Supporting Information

Synthesis, Structure, and Spin Crossover Above Room Temperature of a Mononuclear and Related Dinuclear Double Helicate Iron(II) Complexes

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Fig. S1 TG/DTA curves of $[Fe^{II}(L1^{Me})_2](PF_6)_2$ (**1**).
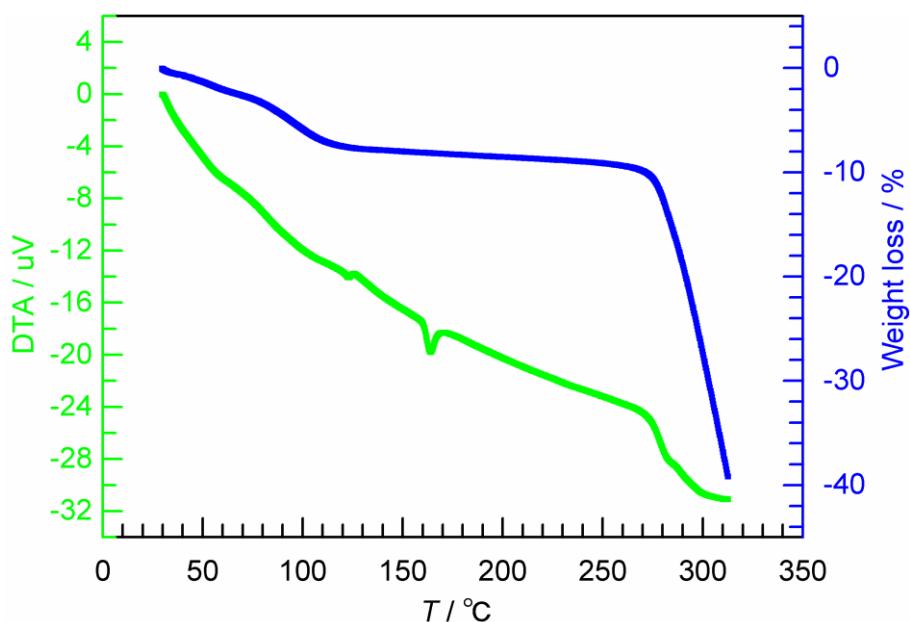
Fig. S2 TG/DTA curves of $[Fe^{II}_2(L2^{C2})_2](PF_6)_4 \cdot 5H_2O \cdot MeCN$ (**2**).
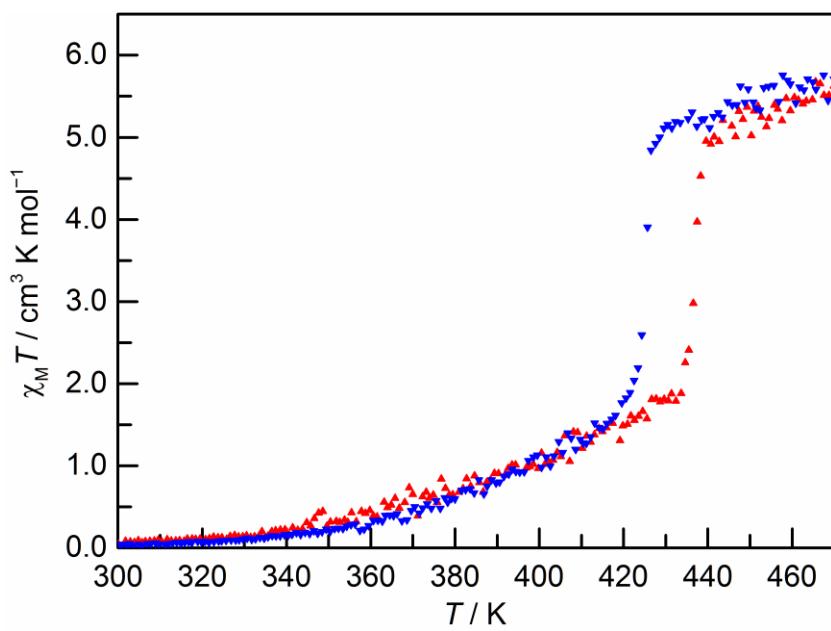
Fig. S3 The magnetic behaviour of desolvated sample **2'** in the form of the $\chi_M T$ vs. T plots. **2'** was warmed from 300 to 470 K (filled triangles; red), and then cooled from 470 to 300 K (filled inverted triangles; blue) at a sweep rate of 1 K min^{-1}.
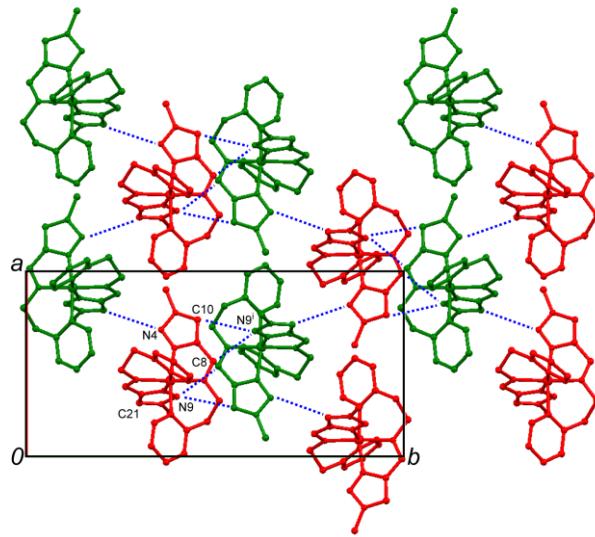
Fig. S4 Heterochiral 2D structure of $[Fe^{II}(L1^{Me})_2](PF_6)_2$ (**1**) at 150 K. Δ-$[Fe^{II}(L1^{Me})_2]^{2+}$ (green) and Λ-$[Fe^{II}(L1^{Me})_2]^{2+}$ (red) enantiomers are linked alternately *via* CH···N hydrogen bonds (blue dotted line) and enantiomers of same chirality are not directly connected in a 2D layer.
