Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Heteroleptic Iron(III) Schiff Base Spin Crossover Complexes; Halogen Substitution, Solvent Loss and Crystallite Size Effects

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Figure S 1 The asymmetric unit of a) **3·0.5MeCN**, b) **2** and c) **4**

Figure S 2 The crystal packing of **2·MeCN** and **3·0.5MeCN** at 100 K in 1D chain, double chains along the *c* axis through π-π interactions regarding to thsa. This gives rise to a free hole for MeCN solvents to occupy.

Figure S 3 The packing comparison between **2·MeCN** and **3·0.5MeCN** in 2D via P4AE (Parallel Four Fold Aryl Embrace) interactions[1] showing they are isostructural. The model represents compound **2·MeCN**

Figure S 4 The crystal packing of compound **1·2.5MeCN** at 100 K and related simple models describing interactions that connect the Fe(III) molecules in *pseudo*-three dimensional structure.

Figure S 5 The crystal packing of compound **4·MeCN** at 100 K and related simple models describing interactions that connect the Fe(III) molecules in *pseudo*-three dimensional structure.

Figure S 6 The χ_MT versus T plots for a) **1** slow cooling, powder form; cooling from 270 K black circles; heating back up to 350 K, red triangles; b) heated sample and c) dry in air for 10 days of **2·MeCN**

Figure S 7 PXRD patterns of the compounds in comparison with the simulated PXRD from single crystal data for compound **2·MeCN** in various conditions.

Figure S 8 TGA data for compound a) **1·2.5MeCN**, b) **2·MeCN**, c) **3·MeCN** with 5 $Kmin^{-1}$ rate and d) **4·MeCN** with various heating rate as shown.

Figure S 9 FT-IR spectra of the compounds showing similar pattern between solvate and de-solvate compounds. Free MeCN is observed at 2250 cm^{-1} for fresh compound **1·2.5MeCN**.

Table S 1 Intermolecular interactions in compound **2·MeCN**, **2**, **3·MeCN** and **3·0.5MeCN**

Table S 2 Intermolecular interactions in compound **1·MeCN** at various temperatures

Table S 3 Intermolecular interactions in compound **4·MeCN and 4** at 100 K

Table S 4 Related halogen interactions in each compounds

Table S 5 Mössbauer spectroscopic data of **1·2.5MeCN**.

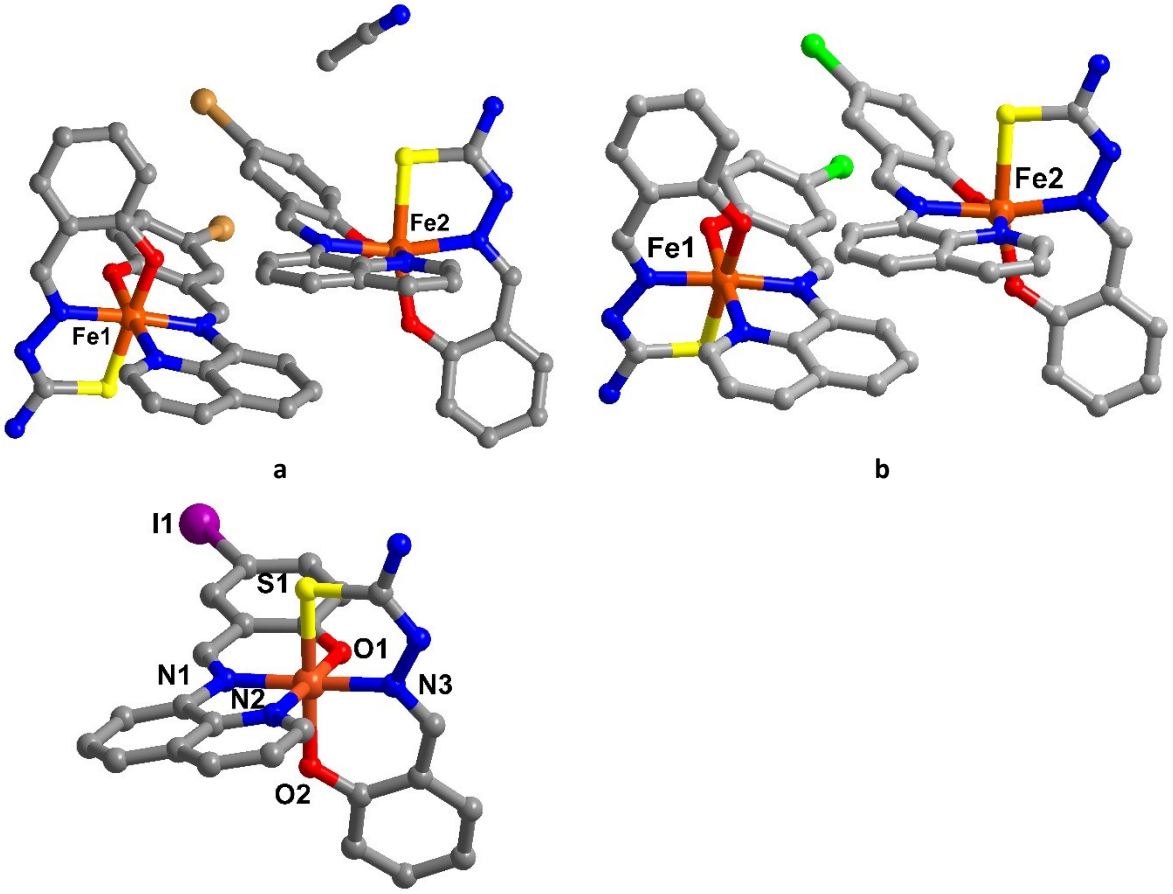
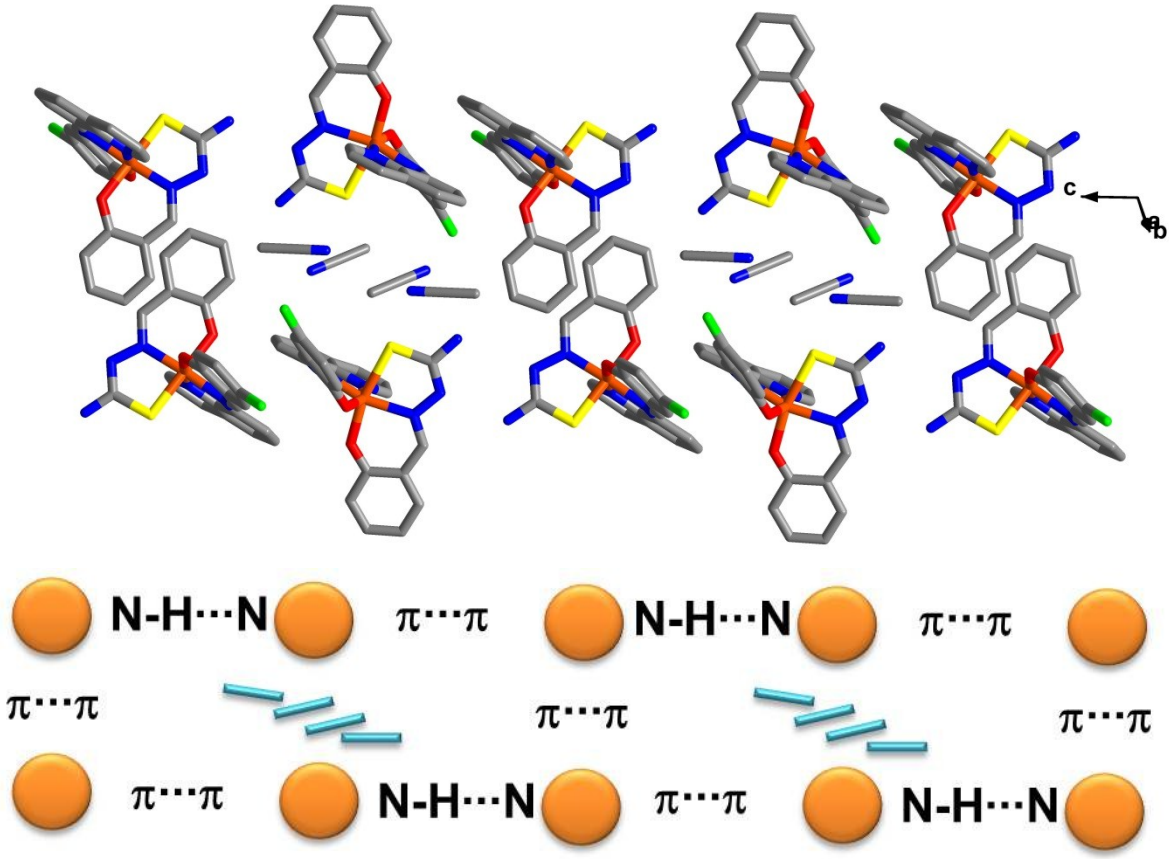


