Water Molecule Induced Reversible Single-Crystal-to-Single-Crystal Transformation Between Two Trinuclear Fe(II) Complexes with Different Spin Crossover Behavior

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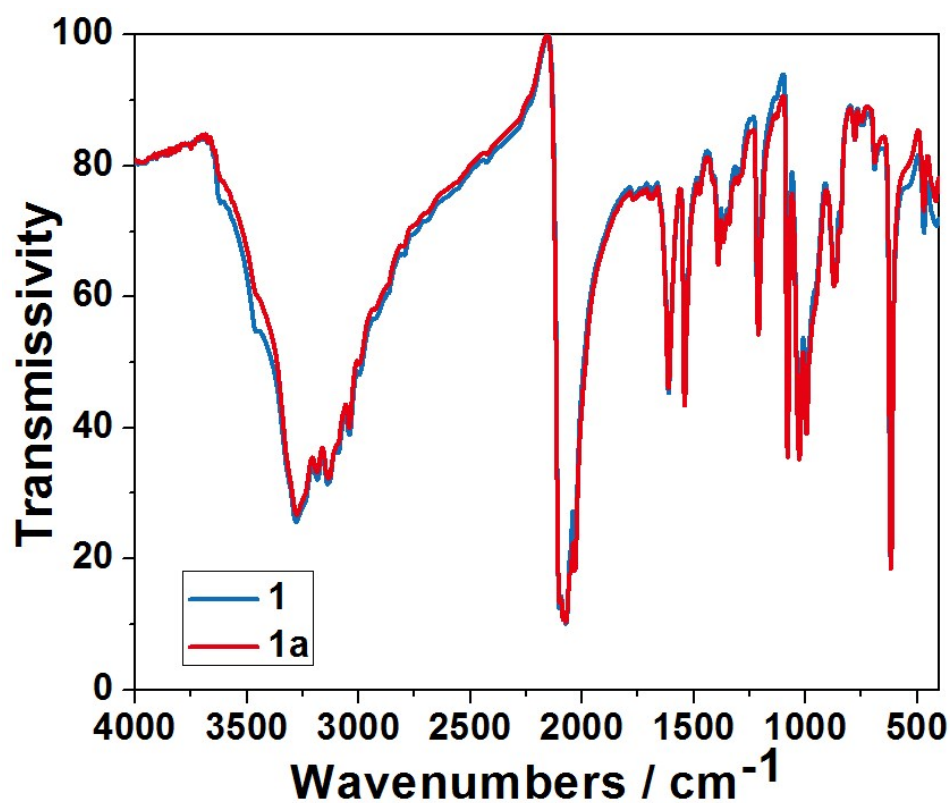
Fig. S1 IR of complex **1** and **1a**.

Table S1. Selected bond distances for Fe3 in complex **1** and **1a** at different temperatures.

	1				**1a**		
	100 K	150 K	293 K		100 K	150K	293K
Fe(3)-N(14)	2.155(3)	2.178(4)	2.178(7)	Fe(3)-N(14)	2.162(5)	2.162(9)	2.168(6)
Fe(3)-N(18)	2.185(3)	2.184(4)	2.197(6)	Fe(3)-N(18)	2.195(6)	2.210(11)	2.217(8)
Fe(3)-N(22)	2.143(3)	2.146(4)	2.210(6)	Fe(3)-N(22)	2.174(7)	2.138(12)	2.165(8)
Fe(3)-N(27)	2.086(3)	2.090(4)	2.112(6)	Fe(3)-N(27)	2.122(7)	2.139(10)	2.137(8)
Fe(3)-N(28)	2.142(3)	2.133(4)	2.129(8)	Fe(3)-N(28)	2.114(7)	2.111(13)	2.119(10)
Fe(3)-O(2)	2.184(3)	2.176(3)	2.196(6)	Fe(3)-N(29)	2.149(7)	2.149(13)	2.175(9)
Average Fe(3)-N	2.142	2.146	2.165	Average Fe(3)-N	2.152	2.152	2.164

Table S2. Information of hydrogen bonds in complex **1** at 100K obtained by PLATON tables.

