Supporting Information for:

Isostructural iron(III) spin crossover complexes with a tridentate Schiff base-like ligand: X-ray structures and magnetic properties

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Experimental:

The ligand HL was synthesised as published previously.[1] All other chemicals were commercially available and used without further purification. CHN analyses were measured with a Vario El III from Elementar AnalysenSysteme. Samples were prepared in a tin boat, and acetanilide was used as standard. Mass spectra were recorded with a Finnigan MAT 8500 with a data system MASPEC II. IR spectra were recorded with a Perkin Elmer Spectrum 100 FT-IR spectrometer.

$[FeL_2]BF_4$ (**1**). HL (0.2 g, 0.9 mmol, 1 eq), sodium acetate (0.05 g, 0.9 mmol, 1 eq), and iron(III) nitrate nonahydrate (0.22 g, 0.55 mmol, 0.6 eq) were dissolved in ethanol (20 mL) and the resulting purple solution was heated to reflux for 1 h. After cooling to room temperature, approximately half of the solvent was removed under reduced pressure. Sodium tetrafluoroborate (1.14 g, 10 mmol, 25 eq) was dissolved in 20 mL water and added to the purple solution. The mixture was stirred at room temperature for 10 min, the resulting purple solid was filtrated, washed with a few mL of water and dried *in vacuo*. Yield: 0.10 g (577.15 $g \cdot mol^{-1}$, 40 %). Elemental analysis ($C_{24}H_{26}BF_4FeN_4O_4$, %) measured (calcd.): C 49.32 (49.95), H 4.30 (4.54), N 9.56 (9.71). MS (EI, pos.) *m/z* (%): 490 ($C_{24}H_{26}FeN_4O_4$, 36), 93 (C_6H_6N, 100) 43 (C_2H_3O, 25). IR: ν = 1579 (s, C=O), 1568 (s, C=O) cm^{-1}.

$[FeL_2]ClO_4$ (**2**). HL (0.2 g, 0.9 mmol, 1 eq), sodium acetate (0.05 g, 0.9 mmol, 1 eq), and iron(III) nitrate nonahydrate (0.22 g, 0.55 mmol, 0.6 eq) were dissolved in ethanol (20 mL) and the resulting purple solution was heated to reflux for 1 h. After cooling to room temperature, approximately half of the solvent was removed under reduced pressure. Barium perchlorate trihydrate (5.37 g, 10 mmol, 25 eq) was dissolved in 20 mL water and added to the purple solution. The mixture was stirred at room temperature for 10 min, the resulting purple solid was filtrated, washed with a few mL of water and dried *in vacuo*. Yield: 0.14 g (589.79 $g \cdot mol^{-1}$, 43 %). IR: ν = 1579 (s, C=O), 1567 (s, C=O) cm^{-1}.

Single crystal X-ray structure analysis

X-ray structure analysis of the crystals was performed with a Stoe StadiVari diffractometer using graphite-monochromated MoKα radiation. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SIR-97)[2]and refined by fullmatrix least-square techniques against Fo^2–Fc^2 (SHELXL-2017).[3] All hydrogen atoms were calculated in idealised positions with fixed displacement parameters. ORTEP-III[4] was used for the structure representation, SCHAKAL-99[5] to illustrate molecule packing. The Hirshfeld surfaces were mapped with d_{norm}, and 2D fingerprint plots were generated using CrystalExplorer 17.5.[6] Graphical plots of the molecular Hirshfeld surfaces use a red-white-blue colour scheme. Red highlights contacts shorter than the van der Waals separation, contacts around the van der Waals separation are white, and blue is used for longer contacts.

CCDC (1898802–1898805) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Magnetic measurements

Magnetic measurements on the compounds were carried out using a SQUID MPMS-XL5 from Quantum Design with an applied field of 5000 G, and in the temperature range from 300 to 50 K in settle and in sweep (5 K/min) mode. The sample was prepared in a gelatine capsule held in a plastic straw. The raw data were corrected for the diamagnetic part of the sample holder and the diamagnetism of the organic ligand using tabulated Pascal's constants.[7]

Table S1. Crystallographic data for the complexes at different temperatures presented in this work.

