Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for

High temperature Fe(III) spin crossover behaviours in three unprecedented Fe^{III}–M^{II}–Fe^{III} (M = Fe, Cd) linear trinuclear Complexes

Contents of the Supporting Information

Table S1. Crystallographic parameters for complexes **1–3**

Identification code	Complex_**1**	Complex_**2**	Complex_**3**
Empirical formula	$C_{60}H_{74}Fe_3N_{28}O_{19}$	$C_{60}H_{74}CdFe_2N_{28}O_{19}$	$C_{56}H_{60}Fe_3N_{28}O_{16}$
Formula weight	1659.02	1715.57	1548.87
Temperature/K	100.15	100.01(10)	100.01(11)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	12.547(3)	12.80010(10)	9.3846(3)
b/Å	14.079(4)	14.22150(10)	12.7707(3)
c/Å	19.628(5)	19.6539(2)	13.7327(3)
α/°	90	90	90.334(2)
β/°	95.264(5)	95.4610(10)	96.623(3)
γ/°	90	90	98.580(3)
Volume/Å^3	3452.7(16)	3561.49(5)	1616.11(7)
Z	2	2	1
ρ_{calc}g/cm^3	1.596	1.600	1.591
μ/mm^{-1}	0.717	6.377	6.112
F(000)	1720.0	1764.0	798.0
2θ range for data collection/°	3.566 to 56.774	7.686 to 153.928	6.482 to 154.646
Reflections collected	21616	23014	19369
Independent reflections	8448 [R_{int} = 0.0988, R_{sigma} = 0.1502]	7251 [R_{int} = 0.0324, R_{sigma} = 0.0322]	6547 [R_{int} = 0.0521, R_{sigma} = 0.0547]
Data/restraints/parameters	8448/0/508	7251/12/508	6547/0/476
Goodness-of-fit on F^2	0.993	1.079	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0749, wR_2 = 0.1822	R_1 = 0.0559, wR_2 = 0.1444	R_1 = 0.0565, wR_2 = 0.1490
Final R indexes [all data]	R_1 = 0.1459, wR_2 = 0.2281	R_1 = 0.0580, wR_2 = 0.1460	R_1 = 0.0658, wR_2 = 0.1560
Largest diff. peak/hole / e Å^{-3}	1.47/-0.93	1.91/-1.92	1.35/-0.99
CCDC Number	1911665	1911662	1911663

Table S2. Fe–O, Fe–N, Cd–O, Cd–N Bond distances (Å) around Fe(III), Fe(II) and Cd(II) centers and BVS values for Fe atoms in complexes **1**–**3**

Complex 1

Bond	Bond Length / Å	Bond Valence	Bond	Bond Length / Å	Bond Valence
Fe(1)–O(1)	1.886(3)	0.692	Fe(2)–O(5)	2.133(3)	0.319
Fe(1)–O(3)	1.904(3)	0.660	Fe(2)–O(5')	2.133(3)	0.319
Fe(1)–N(1)	1.905(4)	0.575	Fe(2)–O(6)	2.113(3)	0.336
Fe(1)–N(6)	1.901(4)	0.581	Fe(2)–O(6')	2.113(3)	0.336
Fe(1)–N(7)	1.907(4)	0.572	Fe(2)–N(4)	2.153(4)	0.346
Fe(1)–N(12)	1.900(4)	0.582	Fe(2)–N(4')	2.153(4)	0.346
	∑v(Fe) = 3.662			∑v(Fe) = 2.002	

Complex 2

Bond	Bond Length / Å	Bond Valence	Bond	Bond Length / Å
Fe(1)–O(1)	1.896(3)	0.674	Cd(1)–O(5)	2.335(3)
Fe(1)–O(3)	1.917(3)	0.637	Cd(1)–O(6)	2.293(3)
Fe(1)–N(1)	1.921(3)	0.550	Cd(1)–N(4)	2.283(3)
Fe(1)–N(6)	1.914(3)	0.561		
Fe(1)–N(7)	1.919(3)	0.553		
Fe(1)–N(12)	1.912(3)	0.568		
	∑v(Fe) = 3.543			