Hydrogen Bond	Bond Distances (Å)	Bond Angles (^{o})	Symmetry of the acceptor
O2--H2A...N29	2.8564(1)	166	x-1/2,-y+1/2,-z
O1--H1A...N12	2.9023(1)	147	-x+1,y+1/2,-z+1/2
N20--H20A...N30	2.9220(1)	146	x,y-1,z
N4--H4B...N29	2.9684(1)	164	
C7--H7...O3	3.0970(1)	168	-x+1,y-1/2,-z+1/2
C10--H10...N16	3.1532(1)	135	x+1/2,-y+1/2,-z
N16--H16A...N29	3.2103(1)	136	
O1--H1B...S2	3.2780(1)	156	-x+1,y-1/2,-z+1/2
O2--H2B...S3	3.2785(1)	164	x-1/2,-y+1/2,-z
N24--H24A...S6	3.3099(1)	117	x+1/2,-y+1/2,-z
N24--H24A...N16	3.3144(1)	136	x+1/2,-y+1/2,-z
N8--H8B...S1	3.3308(1)	141	-x,y+1/2,-z+1/2
O3--H3B...S5	3.3336(1)	165	x+1,y,z
N20--H20B...S4	3.3367(1)	146	x-1/2,-y-1/2,-z
N16--H16B...S1	3.3523(1)	147	-x,y+1/2,-z+1/2
N12--H12A...S4	3.3659(1)	140	x+1/2,-y-1/2,-z
N4--H4A...S1	3.3744(1)	141	-x+1,y+1/2,-z+1/2
N24--H24B...S3	3.3993(1)	127	x+1/2,-y+1/2,-z
N8--H8A...S5	3.4621(1)	136	-x,y-1/2,-z+1/2
C5--H5...S6	3.6077(1)	173	x,y-1,z

Table S3. Information of hydrogen bonds in complex **1a** at 100K obtained by PLATON tables.

Hydrogen Bond	Bond Distances (Å)	Bond Angles (°)	Symmetry of the acceptor
N20--H20A...N30	2.8358(12)	144	x,y-1,z
O1--H1B...N12	2.8833(13)	156	-x+1,y+1/2,-z+1/2
C10--H10...N16	3.0934(14)	132	x+1/2,-y+1/2,-z
N12--H12B...N4	3.1223(14)	135	x,y-1,z
O1--H1A...S2	3.2274(14)	157	-x+1,y-1/2,-z+1/2
N20--H20B...S4	3.2425(14)	136	x-1/2,-y-1/2,-z
N16--H16B...S1	3.3072(14)	147	-x,y+1/2,-z+1/2
N24--H24A...S3	3.3152(15)	136	x+1/2,-y+1/2,-z
N4--H4A...S1	3.3181(15)	127	-x+1,y+1/2,-z+1/2
C4--H4...N30	3.3651(15)	140	-x,y-1/2,-z+1/2
N16--H16A...S5	3.3718(15)	143	x+1/2,-y+1/2,-z
N4--H4B...S5	3.3866(15)	150	x+1/2,-y+1/2,-z
N12--H12B...S4	3.3925(15)	136	x+1/2,-y-1/2,-z
N12--H12A...S6	3.6041(16)	162	x,y-1,z
C11--H11...S6	3.6593(16)	175	

Table S4. Information of hydrogen bonds in complex **2** obtained by PLATON tables.[1]

