Supporting Information

Spin-state switching sublimable complexes of the {$Fe^{II}(L)[(H_2B(pz)_2]_2$}-type prepared as bulk and thin films. Resistive sensing of spin crossover in graphene based devices.

Figure S1. (a) Thermal analysis of **1·CH_3CN**. (b) Comparison of calculated and experimental XRPD for **1·CH_3CN** and its desolvated form **1**.

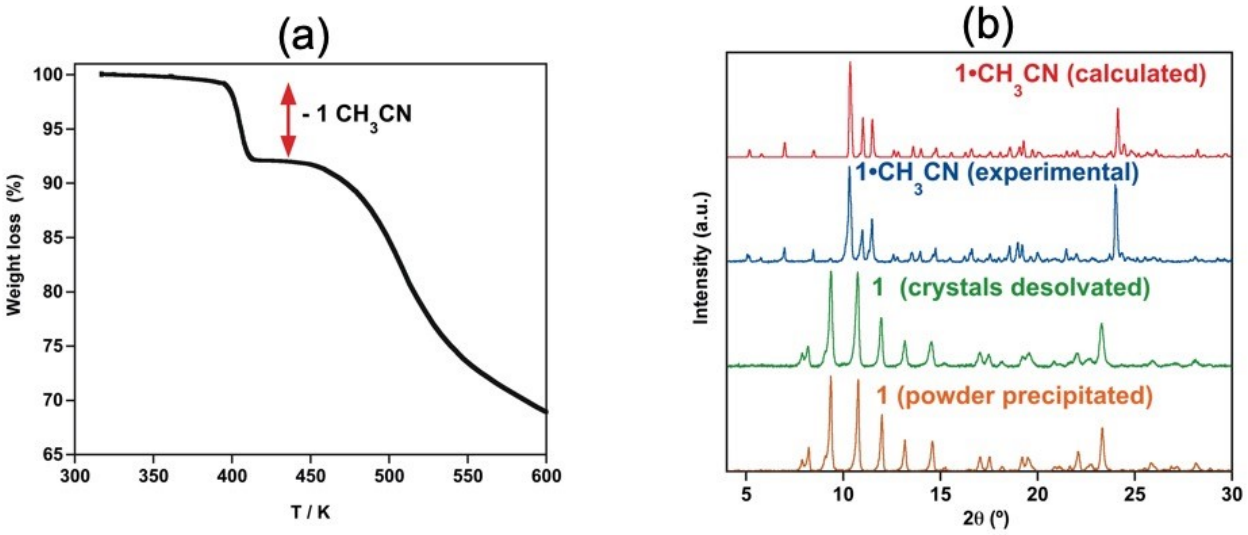

Figure S2. Thermal analysis of **3·1/2CH_2Cl_2**.

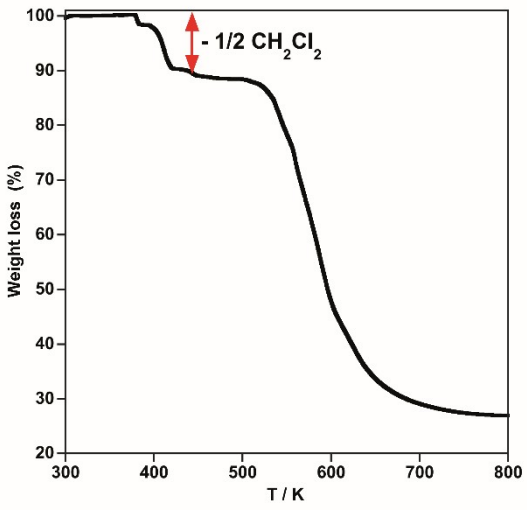

Figure S3. Molecular unit of **1·CH$_3$CN**, site Fe(2).