Complex 3

Bond	Bond Length / Å	Bond Valence	Bond	Bond Length / Å	Bond Valence
Fe(1)–O(1)	1.898(2)	0.670	Fe(2)–O(5)	2.155(2)	0.300
Fe(1)–O(3)	1.887(2)	0.691	Fe(2)–O(5')	2.155(2)	0.300
Fe(1)–N(1)	1.932(2)	0.534	Fe(2)–O(6)	2.126(2)	0.325
Fe(1)–N(6)	1.902(2)	0.579	Fe(2)–O(6')	2.126(2)	0.325
Fe(1)–N(7)	1.925(2)	0.544	Fe(2)–N(4)	2.166(2)	0.334
Fe(1)–N(12)	1.909(2)	0.568	Fe(2)–N(4')	2.166(2)	0.334
	∑v(Fe) = 3.586			∑v(Fe) = 1.918	

Bond Valence = $\exp[(R_0-d_{ij})/b]$, R_0 = 1.70 for Fe(1)–N, 1.75 for Fe(1)–O, 1.76 for Fe(2)–N and 1.71 for Fe(2)–O, b = 0.37.[1]

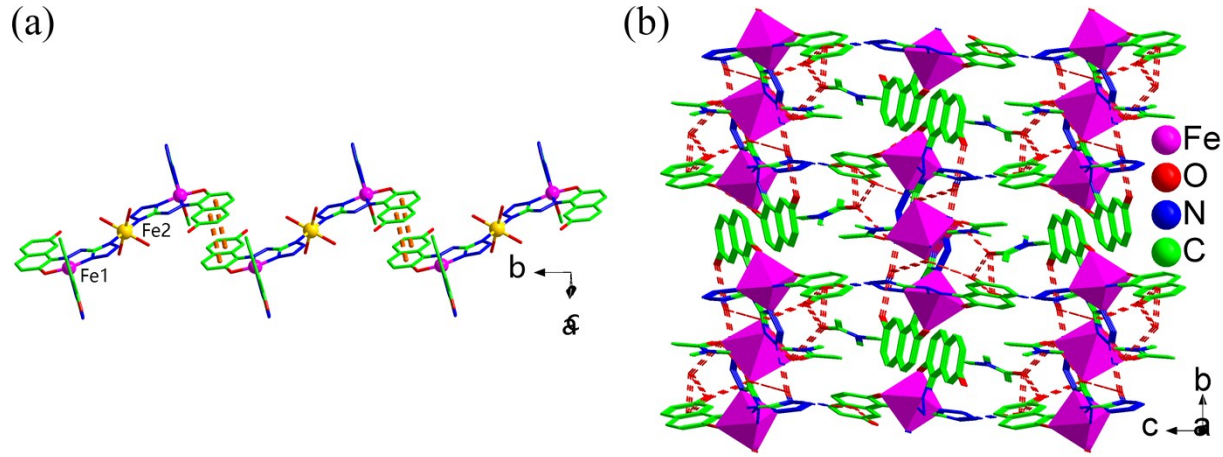

Fig. S1 Crystal packing of 1D chain (a) and 3D supramolecular structure (b) for complex **1** at 100 K. Hydrogen atoms have been omitted for clarity.