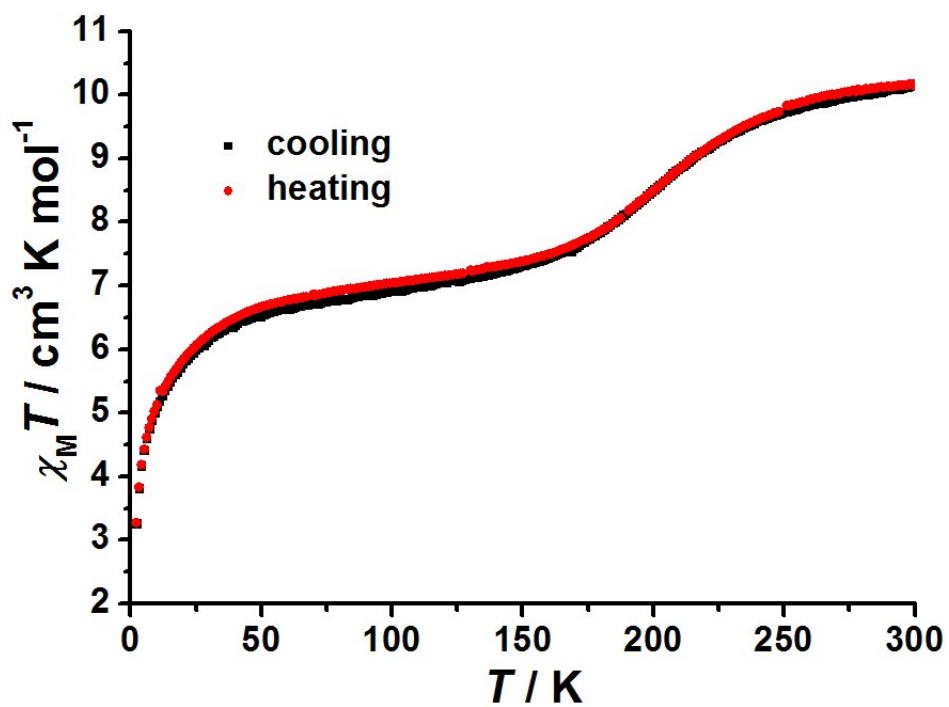| Hydrogen Bond	Bond Distances (Å)	Bond Angles (°)	Symmetry of the acceptor
O1--H1A...S2	3.221(4)	146	1/2+x,1/2-y,-1/2+z
O1--H1B....N30	2.731(8)	169	2-x,1-y,1-z
O2--H2B...N6	3.174(6)	180	
O3--H3A...N13	3.030(18)	145	-1+x,y,z
O3--H3A...N14	3.007(19)	178	-1+x,y,z
O3--H3A...N15	3.176(17)	128	-1+x,y,z
N4--H4A...S1	3.414(5)	142	1-x,-y,2-z
N4--H4B...S6	3.681(5)	155	x,-1+y,z
O4--H4C...N16	2.948(7)	178	1-x,-y,1-z
N8-H8A...S3	3.331(4)	152	1+x,y,z
N12--H12A...O4	3.069(8)	174	1/2+x,1/2-y,1/2+z
N12--H12B...S4	3.599(5)	150	-1/2+x,1/2-y,1/2+z
N16--H16A...S1	3.251(4)	111	2-x,-y,2-z
N16--H16A...S5	3.490(4)	130	2-x,-y,1-z
N16--H16B...N30	2.904(8)	124	x,-1+y,z
N20--H20B...S4	3.381(5)	142	1/2+x,1/2-y,1/2+z
N24--H24A...N29	3.146(6)	168	1-x,-y,1-z
N24--H24B...S6	3.368(4)	131	1-x,1-y,1-z
C1--H1...N24	3.446(6)	169	1-x,-y,1-z
C3--H3...O3	3.05(2)	152	1+x,y,z
C4--H4...N12	3.265(6)	151	1/2+x,1/2-y,1/2+z
C5--H5...N8	3.527(6)	171	-1/2+x,1/2-y,-1/2+z
C7--H7...O2	3.272(7)	171	
C9--H9...S6	3.523(5)	169	3/2-x,-1/2+y,3/2-z
C10--H10...N26	3.279(6)	147	1/2+x,1/2-y,-1/2+z
C11--H11...S5	3.644(5)	158	1-x,-y,1-z
C12--H12...N4	3.414(7)	164	1-x,-y,1-z