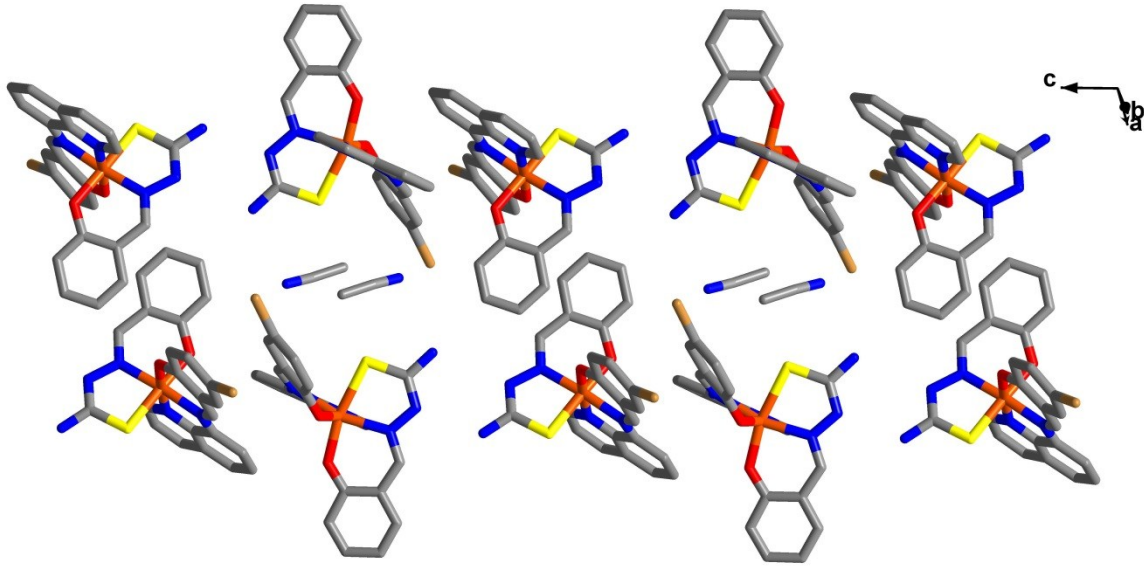
Figure S 1 The asymmetric unit of a) **3·0.5MeCN**, b) **2** and c) **4**

Table S 1 Intermolecular interactions in compound **2·MeCN**, **2**, **3·MeCN** and **3·0.5MeCN**

100 K	**2·MeCN**	**2**	**3·MeCN**	**3·0.5MeCN**
in 1D along the c axis				
π-π	3.716	3.732	3.757	3.764
π-π	3.037	3.022	3.049	3.066
C33-H33···O2	2.363(2)	2.363(2)	2.380(5)	2.402(4)
N5-H5A···N8	2.035(3)	2.012(3)	2.026(6)	2.018(6)
N10-H10A···N4	2.462(2)	2.333(3)	2.480(6)	2.437(5)
diagonal on b plane				
C20-H20···O1	2.694(2)	2.866(2)	2.720(5)	2.740(4)
π-π	3.611	3.790	3.630	3.684
C5-H5···S1	2.949(1)	3.068(1)	2.975(2)	3.026(2)
C7-H7···S1	2.639(1)	2.680(1)	2.652(2)	2.665(2)
C9-H9···S1	2.989(1)	3.044(1)	2.983(2)	3.018(2)
N5-H5B···O3	2.198(2)	2.269(2)	2.205(5)	2.234(4)
along the a axis				
C11-H11···X2	2.930(1)	2.998(1)	2.957(1)	2.987(1)
C43-H43···X1	2.889(1)	2.802(1)	2.969(1)	2.930(1)
P4AE Fe1-Fe1				
C13-H13···π	3.070	3.086	3.116	3.081
π-π	3.154	3.167	3.122	3.160
P4AE Fe2-Fe2				
C37-H37···π	3.275	3.273	3.259	3.235
π-π	3.368	3.339	3.333	3.323
interaction to solvent				
N10-H10B···N11	2.636(4)	-	2.615(10)	2.627(14)
C18-H18···N11	2.551(3)	-	2.580(9)	2.572(11)
C50-H50A···S2	2.971(1)	-	3.017(2)	2.986(2)
C50-H50A···π	2.741	-	2.804	2.704
C50-H50B···N12	2.688(7)	-	2.712(20)	-
C39-H39···N12	2.685(6)	-	2.693(17)	-



[Fe(qsal-Cl)(thsa)]·MeCN, **2·MeCN** at 100 K (isostructural with **3·MeCN**)