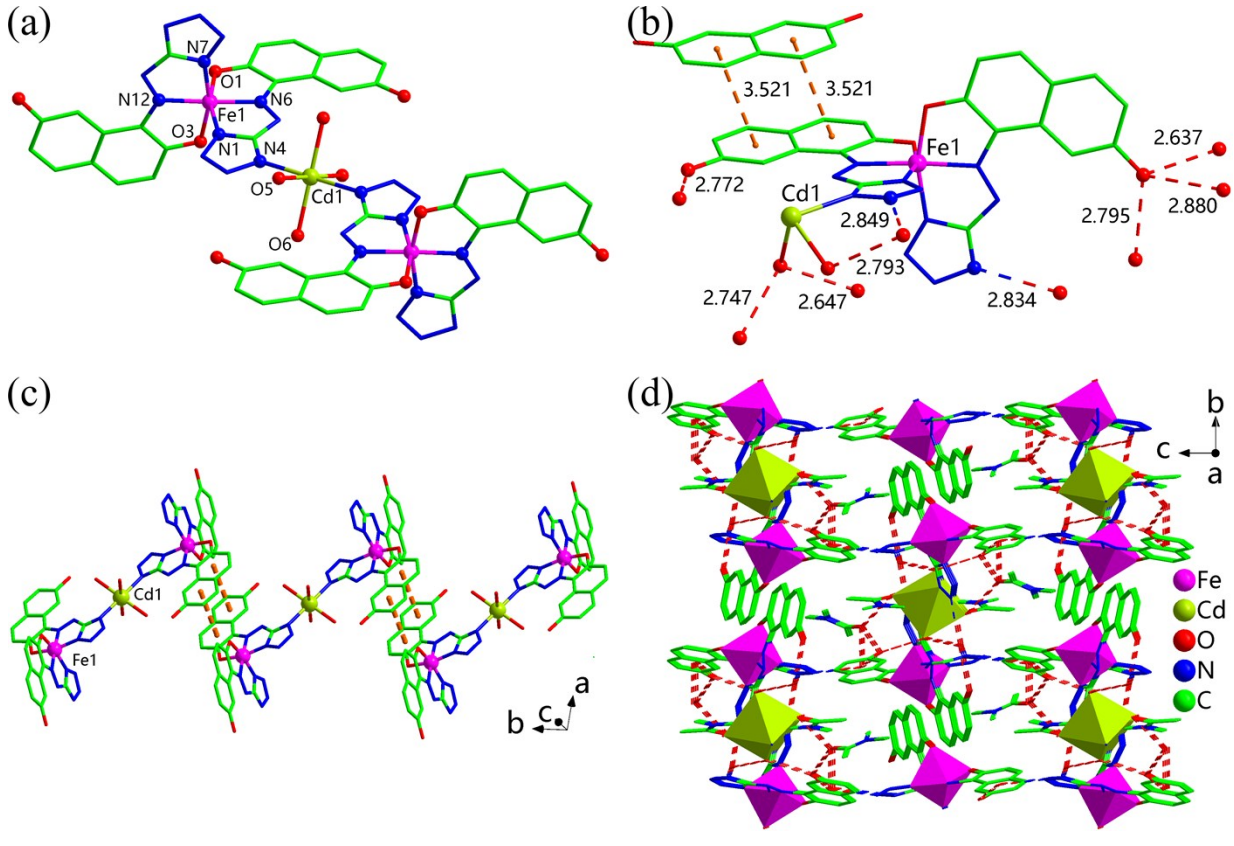

Fig. S2 Structural illustrations of **2**: Coordination environment of Fe and Cd (a); Intermolecular face-to-face π···π and O–H···N and O–H···O hydrogen-bonding interactions (dashed lines, b); Crystal packing of 1D chain (c); 3D supramolecular structure (d). Hydrogen atoms were omitted for clarity.

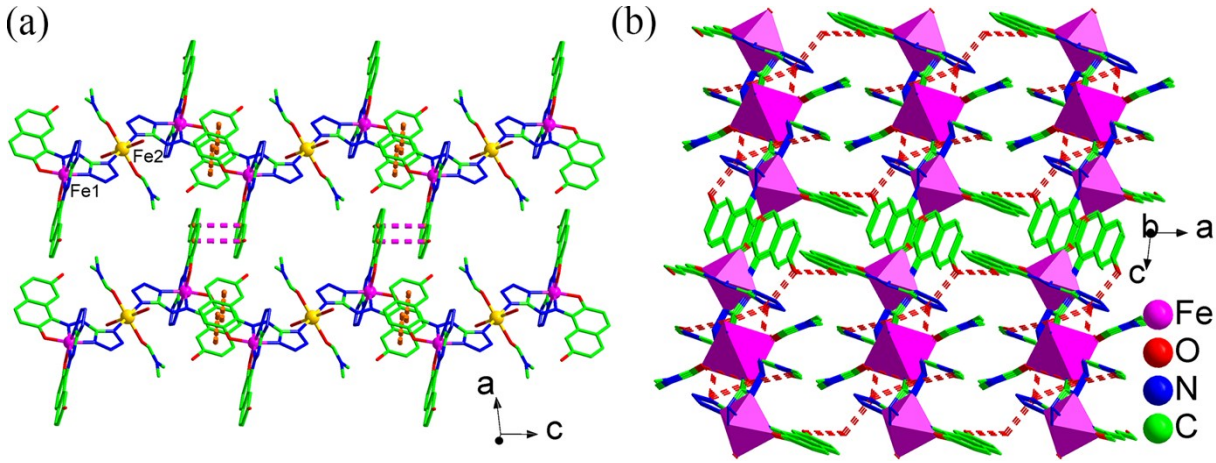

Fig. S3 Crystal packing of 1D chain (a) and 3D supramolecular structure (b) for complex **3** at 100 K. Hydrogen atoms were omitted for clarity.