Fig. S2. Plots of $\chi_M T$ vs. T for **1**. The black shows the cooling progress and the red line indicates the heating progress.
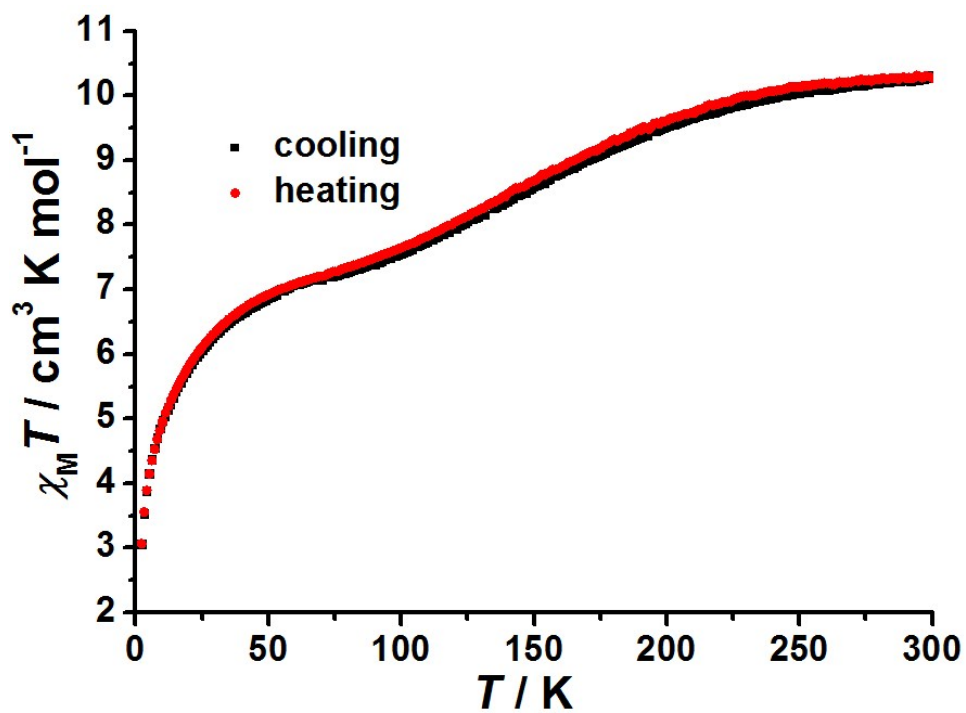