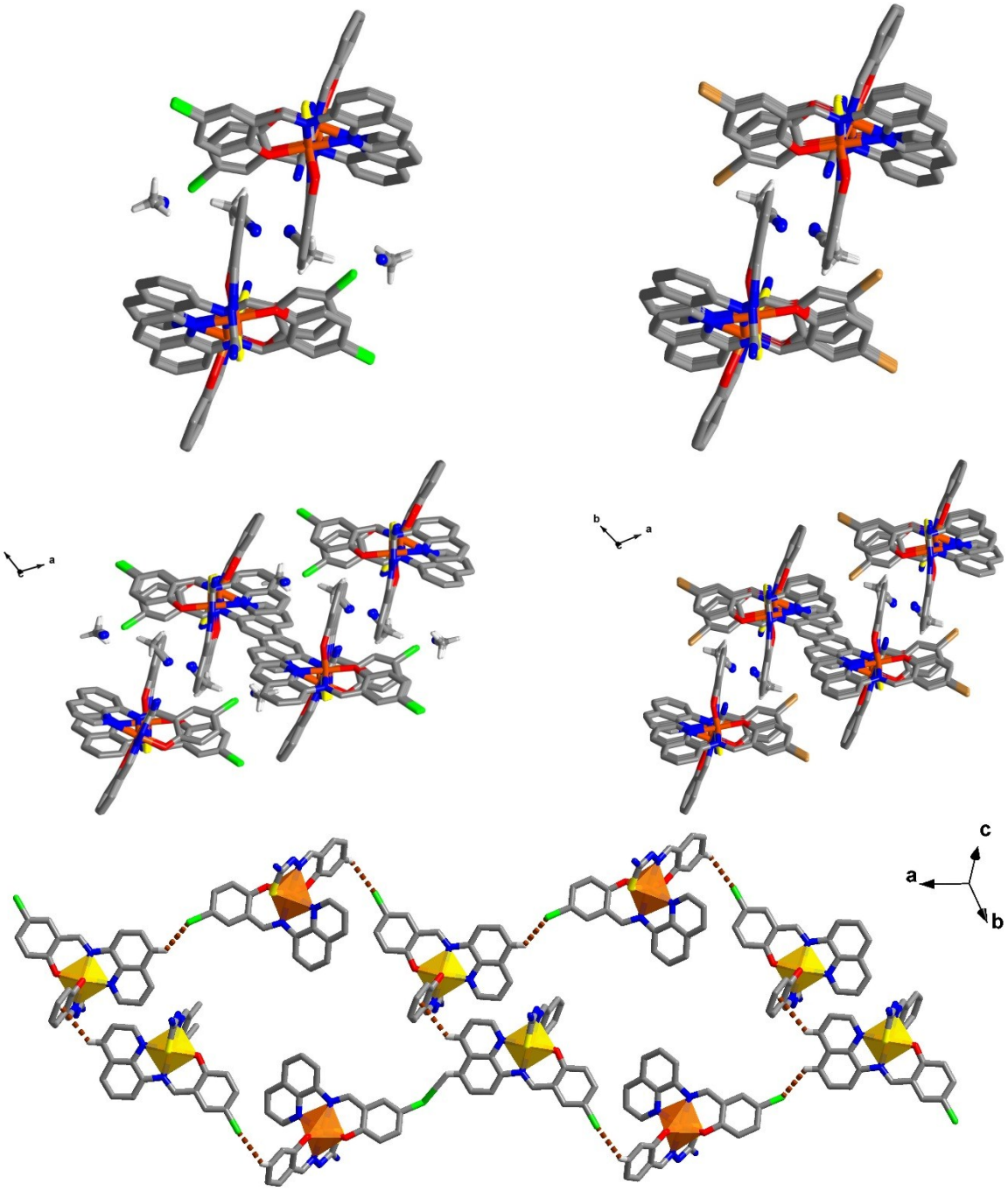


[Fe(qsal-Br)(thsa)]·0.5MeCN, **3·0.5MeCN** at 100 K

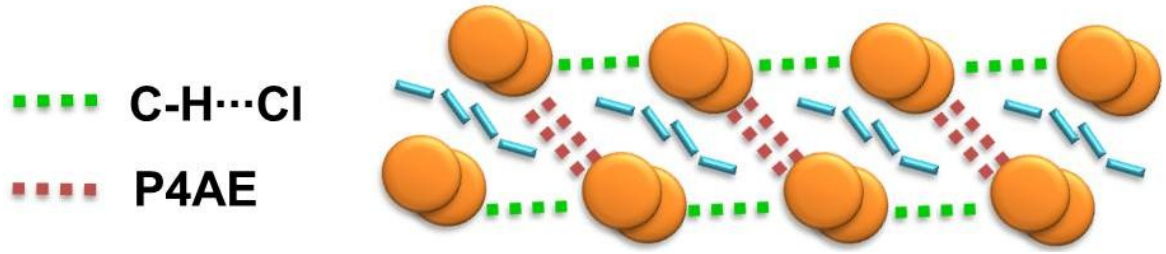
Figure S 2 The crystal packing of **2·MeCN** and **3·0.5MeCN** at 100 K in 1D chain, double chains along the *c* axis through π-π interactions regarding to thsa. This gives rise to a free hole for MeCN solvents to occupy.

X = Cl, **2·MeCN**

X = Br, **3·0.5MeCN**



C-H···Cl



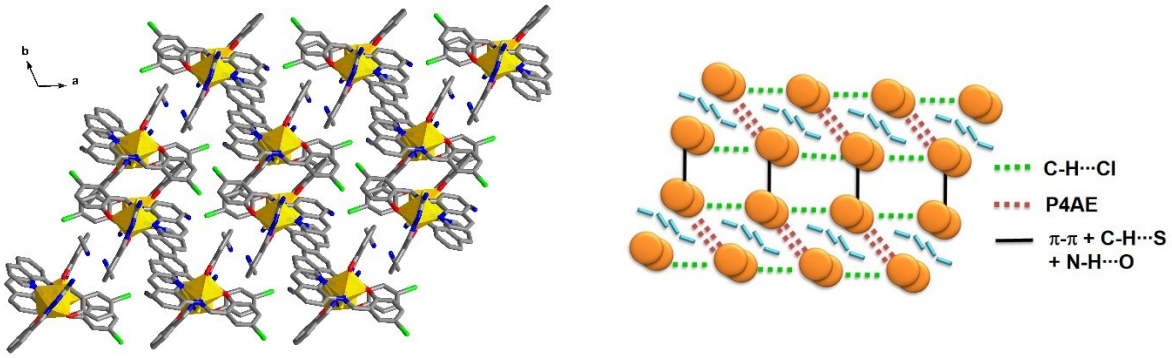
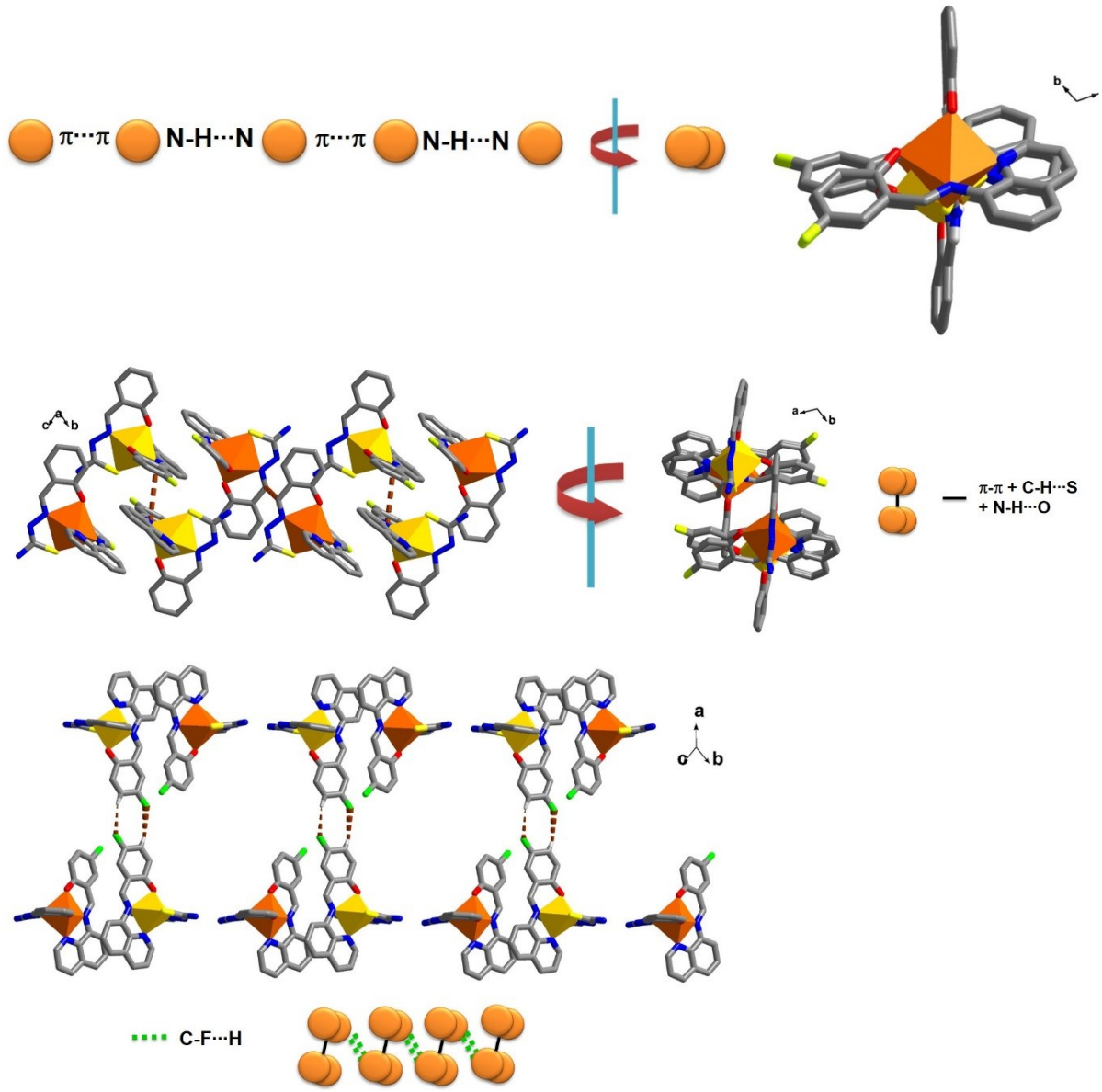