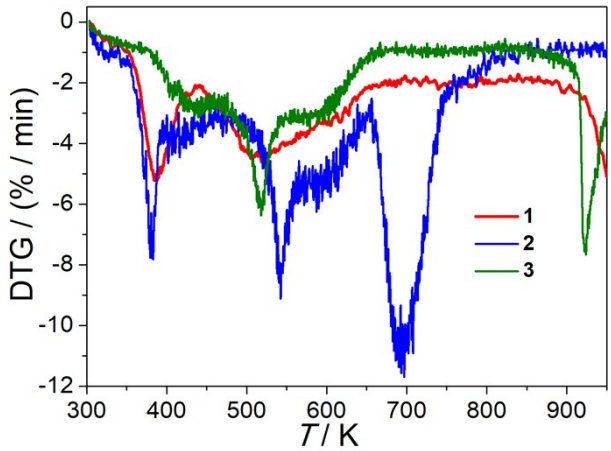

Fig. S4 DSC curves of the thermal analysis for complexes **1**–**3**

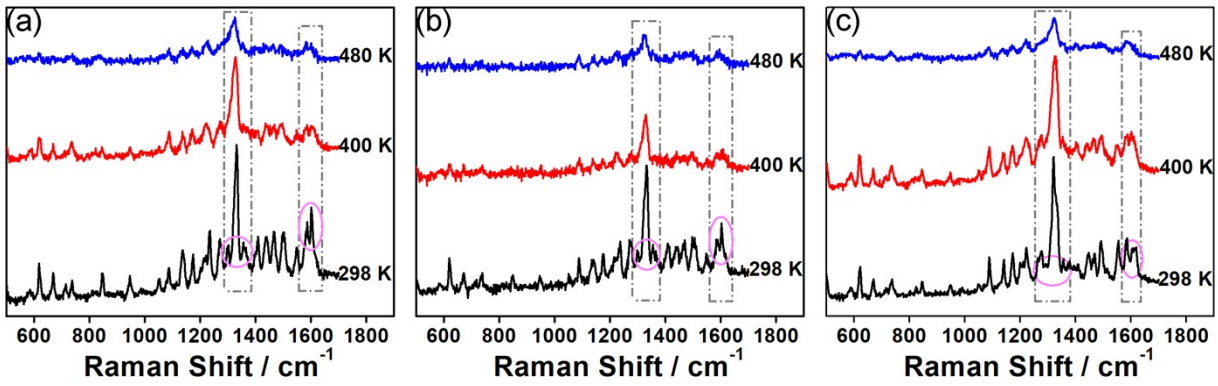

Fig. S5 Solid-state variable-temperature Raman spectra for complexes **1**(a), **2**(b) and **3**(c).

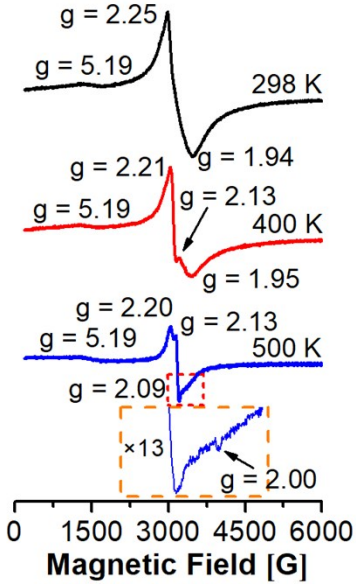

Fig. S6 Solid-state variable-temperature EPR spectra for complex **3**.

References

1 H. Zheng, K. M. Langner, G. P. Shields, J. Hou, M. Kowiel, F. H. Allen, G. Murshudov and W. Minor, *Acta Crystallographica. Section D, Structural biology*, 2017, **73**, 316-325.