Fig. S3. Plots of $\chi_M T$ vs. T for **1a**. The black shows the cooling progress and the red line indicates the heating progress.
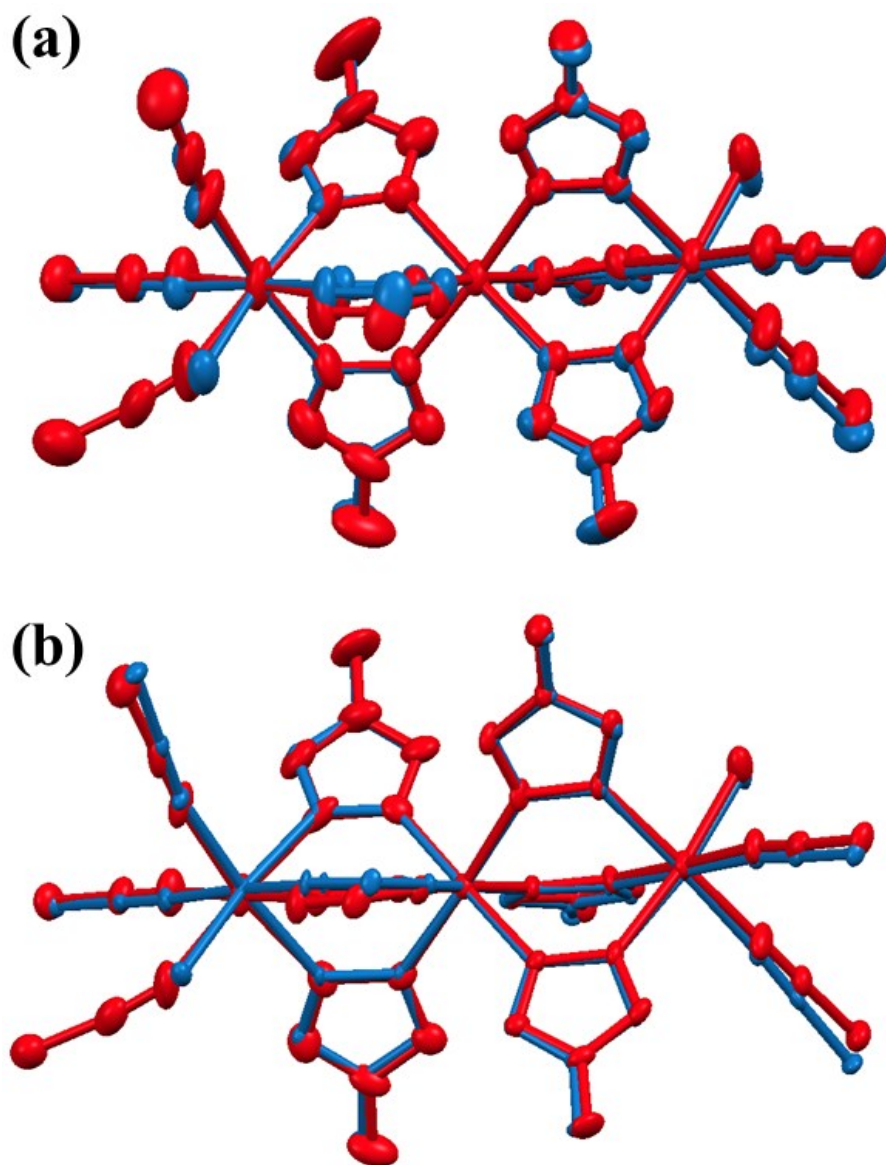
Fig. S4 Superposition of the two core structures of **1** (blue) and **1a** (red) between the HS (a) and
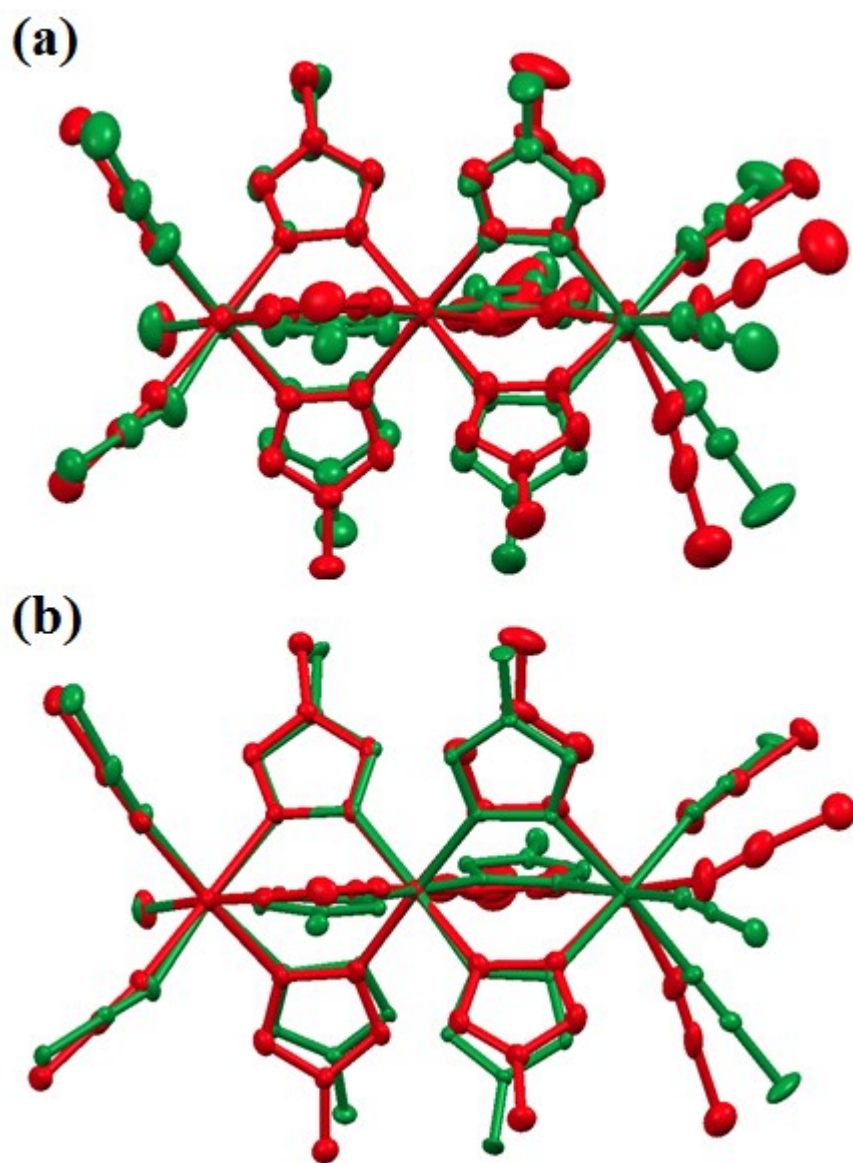
LS (b) states.