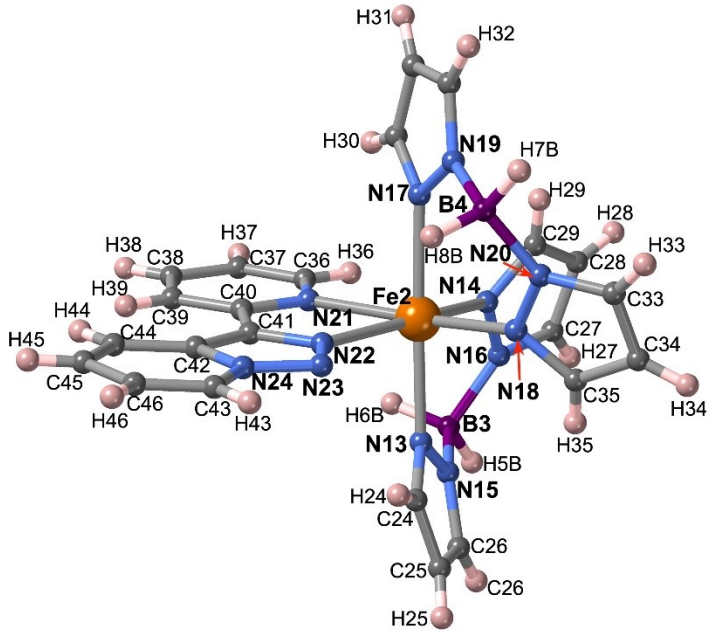

Figure S4. Short intermolecular contacts for **2** (see also Table S8).

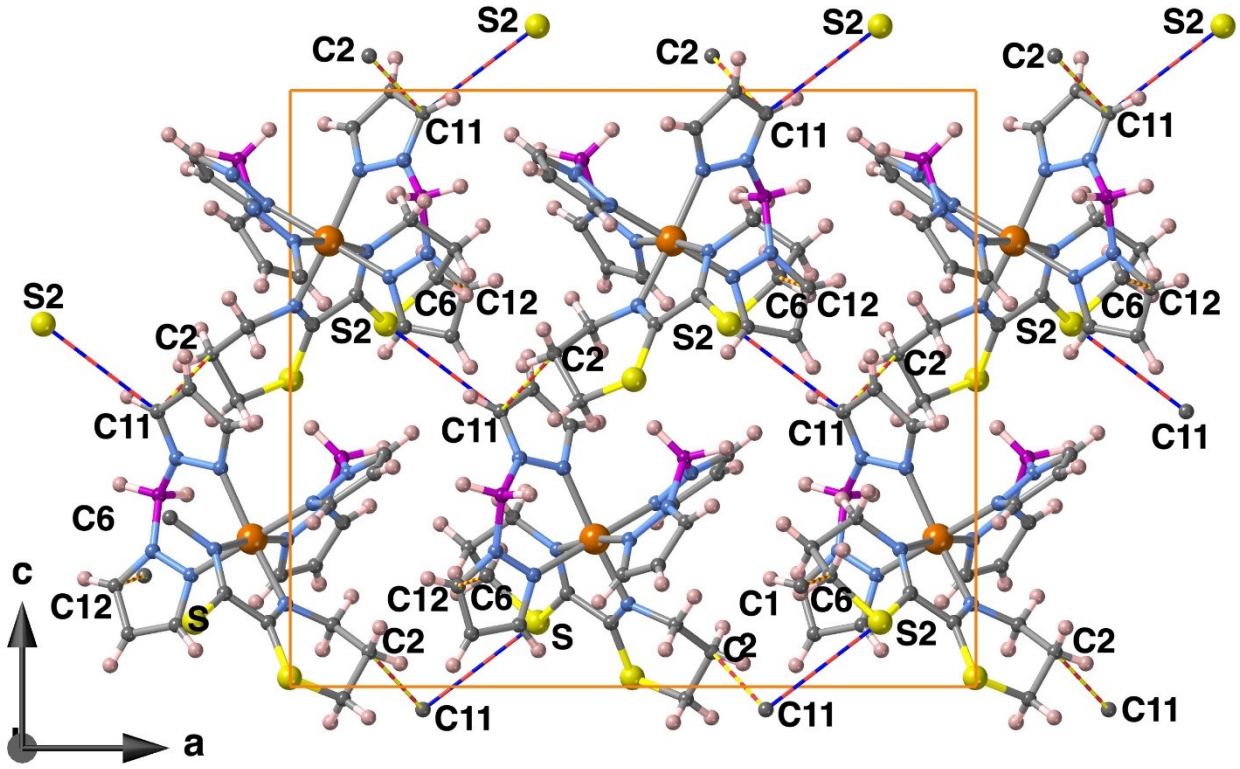

Figure S5. Crystal packing of **3·1/2CH_2Cl_2** (a) and **3** (see also Table S8).