Figure S 3 The packing comparison between **2·MeCN** and **3·0.5MeCN** in 2D via P4AE (Parallel Four Fold Aryl Embrace) interactions[1] showing they are isostructural. The model represents compound **2·MeCN.**



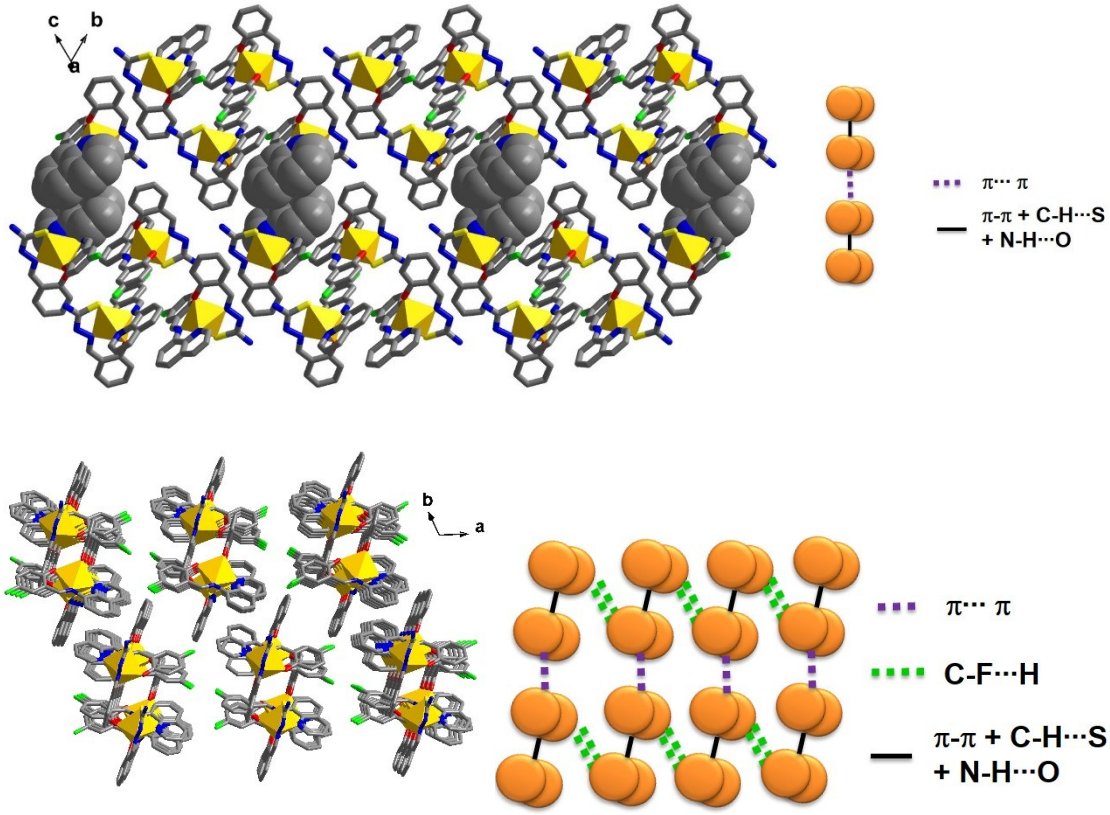
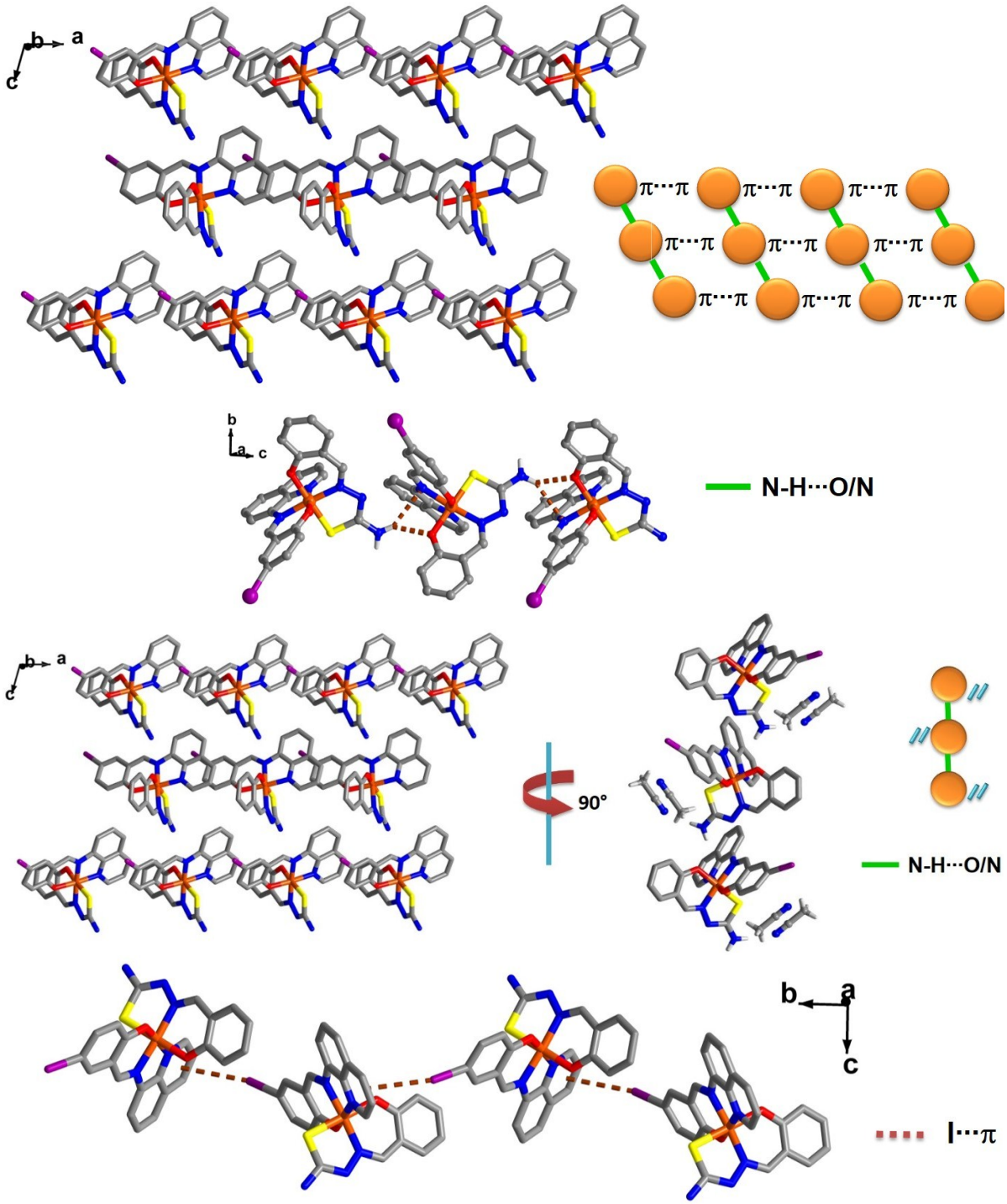