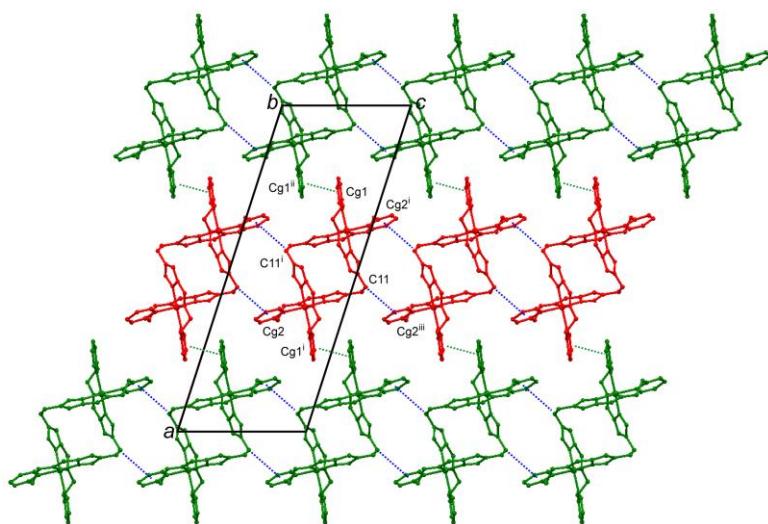
Fig. S5 Heterochiral 2D layer of $[Fe^{II}_2(L2^{C2})_2](PF_6)_4 \cdot 5H_2O \cdot MeCN$ (**2**) at 120 K. Green and red colours indicate $\Delta-\Delta$-$[Fe^{II}_2(L2^{C2})_2]^{4+}$ and $\Lambda-\Lambda$-$[Fe^{II}_2(L2^{C2})_2]^{4+}$ enantiomers, respectively. Homochiral cations are connected by CH/π (blue dotted line) interactions along the *c*-axis ($\Delta-\Delta\cdots\Delta-\Delta\cdots\Delta-\Delta\cdots$ or $\Lambda-\Lambda\cdots\Lambda-\Lambda\cdots\Lambda-\Lambda\cdots$) and cations of opposite chiral pair are linked alternately *via* $\pi-\pi$ interactions (green dotted line) along the (*a+c*)/2 direction ($\Delta-\Delta\cdots\Lambda-\Lambda\cdots\Delta-\Delta\cdots\Lambda-\Lambda\cdots$).
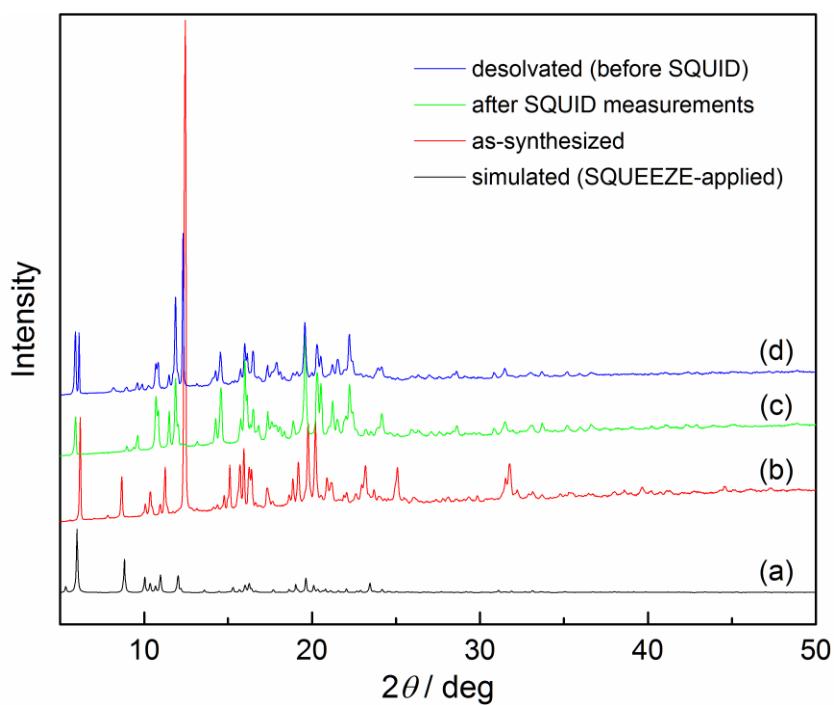
Fig. S6 PXRD patterns of **2** at room temperature in different states: (a) simulated from the SQUEEZE-applied single crystal X-ray data at 120 K; (b) as-synthesized **2**; (c) **2** after SQUID measurements; (d) desolvated **2'** before SQUID measurements.

