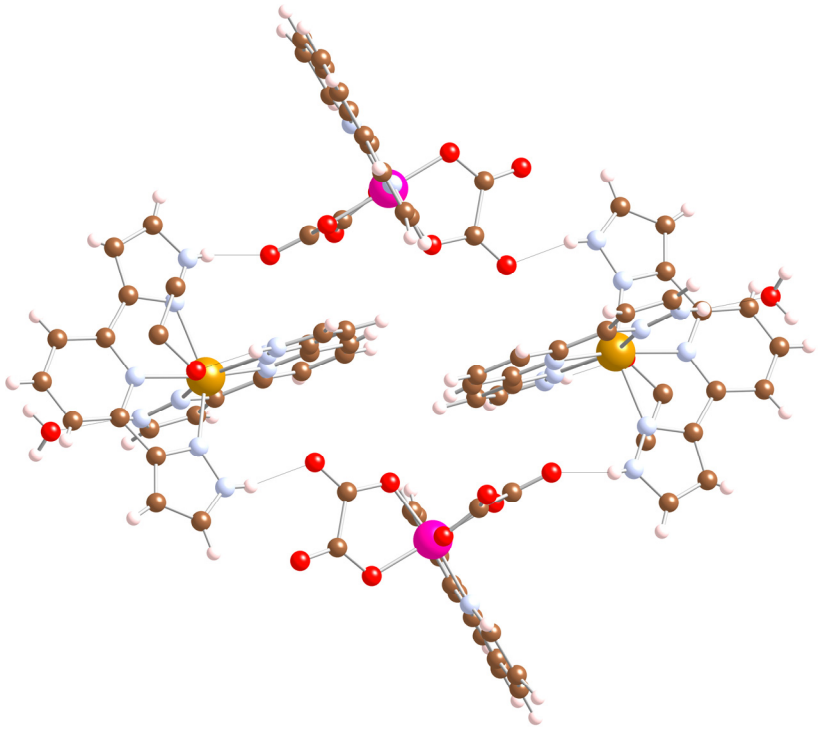

Fig. S1 View of a centrosymmetric Fe_2Cr_2 unit of the crystal structure of **2** showing the second coordination sphere of the iron(II) complex. Colouring of the different atoms: Fe = gold; Cr = magenta; C = brown; H = pink; N = blue; O = red. Thin lines refer to H bonds.