	1-HS	**1-LS**	**2-HS**	**2-LS**
CCDC	1898802	1898803	1898804	1898805
formula	$C_{24}H_{26}FeN_4O_4$, BF_4	$C_{24}H_{26}FeN_4O_4$, BF_4	$C_{24}H_{26}FeN_4O_4$, ClO_4	$C_{24}H_{26}FeN_4O_4$, ClO_4
sum formula	$C_{24}H_{26}BF_4FeN_4O_4$	$C_{24}H_{26}BF_4FeN_4O_4$	$C_{24}H_{26}ClFeN_4O_8$	$C_{24}H_{26}ClFeN_4O_8$
M/ g mol^{-1}	577.15	577.15	589.79	589.79
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
crystal description	purple plate	purple plate	purple plate	purple plate
a/ Å	8.6392(3)	8.6111(3)	8.6776(3)	8.6347(3)
b/ Å	16.7578(5)	16.4406(5)	16.8062(8)	16.5568(7)
c/ Å	17.6029(8)	17.5177(8)	17.6168(6)	17.5497(6)
α/ °	90	90	90	90
β/ °	90	90	90	90
γ/ °	90	90	90	90
V/ Å^3	2548.44(16)	2480.01(16)	2569.19(17)	2508.96(16)
Z	4	4	4	4
ρ_{calcd}/ g cm^{-3}	1.504	1.546	1.525	1.561
μ/ mm^{-1}	0.660	0.678	0.747	0.765
crystal size/ mm	0.115×0.052×0.029	0.115×0.052×0.029	0.087×0.078×0.038	0.087×0.078×0.038
F(000)	1188	1188	1220	1220
T/ K	175	133	150	100
λ/ Å	Mo-K$_\alpha$ 0.71073	Mo-K$_\alpha$ 0.71073	Mo-K$_\alpha$ 0.71073	Mo-K$_\alpha$ 0.71073
Θrange/ °	1.7–28.5	2.3–28.6	2.3–28.5	2.3–28.5
Reflns. collected	12870	14682	13721	13617
Indep. reflns.(R_{int})	5894 (0.054)	5782 (0.062)	6016 (0.045)	5863 (0.039)
Parameters	343	343	343	343
$R1$ (all data)	0.0461	0.0477	0.0405	0.0368
$wR2$	0.0940	0.0975	0.0705	0.0649
GooF	0.89	0.89	0.89	0.90
Flack x	−0.030(17)	−0.02(2)	−0.022(13)	−0.001(12)

Figure S1. ORTEP drawing of **1** in the HS state (top) and LS state (bottom). Ellipsoids were drawn at 50 % probability level. Hydrogen atoms were omitted for clarity.

