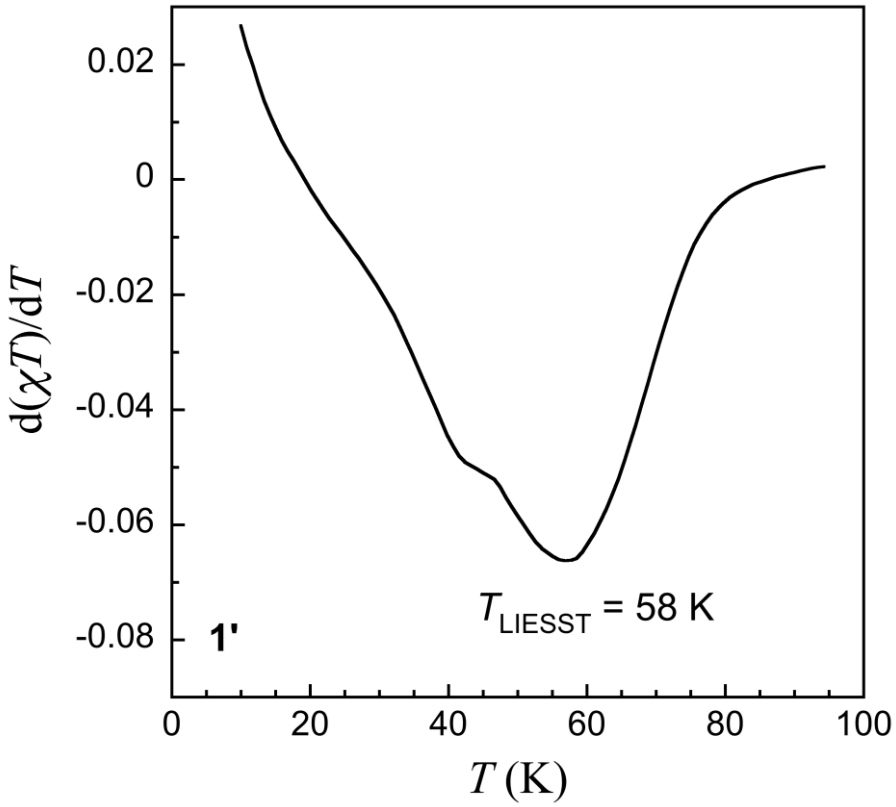

Table S4. Crystal data and structure refinement for ligand **L1**.

Empirical formula	$C_{25}H_{18}N_6O_2$
F_w (g mol^{-1})	434.45
CCDC number	922570
Temperature (K)	250(2)
Crystal system	triclinic
Space group	*P*–1
Crystal size (mm^3)	0.35 × 0.11 × 0.07
a (Å)	10.840(2)
b (Å)	11.894(2)
c (Å)	18.623(3)
α (°)	100.603(2)
β (°)	105.797(2)
γ (°)	104.495(2)
V (Å^3)	2153.4(6)
Z	4
ρ_{calcd}	1.340
μ (mm^{-1})	0.107
F(000)	904
ϑ for data collection (°)	2.90–28.97
Reflections collected / unique	21045 / 8727
Completeness to theta	98.9
Data / restraints / parameters	8727 / 0 / 595
Goodness-of-fit on F^2	1.025
Final R indices [$I>2\sigma(I)$]	R1 = 0.0518, wR2 = 0.1407
R indices (all data)	R1 = 0.0715, wR2 = 0.1553
largest diff. peak and hole (*e* Å^3)	0.207 and –0.251

Figure S6. Representation of the solid-state structure of ligand **L1** obtained by single-crystal X-ray diffraction.