Figure S 4 The crystal packing of compound **1·2.5MeCN** at 100 K and related simple models describing interactions that connect the Fe(III) molecules in *pseudo*-three dimensional structure.

Table S 2 Intermolecular interactions in compound **1·2.5MeCN** at various temperatures

	270 K	**160 K**	**295 K**	**320 K**	**100 K**
In 1D chain along diagonal on *bc* plane					
π-π	3.513	3.512	3.516	3.519	3.498
C33-H33···O2	2.525(1)	2.489(1)	2.526(1)	2.538(1)	2.507(1)
C9-H9···O4	2.754(1)	2.698(1)	2.767(1)	2.779(1)	2.693(1)
N5-H5A···N8	2.126(1)	2.075(1)	2.132(1)	2.133(1)	2.070(1)
N10-H10A···N4	2.249(1)	2.228(1)	2.253(1)	2.266(1)	2.225(1)
C42-H42···O1	2.647(1)	2.596(1)	2.670(1)	2.701(1)	2.610(1)
π-π	3.345	3.294	3.359	3.369	3.251
π-π	3.648	3.640	3.645	3.643	3.631
C5-H5···S1	2.970(1)	2.928(2)	2.971(1)	2.983(1)	2.914(1)
C7-H7···S1	2.809(1)	2.762(2)	2.814(1)	2.820(1)	2.748(1)
N5-H5B···O3	2.246(1)	2.219(1)	2.248(1)	2.244(1)	2.187(1)
Diagonal on *a* axis					
C4-F1···H3	2.535(1)	2.548(1)	2.537(1)	2.541(1)	2.553(1)
Diagonal on *bc* plane					
π-π	3.539	3.503	3.542	3.551	3.534


b
a
c
π···π
N-H···O/N
90°
N-H···O/N
I···π

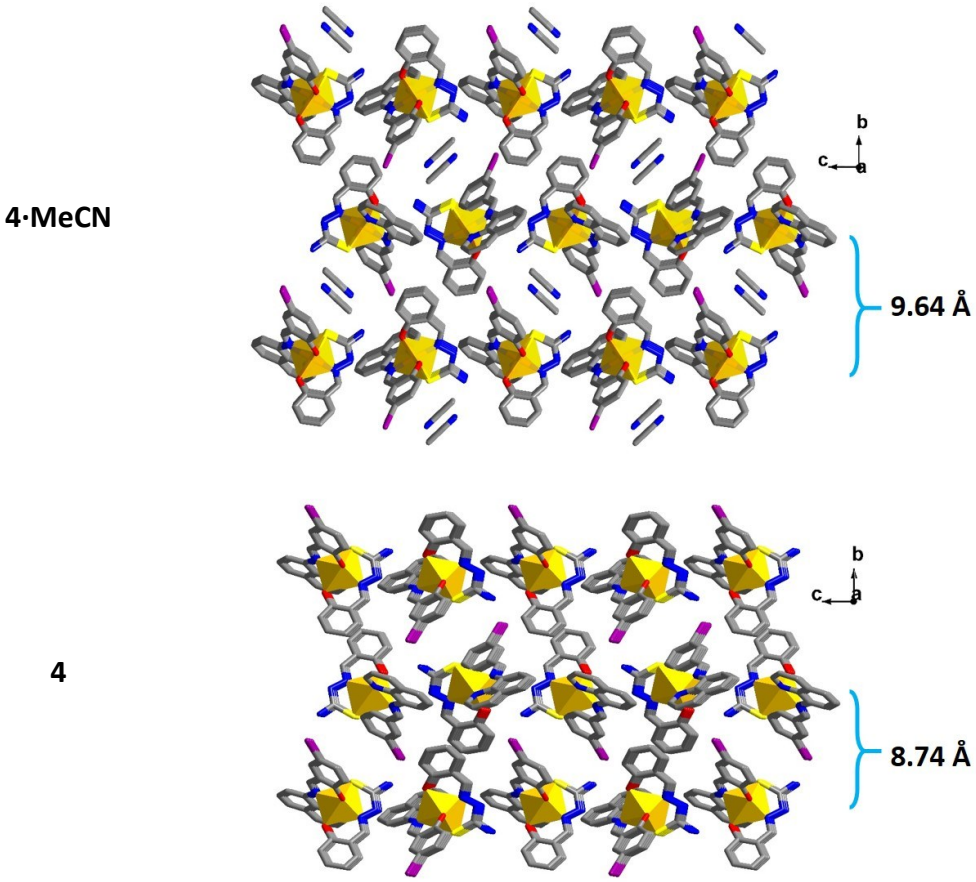
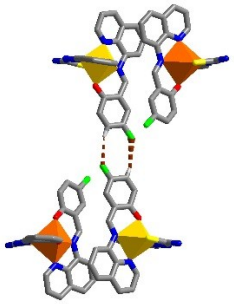
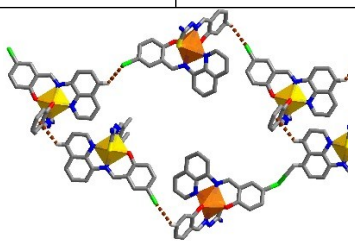
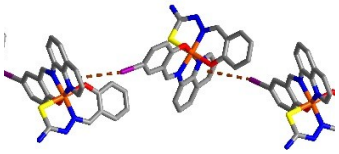
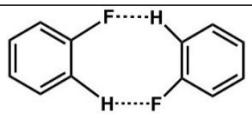
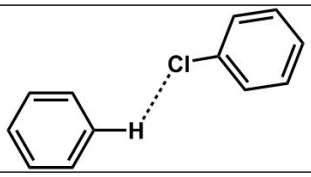