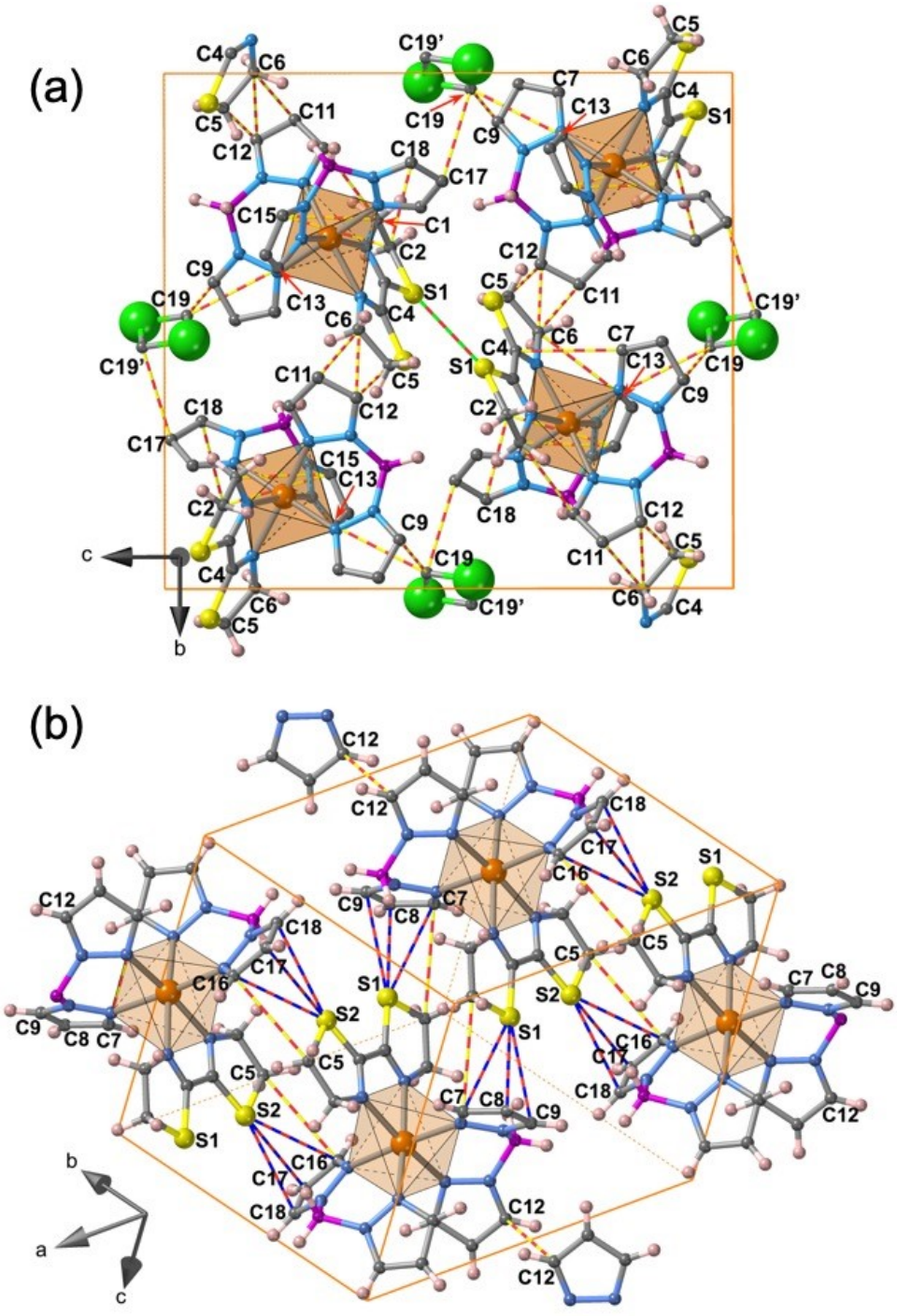

Figure S6. Thickness profiles of a) **TF1** and b) **TF2** integrated onto CVD-graphene devices before and after the performance of the variable temperature resistance measurements. For the collection of this data the measurements were performed at the edge of the chip were a step (thickness) of the film was measurable without requiring to scratch the surface and possibly damaging the device.