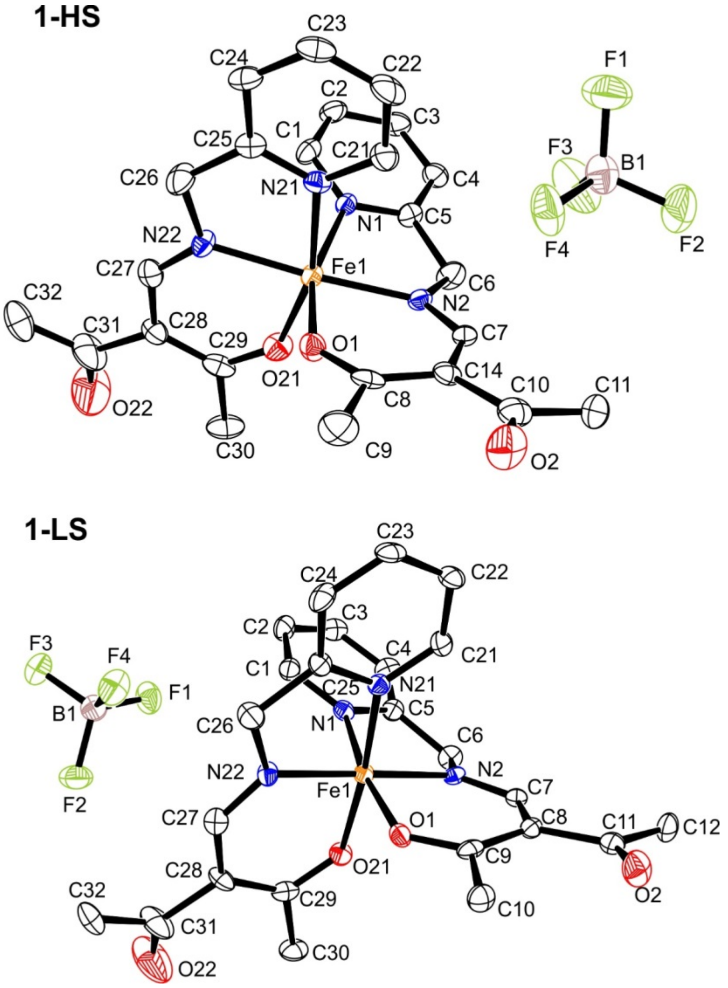
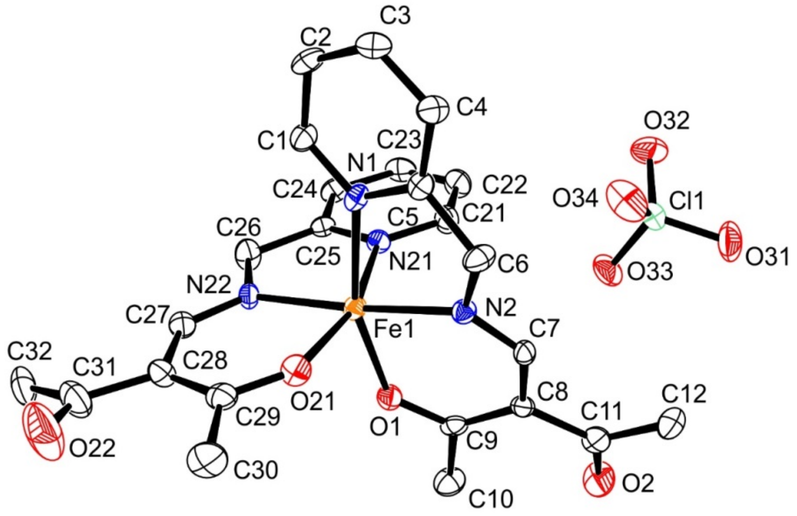


Figure S2. ORTEP drawing of **2** in the HS state (top) and LS state (bottom). Ellipsoids were drawn at 50 % probability level. Hydrogen atoms were omitted for clarity.