Fig. S5 Superposition of the two core structures of **1a** (red) and **2** (green) between the HS (a) and
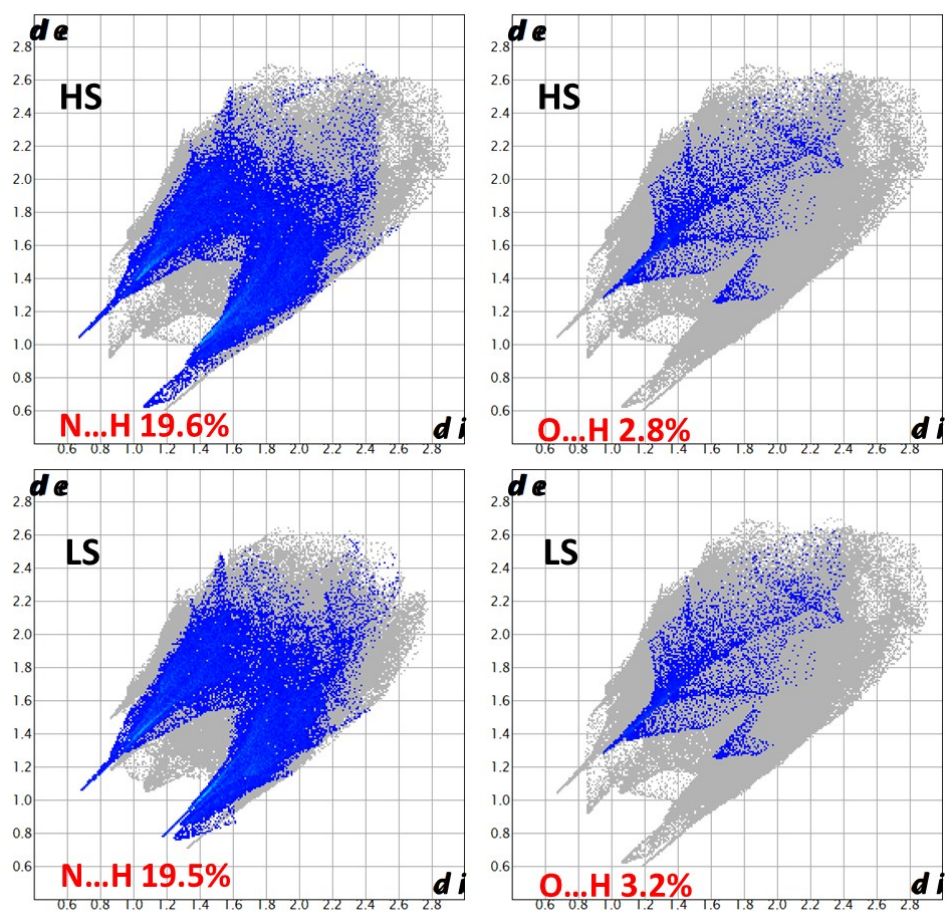
LS (b) states.

2

Fig. S6 Fingerprints of the intermolecular interactions in **2** within the HS (up) and LS (down) crystal packings from Single-Crystal X-ray Diffraction data. Grey zones represent all of the interactions and the blue zones account for the corresponding selected interaction, i.e. N···H (left) and O···H (right).

References

1 W.-B. Chen, J.-D. Leng, Z.-Z. Wang, Y.-C. Chen, Y. Miao, M.-L. Tong and W. Dong, *Chem. Commun.*, 2017, **53**, 7820-7823.