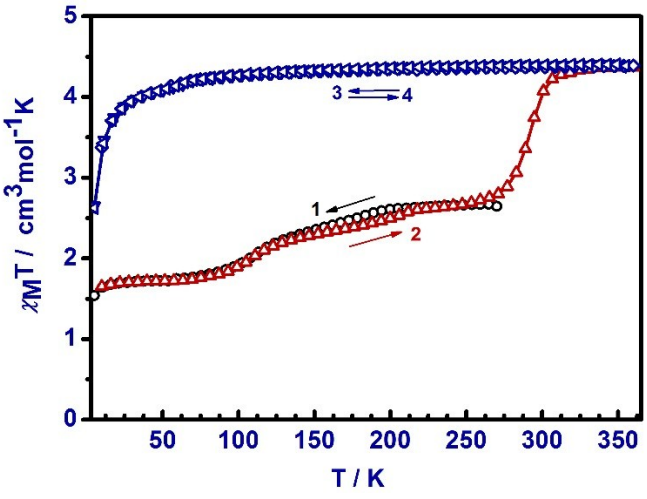
Figure S 5 The crystal packing of compound **4·MeCN** at 100 K and related simple models describing interactions that connect the Fe(III) molecules in *pseudo*-three dimensional structure.

Table S 3 Intermolecular interactions in compound **4·MeCN and 4** at 100 K

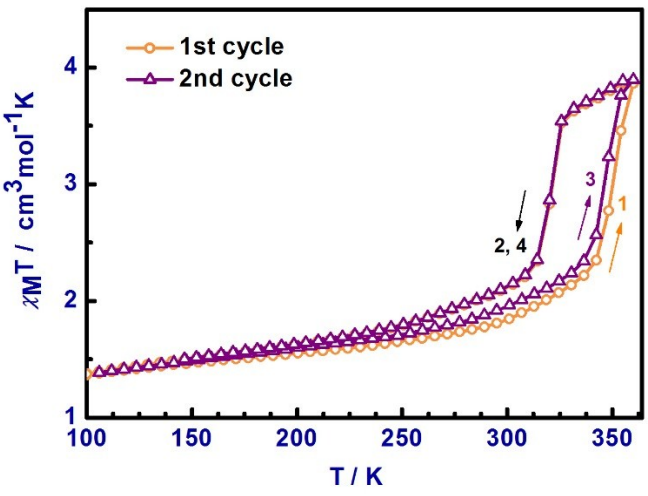
	4·MeCN	**4**
In 1D along the a axis		
π-π	3.364	3.372
C3-H3···S1	2.834(4)	2.890(1)
C14-H14···π	2.606	2.571
In 1D along the c axis		
N5-H5A···O2	2.274(8)	2.269(1)
N5-H5A···N1	2.727(9)	(2.959(1))
C18-H18···N5	(2.836(12))	2.629(1)
C11-H11···N4	2.554(11)	2.668(1)
along the b axis		
π-π	3.673	3.624
C4-I1···π	3.637	3.628
MeCN interactions		
N5-H5B···N6	2.159(20)	-
C26-H26C···S1	2.976(4)	-

Table S 4 Related halogen interactions in each compounds

Comp	X = F, 1·2.5MeCN	X = Cl, 2·MeCN	X = Br, 3·MeCN	X = I, 4·MeCN
interactions	C-F···H	C-Cl···H	C-Br···H	C-I···π
				
Model				



a



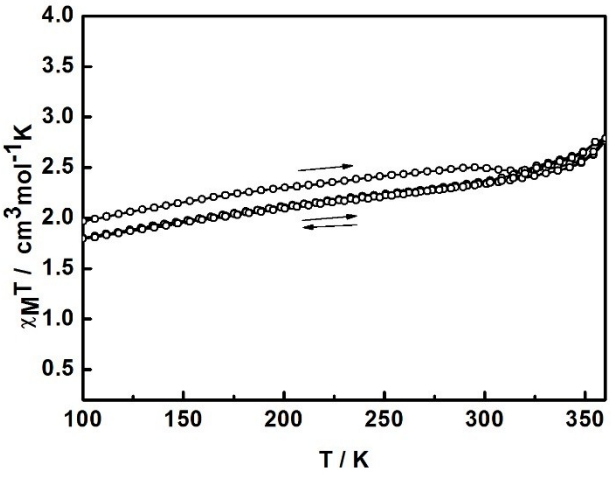
Cycle	$T_{1/2}\uparrow$/K	$T_{1/2}\downarrow$/K
1	349	320
2	345	320

$$\%\ SCO\ = \frac{\chi MTmax - \chi MTmin}{4.375 - \ 0.375\ (ideal\ \chi MT\ value\ for\ HS\ and\ LS, respectively)}$$

$$\%\ SCO\ for\ heated\ powder\ of\ 2 = \frac{3.86 - 1.5}{4} = 59\%$$

$$\%\ SCO\ for\ heated\ crystal\ of\ 2 = \frac{2.75 - 1.5}{4} = 31\%$$

b



c

Figure S 6 The χ_MT versus T plots for a) **1·2.5MeCN** slow cooling, powder form; cooling from 270 K black circles; heating back up to 350 K, red triangles; b) heated sample and c) dry in air for 10 days of **2·nMeCN** (n<0.1)