2-HS



2-LS

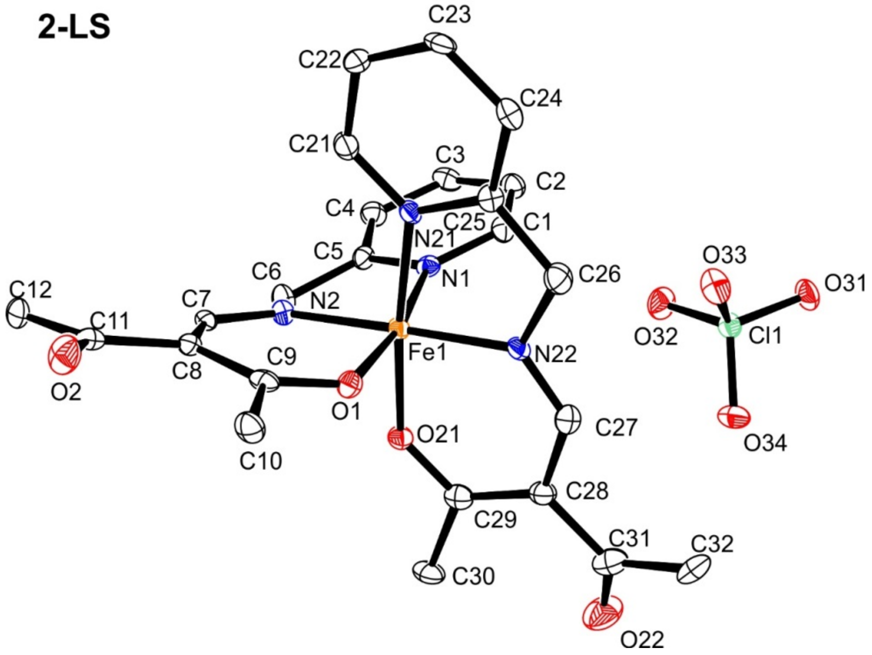


Table S2. Summary of the C–H···π interactions of the complexes presented in this work.

		C$_g$	H···C$_g$/Å Y···C$_g$/Å	X–H···C$_g$/° X–Y···C$_g$/°	X···C$_g$/Å
1-HS	C3–H3	Fe1–O21–C29–C28–C27–N22[a]	2.95	153	3.818(6)
	C30–H30B	N21–C21–C22–C23–C24–C25[b]	2.72	134	3.470(5)
1-LS	C30–H30B	N21–C21–C22–C23–C24–C25[c]	2.61	143	3.444(5)
2-HS	C3–H3	Fe1–O21–C29–C28–C27–N22[d]	2.95	153	3.824(4)
	C30–H30C	N21–C21–C22–C23–C24–C25[c]	2.73	134	3.481(4)
2-LS	C30–H30C	N21–C21–C22–C23–C24–C25[b]	2.59	148	3.465(4)

a: 3/2−x, 2−y, −1/2+z; b: 1+x, y, z; c: −1+x, y, z; d: 1/2−x, −y, 1/2+z.

Table S3. Hydrogen bonds and angles of complexes presented in this work.

	Donor	Acceptor	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
1-HS	C1–H1	F2[a]	0.95	2.54	3.008(6)	111
	C7–H7	O2[b]	0.95	2.50	3.090(6)	121
	C21–H21	F4[c]	0.95	2.43	3.089(6)	126
	C23–H23	F2[d]	0.95	2.42	3.179(6)	137
	C24–H24	F1[d]	0.95	2.52	3.357(6)	146
	C26–H26B	F3[a]	0.99	2.52	3.380(6)	145
	C32–H32B	O22[e]	0.98	2.31	3.253(8)	161
	C32–H32A	F1[a]	0.98	2.49	3.320(6)	142
1-LS	C7–H7	O2[f]	0.95	2.49	3.187(6)	131
	C21–H21	F4[g]	0.95	2.47	3.346(6)	152
	C23–H23	F1[h]	0.95	2.41	3.120(6)	132
	C24–H24	F2[h]	0.95	2.48	3.340(6)	151
	C32–H32A	F2[c]	0.98	2.54	3.327(6)	137
	C32–H32B	O22[i]	0.98	2.36	3.308(7)	170
2-HS	C1–H1	O31[k]	0.95	2.60	3.039(5)	109
	C7–H7	O2[l]	0.95	2.48	3.076(5)	120
	C21–H21	O33[c]	0.95	2.53	3.135(4)	121
	C23–H23	O31[m]	0.95	2.43	3.192(5)	137
	C24–H24	O32[m]	0.95	2.55	3.384(5)	147
	C26–H26A	O34[k]	0.99	2.52	3.377(5)	145
	C32–H32B	O22[n]	0.98	2.31	3.264(6)	166
	C32–H32C	O32[k]	0.98	2.54	3.323(6)	137
2-LS	C7–H7	O2[o]	0.95	2.49	3.198(4)	132
	C21–H21	O33[p]	0.95	2.51	3.383(4)	153
	C23–H23	O32[q]	0.95	2.44	3.150(4)	131
	C24–H24	O34[q]	0.95	2.50	3.364(4)	152
	C26–H26A	O33[c]	0.99	2.58	3.395(4)	140
	C32–H32B	O22[r]	0.98	2.39	3.347(4)	165
	C32–H32C	O34[c]	0.98	2.55	3.298(4)	133