Table S1 X-ray Crystallographic Data for $[Fe^{II}(L1^{Me})_2](PF_6)_2$ (**1**) at 150 and 448 K and $[Fe^{II}_2(L2^{C2})_2](PF_6)_4 \cdot 5H_2O \cdot MeCN$ (**2**) at 120 K

Complex	Mononuclear **1**		Dinuclear **2**[a]
Temperature	150 K	448 K	120 K
Formula		$C_{22}H_{26}N_{10}P_2F_{12}Fe$	$C_{46}H_{51}N_{21}P_3F_{18}Fe_2$
Formula weight		776.32	1444.68
Crystal system		Monoclinic	Monoclinic
Space group		$P2_1/a$	$C2/c$
a, Å	12.1982(16)	12.647(3)	30.932(8)
b, Å	21.725(3)	22.117(4)	20.020(5)
c, Å	12.2925(16)	12.703(4)	11.614(3)
β, deg	118.8092(12)	119.722(2)	107.907(3)
V, Å^3	2854.4(6)	3085.8(13)	6844(3)
Z	4	4	4
T, K	150(2)	448(2)	120 K(2)
d_{calcd}, g cm^{-3}	1.806	1.671	1.402
μ, mm^{-1}	0.756	0.699	0.591
R_1[b] (I>2sigma(I))	0.0404	0.0930	0.0956
wR_2[c] (I>2sigma(I))	0.0967	0.2253	0.2032
R_1[b] (all data)	0.0442	0.1291	0.1358
wR_2[c] (all data)	0.0998	0.2449	0.2215
S	1.064	1.434	1.001
CCDC number	1491569	1491570	1491571

[a] The PLATON SQUEEZE program[1] was used to treat regions having highly disordered solvent molecules and counter anions which could not be sensibly modelled in terms of atomic sites. Available void volume is 1386.1 Å^3. 473 electrons per unit cell were located and these were assigned to 1 PF_6 and 5 H_2O molecules per complex [473/4 = 119 e per complex; PF_6 (69) + 5 H_2O (10) = 119 electrons].

[b] $R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$.

[c] $wR_2 = [\Sigma w(|Fo^2|-|Fc^2|)^2/\Sigma w|Fo^2|^2]^{1/2}$.

Table S2 Relevant coordination bond lengths (Å) and angles (°) for $[Fe^{II}(L1^{Me})_2](PF_6)_2$ (**1**) at 150 and 448 K and $[Fe^{II}_2(L2^{C2})_2](PF_6)_4 \cdot 5H_2O \cdot MeCN$ (**2**) at 120 K