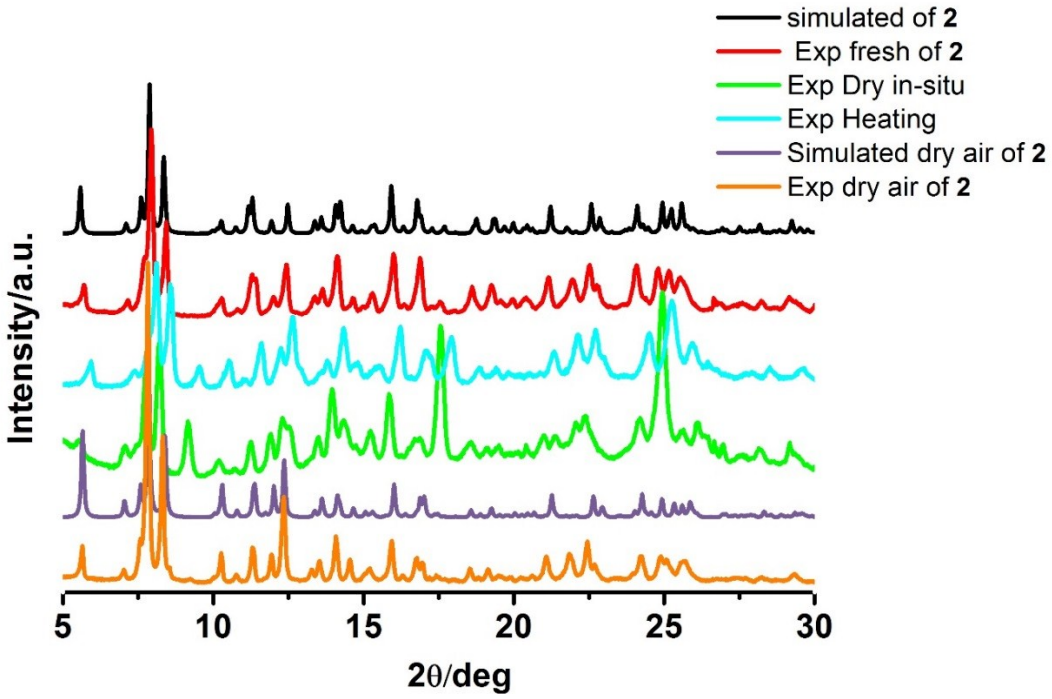


Figure S 7 PXRD patterns of the compounds in comparison with the simulated PXRD from single crystal data for compound **2·MeCN** in various conditions. (Note label **2** in the picture is compound **2·MeCN**)

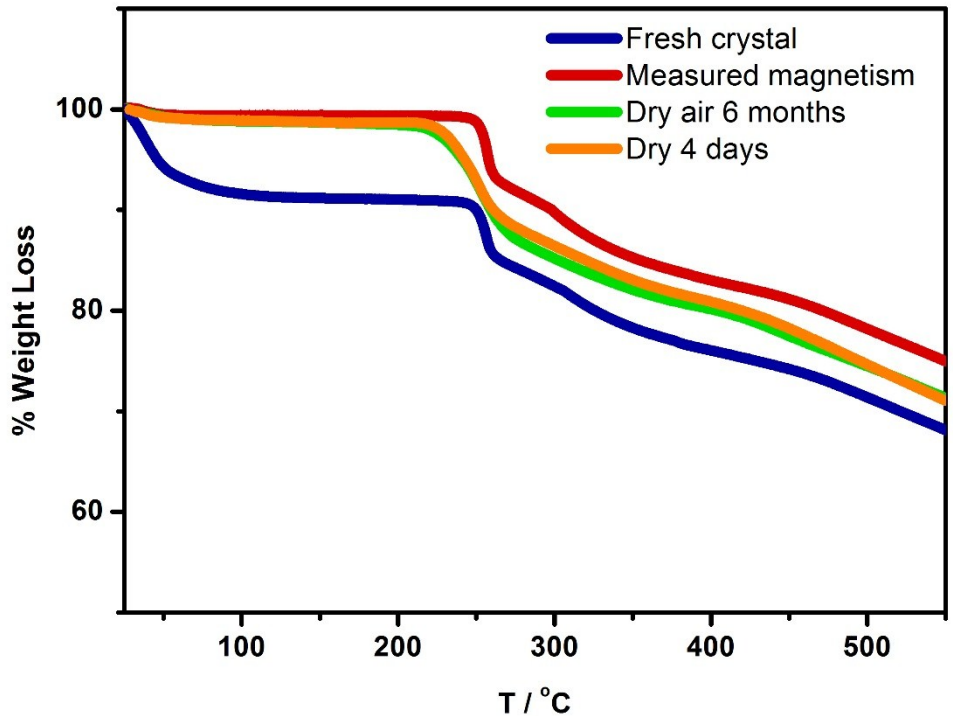
Table S 5 Mössbauer spectroscopic data of **1·2.5MeCN**.

T (K)	Species	δ (mm/s)	ΔE_Q (mm/s)	$\Gamma_{L(R)}$ (mm/s)	I (%)
5.5	LS	0.23	2.81	0.33(0.27)	62
	HS	0.52	0.90	0.90[a](0.57)	38
160	LS	0.20	2.80	0.27(0.25)	54
	HS	0.48	0.91	0.68(0.54)	46
295					
(0-2.5 days)	LS	0.14	2.69	0.33(0.28)	49
	HS	0.41	0.84	0.63(0.63)	51
295[b]					
(2.5-5.5 days)	LS	0.15	2.68	0.35(0.32)	31
	HS	0.41	0.83	0.50(0.49)	69
Desolvated (1) (heated for 120 min at 330 K)					
5.4	LS	0.24	2.74	0.37(0.28)	33
	HS	0.54	0.89	0.45	67

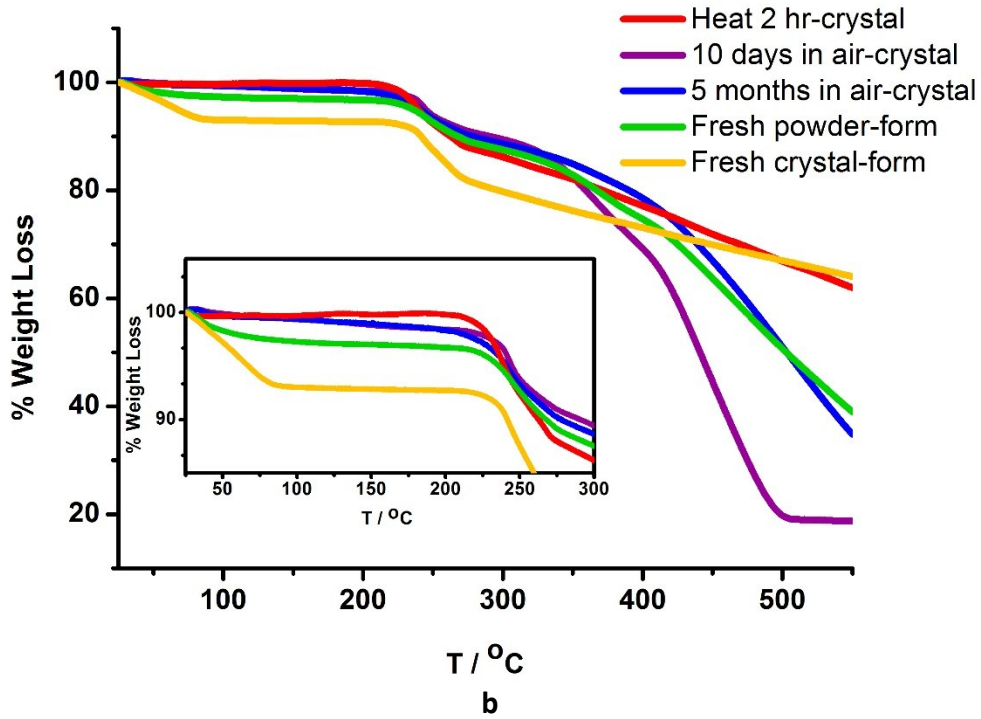
295	LS	-	-	-	-
	HS	0.42	0.84	0.38(0.39)	100

[a] very broad

[b] 2.5-5.5 day spectrum is made by subtracting the 2.5 day spectrum from the 5.5 day spectrum.