a: 1−x, −1/2+y, 3/2−z; b: 1/2+x, 5/2−y, 2−z; c: x, y, z; d: −x, −1/2+y, 3/2−z; e: −1/2+x, 3/2−y, 2−z; f: −1/2+x, 5/2−y, 2−z; g: 2−x, −1/2+y, 3/2−z; h: 1+x, y, z; i: 1/2+x, 7/2−y, 2−z; k: 1−x, 1/2+y, 3/2−z; l: −1/2+x, −1/2−y, 1−z; m: 2−x, 1/2+y, 3/2−z; n: 1/2+x, 1/2−y, 1−z; o: 1/2+x, 1/2−y, −z; p: 1−x, 1/2+y, 1/2−z; q: −1+x, y, z; r: −1/2+x, −1/2−y, −z.

Figure S3. Hirshfeld surface mapped with d_{norm} (top left), fingerprint plots: full (top right), resolved into H···O/O···H (bottom left), and H···F/F···H (bottom right) contacts of complex **1-LS**.

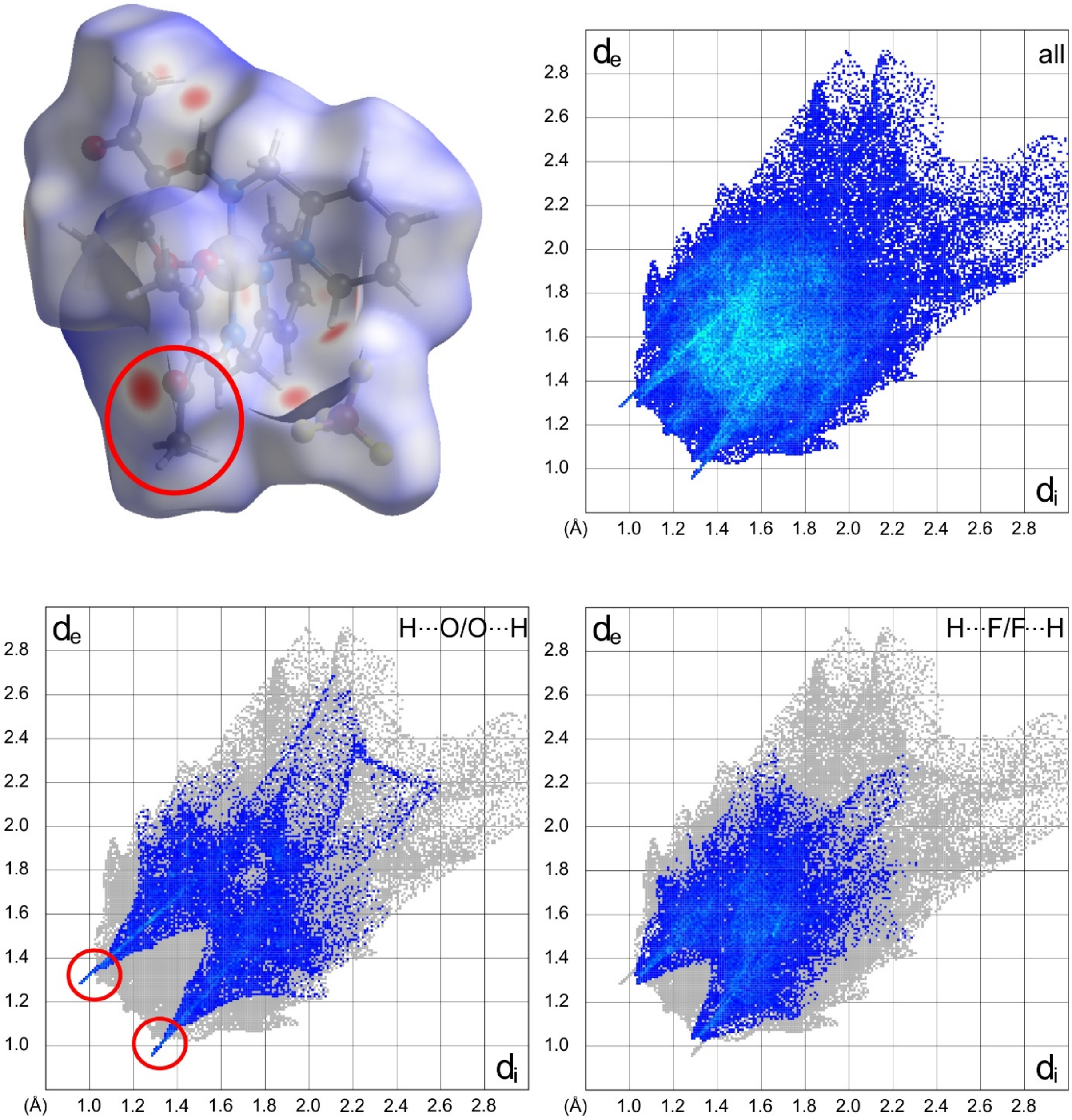


Figure S4. Hirshfeld surface mapped with d_{norm} (top left), fingerprint plots: full (top right), and resolved into H···O/O···H (bottom left) of complex **2-HS**.