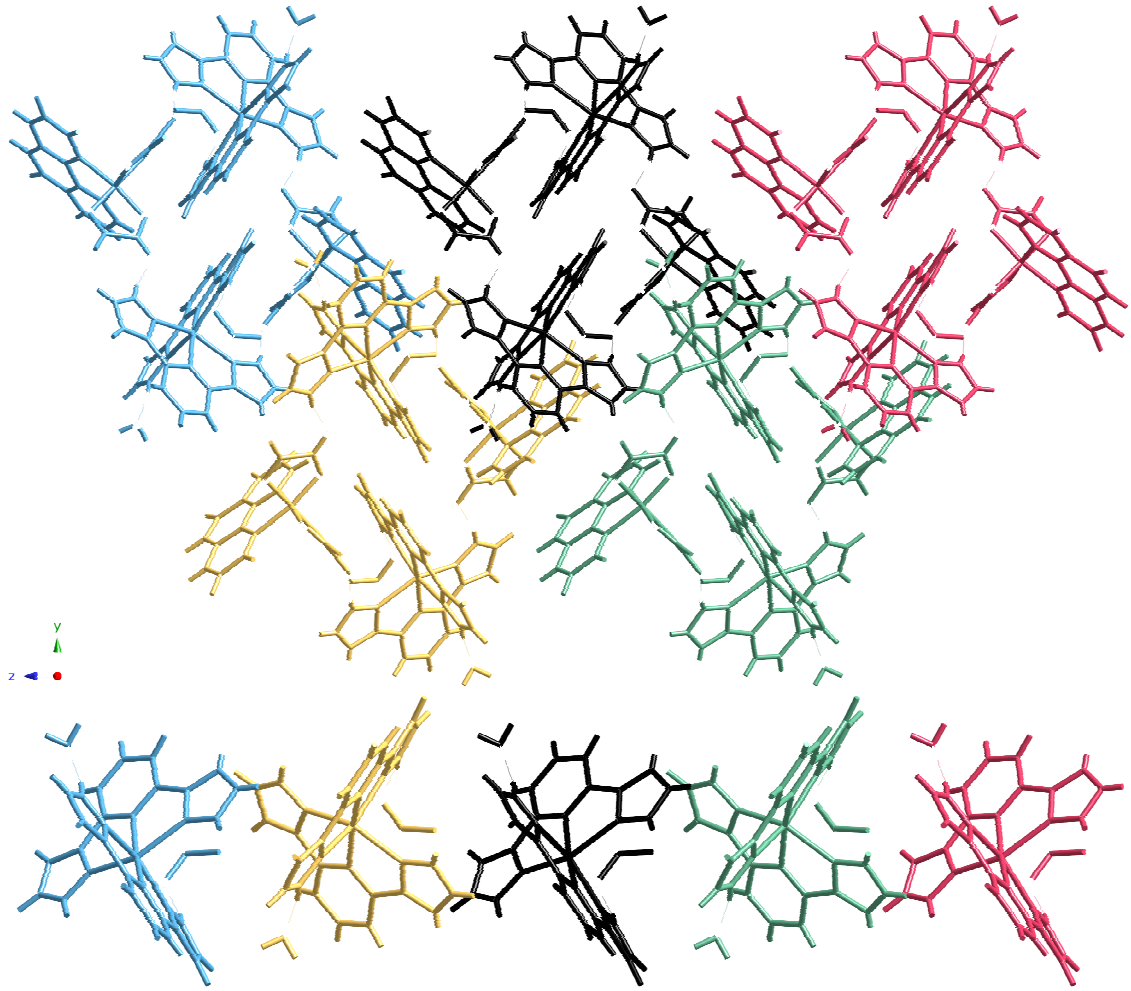

Fig. S2 Projection of the packing of cyclic Fe_2Cr_2 tetramers of **2** onto the *bc* plane. Perchlorate anions are omitted for clarity. A detailed view of the zigzag chains of $[Fe(bpp)_2]^{2+}$ cations is also shown.

Table S1 Intermolecular hydrogen bonds in the crystal structure of **1**.

D–H	d_{D-H}/Å	$d_{H\cdots A}$/Å	$d_{D\cdots A}$/Å	α/º	A
O100-H100	0.820	1.968	2.780	170.66	O7 [$x, -y + 5/2, z + 1/2$]
N3-H3	0.860	1.870	2.721	170.08	O8 [$x + 1, y, z + 1$]
N7-H7A	0.860	2.041	2.824	150.92	O6 [$-x + 2, -y + 2, -z + 2$]
N7-H7A	0.860	2.295	2.906	128.15	O5 [$-x + 2, -y + 2, -z + 2$]
N8-H8A	0.860	1.929	2.783	171.82	O2W
N12-H121	0.860	1.936	2.778	165.69	O4W [$x, -y + 5/2, z + 1/2$]
O4W-H4W2	0.861				

Table S2 Intermolecular hydrogen bonds in the crystal structure of **2**.

D–H	d_{D-H}/Å	$d_{H\cdots A}$/Å	$d_{D\cdots A}$/Å	α/º	A
N1-H1N	0.860	1.887	2.745	175.94	O3W [$-x + 1, -y + 1, -z + 1$]
N5-H5N	0.860	1.906	2.726	158.87	O100 [$-x + 1, y - 1/2, -z + 3/2$]
N6-H6N	0.860	2.018	2.794	149.72	O4 [$-x + 1, y - 1/2, -z + 3/2$]
N6-H6N	0.860	2.302	2.931	130.08	O3 [$-x + 1, y - 1/2, -z + 3/2$]
N10-H10N	0.860	1.905	2.727	159.46	O7 [$x + 1, -y + 1/2, z + 1/2$]
O100-H100	0.820	2.043	2.844	165.30	O11 [$-x + 1, y + 1/2, -z + 3/2$]
O1W-H1W1	0.971	1.927	2.886	168.46	O1 [$x, y, z - 1$]
O1W-H1W2	0.848	2.259	2.830	124.82	O3 [$-x + 1, -y + 1, -z + 1$]
O2W-H2W1	0.656	2.345	2.998	174.42	O12 [$x, -y + 1/2, z - 1/2$]
O2W-H2W2	0.830	1.984	2.804	169.26	O1W
O3W-H3W1	0.856	2.188	2.633	112.19	O4W [$-x + 1, y + 1/2, -z + 1/2$]
O3W-H3W2	0.860	2.043	2.833	152.16	O2W

Table S3 Enthalpy and entropy changes associated to thermal processes of **1**–**2**.

Compound	Curve[a]	T (K)[b]	$\lvert\Delta H\rvert$ (KJ/mol)	$\lvert\Delta S\rvert$ (J/mol·K)
1	1	364	211.7	575.9
	3	316	32.4	102.7
2	1	326	89.8	274.3
		335	87.3	255.2
		356	20.6	44.0
	3	309	87.8	284.0