Fresh crystal
Measured magnetism
Dry air 6 months
Dry 4 days
% Weight Loss
100
80
60
100
200
300
400
500
T / °C

a


Heat 2 hr-crystal
10 days in air-crystal
5 months in air-crystal
Fresh powder-form
Fresh crystal-form
% Weight Loss
100
80
60
40
20
100
200
300
400
500
T / °C
% Weight Loss
100
90
50
100
150
200
250
300
T / °C

b

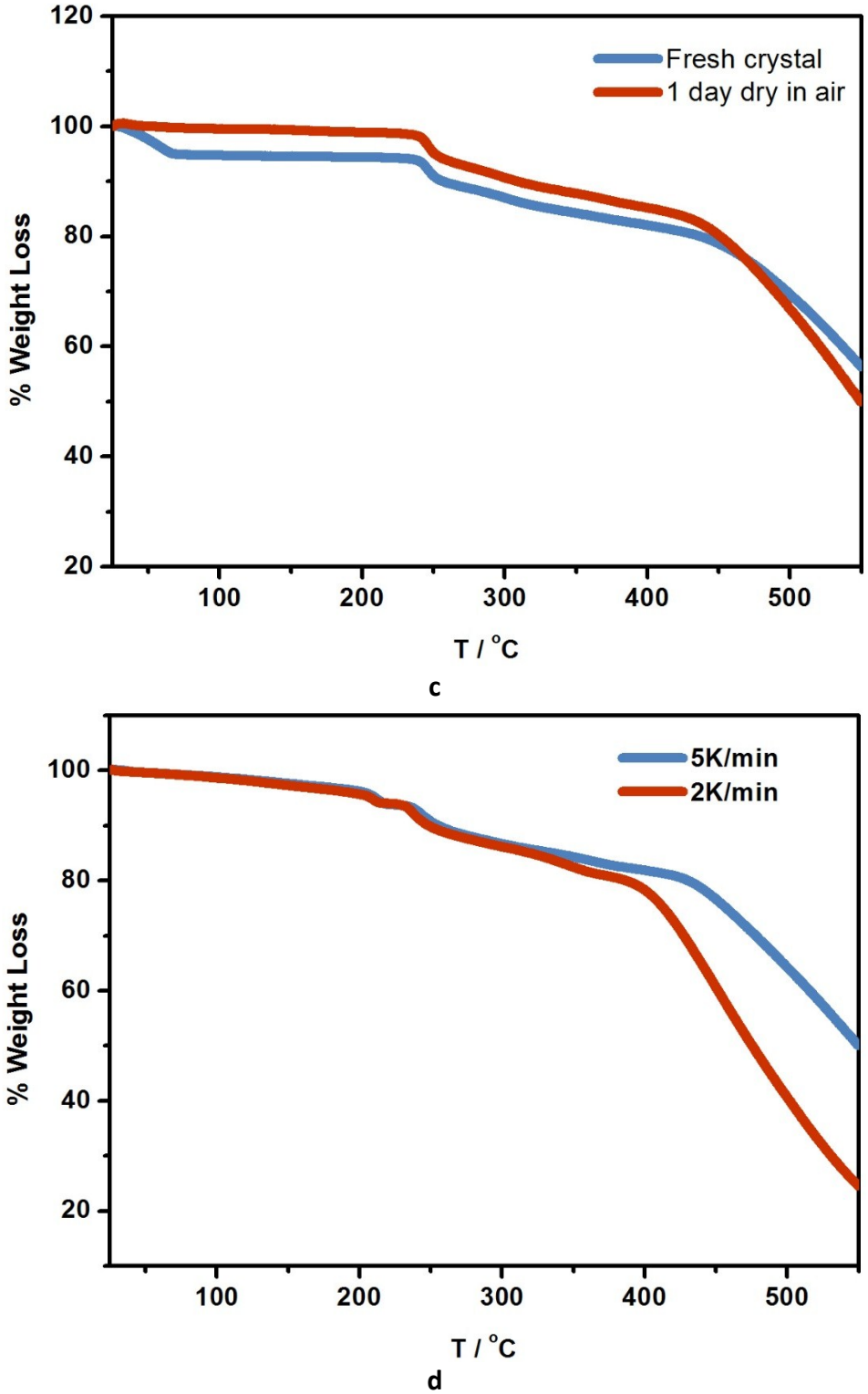


Figure S 8 TGA data for compound a) **1·2.5MeCN**, b) **2·MeCN**, c) **3·MeCN** with 5 $Kmin^{-1}$ rate and d) **4·MeCN** with various heating rate as shown.

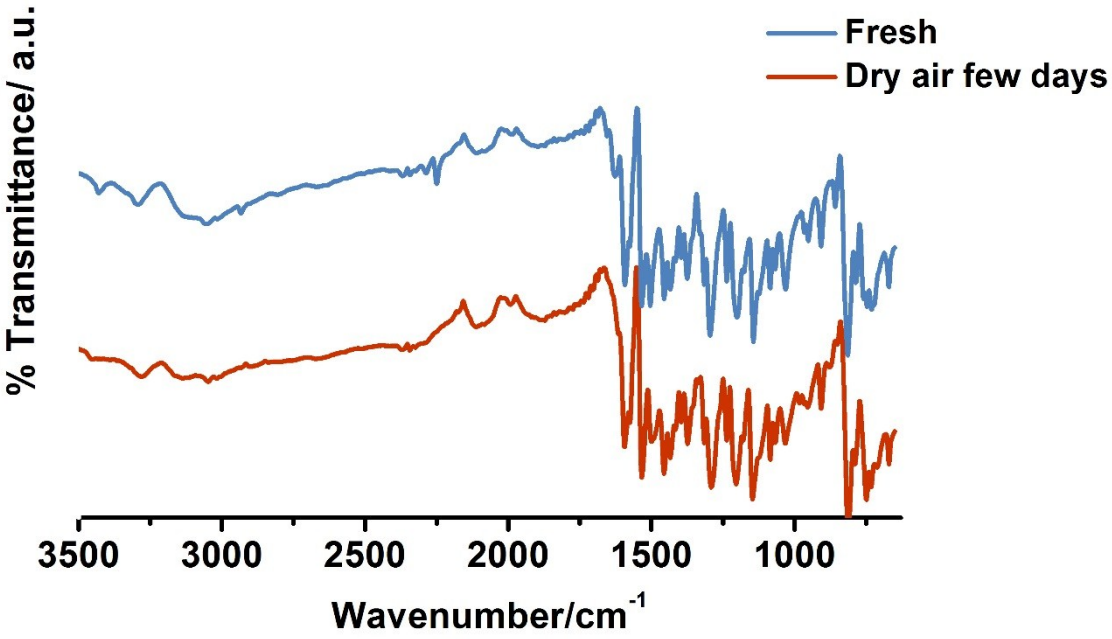


Figure S 9 FT-IR spectra of the compounds showing similar pattern between solvate and de-solvate compounds. Free MeCN is observed at 2250 cm^{-1} for fresh compound **1·2.5MeCN**.

References

1. V. Russell, M. Scudder and I. Dance, *J. Chem. Soc., Dalton Trans.*, 2001, 789-799.