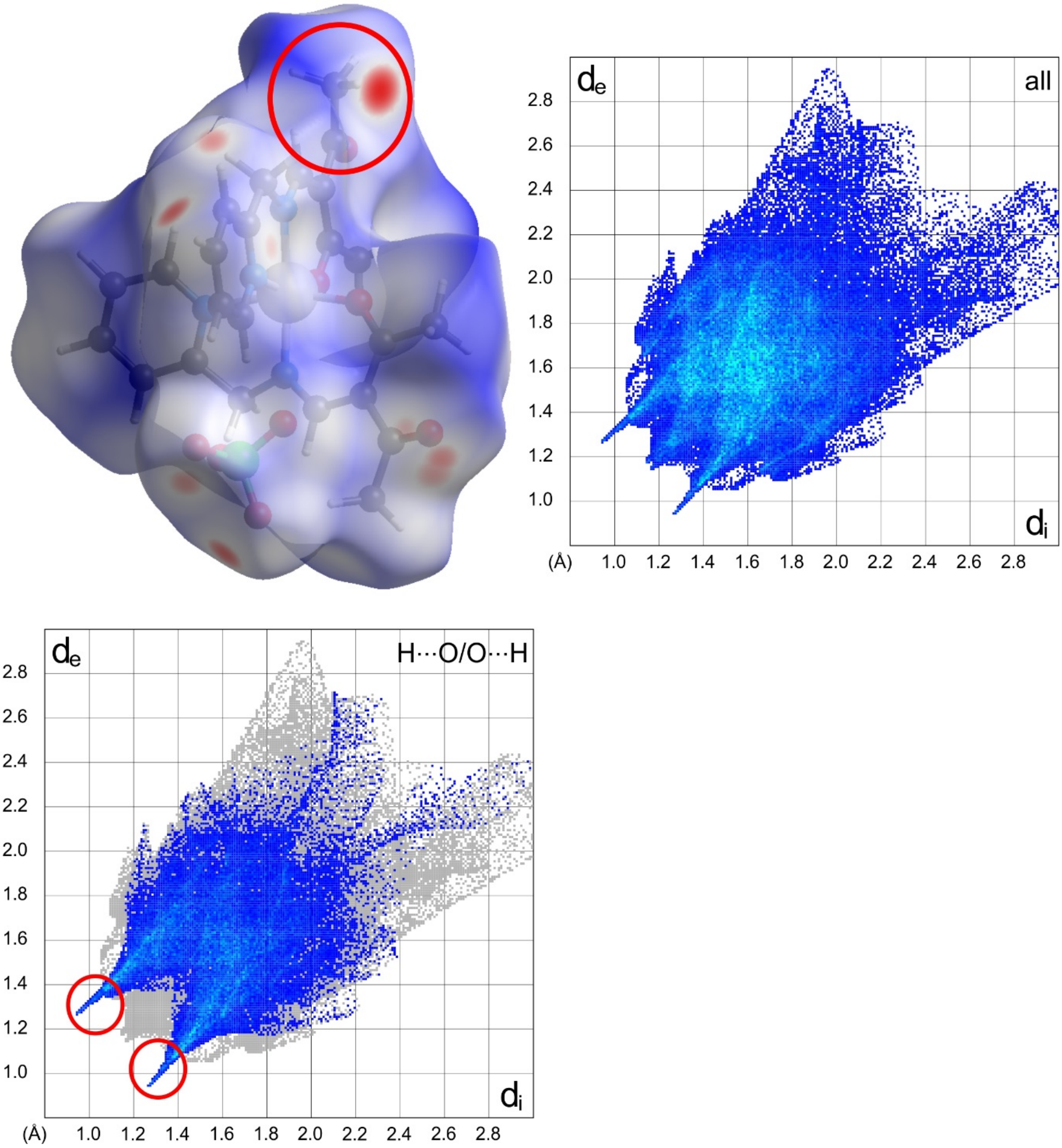


Figure S5. Hirshfeld surface mapped with d_{norm} (top left), fingerprint plots: full (top right), and resolved into H···O/O···H (bottom left) contacts of complex **2-LS**.