Complex	Mononuclear **1**		Dinuclear **2**
Temperature	150 K	448 K	120 K
	Bond Lengths (Å)		
Fe(1)-N(1)	2.0170(16)	2.141(4)	2.017(7)
Fe(1)-N(2)	1.9718(16)	2.085(4)	1.953(5)
Fe(1)-N(3)	1.9915(16)	2.140(4)	1.926(5)
Fe(1)-N(6)^i	2.0196(17)	2.107(5)	2.029(4)
Fe(1)-N(7)^i	1.9814(17)	2.098(4)	1.952(6)
Fe(1)-N(8)^i	1.9954(16)	2.167(4)	1.949(5)
Average Fe-N	1.996	2.123	1.971
	Bond Angles (deg)		
N(1)-Fe-N(2)	91.04(6)	88.23(16)	91.8(2)
N(1)-Fe-N(3)	171.42(7)	165.23(16)	172.8(2)
N(1)-Fe-N(6)^i	88.80(7)	89.68(17)	90.6(2)
N(1)-Fe-N(7)^i	93.40(6)	97.69(16)	98.0(3)
N(1)-Fe-N(8)^i	88.54(7)	88.47(16)	91.7(2)
N(2)-Fe-N(3)	80.43(7)	77.07(15)	81.14(19)
N(2)-Fe-N(6)^i	95.73(7)	101.69(17)	96.29(18)
N(2)-Fe-N(7)^i	171.84(7)	167.32(18)	167.5(3)
N(2)-Fe-N(8)^i	93.52(7)	92.73(16)	91.94(18)
N(3)-Fe-N(6)^i	93.00(7)	94.62(16)	88.89(19)
N(3)-Fe-N(7)^i	94.95(6)	96.47(15)	89.2(2)
N(3)-Fe-N(8)^i	90.99(7)	90.81(15)	89.9(2)
N(6)^i-Fe-N(7)^i	91.21(7)	89.60(18)	91.4(2)
N(6)^i-Fe-N(8)^i	170.42(7)	165.40(16)	171.4(2)
N(7)^i-Fe-N(8)^i	79.77(7)	76.31(18)	80.1(2)
Σ^a	46.3	64.7	42.5
Θ^b	132.8	208.8	133.7

^{a} Σ = the sum of $|90 - \varphi|$ for the 12 *cis* N-Fe-N angles in the octahedral coordination sphere.[2]
^{b} Θ = the sum of $|60 - \theta|$ for the 24 N-Fe-N angles describing the trigonal twist angles.[3]
Symmetry operation relevant only to **2**: (i), $1 - x$, y, $3/2 - z$.

Table S3 Intermolecular contacts (Å) for [Fe^{II}(L1^{Me})$_2$](PF$_6$)$_2$ (**1**) at 150 and 448 K and [Fe^{II}$_2$(L2^{C2})$_2$](PF$_6$)$_4$·5H$_2$O·MeCN (**2**) at 120 K

Complex	Temp.	C-H···X or X···X	d(C-H)	d(H···X)	d(C···X)	<(C-H···X)
Mononuclear **1**	150 K	C(8)-H(9)···N(9)^i	0.950	2.648	3.393(2)	135.63
		C(10)-H(10)···N(9)^i	0.950	2.905	3.527(3)	124.16
		C(21)-H(23)···N(4)^{ii}	0.950	2.687	3.525(3)	147.47
	448 K	C(8)-H(9)···N(9)^i	0.930	2.863	3.633(6)	141.02
		C(21)-H(23)···N(4)^{ii}	0.930	2.735	3.601(8)	155.46
Dinuclear **2**	120 K	Cg1^c···Cg1^{ii}			3.937(4)	
		C(1)···C(4)^{ii}			3.900(9)	
		C(2)···C(4)^{ii}			3.676(13)	
		C(2)···C(5)^{ii}			3.906(11)	
		C(3)···C(4)^{ii}			3.642(14)	
		C(3)···C(5)^{ii}			3.625(12)	
		C(3)···Cg1^{ii}			3.730	
		C(4)···C(4)^{ii}			3.776(11)	
		C(4)···C(5)^{ii}			4.010(9)	
		C(4)···Cg1^{ii}			3.604	
		C(11)-H(11)···Cg2^{d,iii}	0.990	3.681	3.991	101.09
		C(11)-H(12)···Cg2^{iii}	0.989	3.452	3.991	116.44

^{c} Cg1 = Centroid of the N1-C1-C2-C3-C4-C5 ring.
^{d} Cg2 = Centroid of the N6-C12-C13-C14-C15-C16 ring.
Symmetry operations for **1**: (i), 1 − x, 1 − y, 1 − z; (ii), − 1⁄2 + x, 1⁄2 − y, z.
Symmetry operations for **2**: (ii), 1⁄2 − x, 1⁄2 − y, 1 − z; (iii), x, y, 1 + z.

References

1 A. L. Spek, *Acta Cryst.*, 2015, **C71**, 9–18.

2 P. Guionneau, M. Marchivie, G. Bravic, J.-F. Létard and D. Chasseau, *Top. Curr. Chem.*, 2004, **234**, 97–128.

3 M. Marchivie, P. Guionneau, J.-F. Létard and D. Chasseau, *Acta Cryst.*, 2005, **B61**, 25–28.