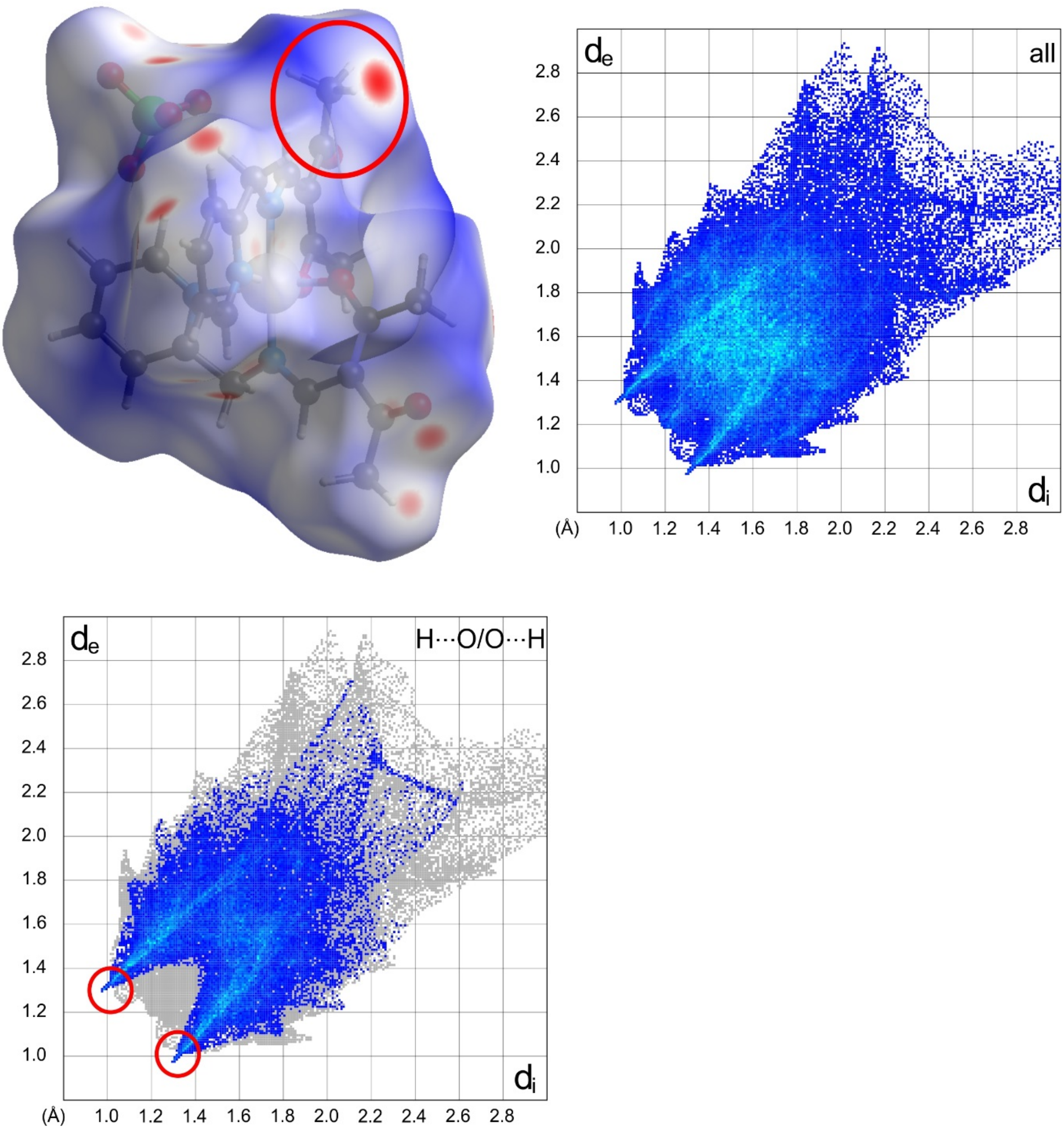
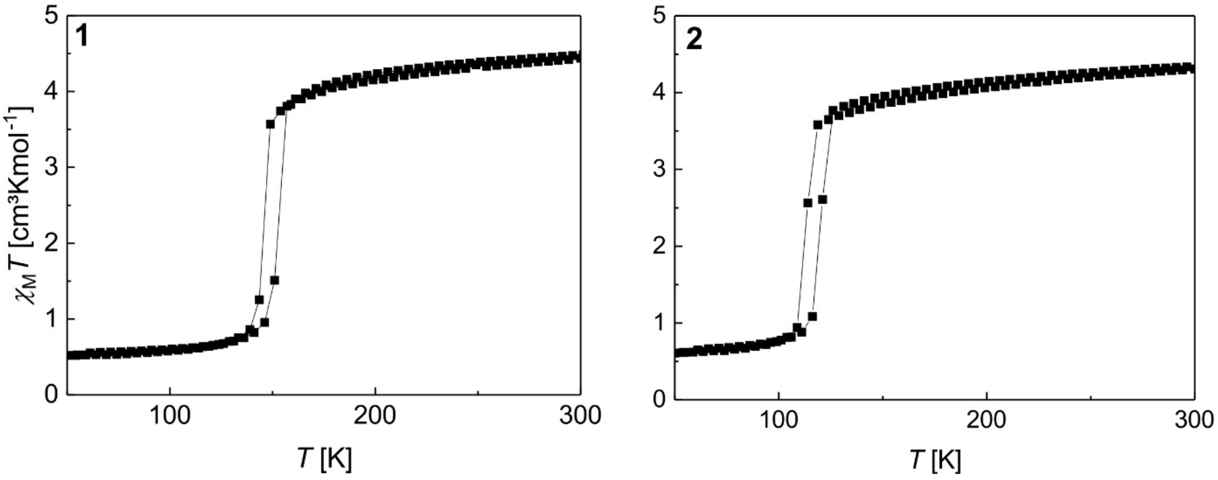


Figure S6. Plot of the $\chi_M T$ product vs. T for complex **1** (left) and **2** (right) measured in sweep mode with a scan rate of 5 K/min.



References

1 K. Dankhoff and B. Weber, *CrystEngComm.*, 2018, **20**, 818–828.

2 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst*., 1999, **32**, 115–119.

3 a) G. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112–122; b) G. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3–8.

4 a) C. K. Johnson and M. N. Burnett, ORTEP-III, Oak-Ridge National Laboratory, Oak-Ridge, TN, 1996; b) L. Farrugia, *J. Appl. Cryst*., 1997, **30**, 565.

5 E. Keller, Schakal-99, University of Freiburg, Freiburg, Germany, 1999.

6 M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka and M. A. Spackman, CrystalExplorer17 (2017). University of Western Australia.

7 O. Kahn, *Molecular Magnetism*, VCH, New York, N.Y, 1993.