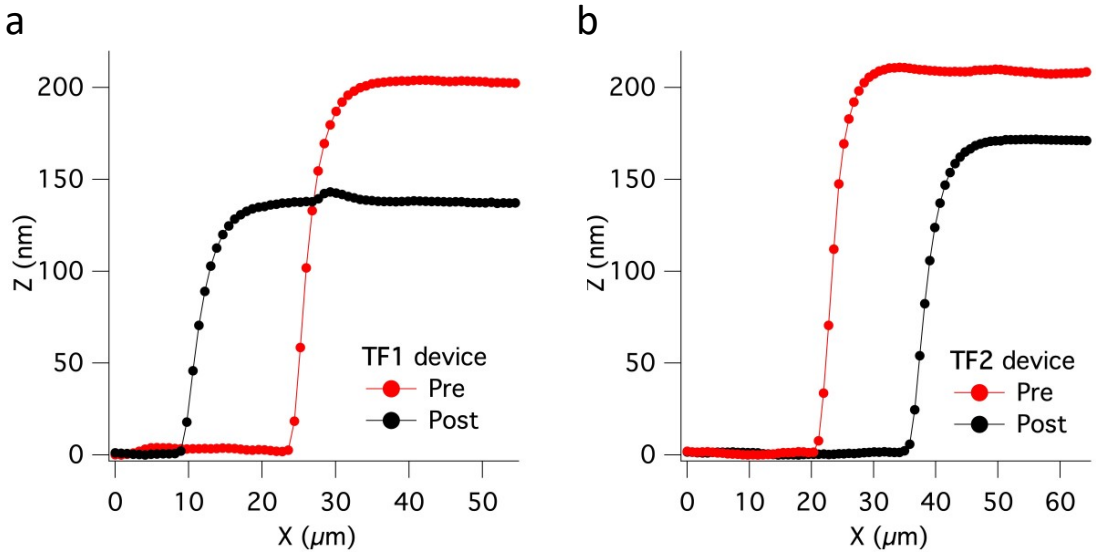

Table S1. Crystal data for **1·CH$_3$CN**.

Temperature	**110**	**250**
Empirical formula	$C_{50}H_{54}B_4N_{26}Fe_2$	
*M*r	1174.13	
Crystal system	triclinic	
Space group	P-1	
a (Å)	10.5203(7)	10.7212(5)
b (Å)	15.3115(12)	15.5314(5)
c (Å)	17.3899(15)	17.7152(8)
α (°)	100.531(7)	100.829(3)
β (°)	100.180(6)	100.994(4)
γ (°)	90.406(6)	90.462(3)
V (Å^3)	2708.4(4)	2841.2(2)
Z	2	
D_c (mg cm^{-3})	1.440	1.372
F(000)	1216	
μ (Mo-K$_\alpha$) (mm^{-1})	0.600	0.572
Crystal size (mm)	0.10x0.10x0.20	
No. of total reflections	13689	14315
No. of reflections [$I>2\sigma(I)$]	8291	8320
R [$I>2\sigma(I)$]	0.1239	0.0586
wR [$I>2\sigma(I)$]	0.2999	0.1252
S	1.061	0.889

$R_1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo|$; $wR = [\, \Sigma \, [w(Fo^2 - Fc^2)^2] \, / \, \Sigma \, [w(Fo^2)^2]]^{1/2}$.
$w = 1/ \, [\sigma^2(Fo^2) + (m \, P)^2 + n \, P]$ where $P = (Fo^2 + 2Fc^2) \, / \, 3$;
m = 0.1571 (**1**) and 0.0758 (**2**);
n = 14.6219 (**1**) and 1.4299 (**2**)

Table S2. Selected bond lengths [Å] and angles [°] for **1·CH_3CN**.

	110 K	**250 K**
Fe(1)-N(1)	2.002(5)	2.137(3)
Fe(1)-N(2)	2.040(6)	2.190(3)
Fe(1)-N(5)	2.029(6)	2.145(3)
Fe(1)-N(6)	2.014(6)	2.182(3)
Fe(1)-N(9)	2.026(6)	2.250(3)
Fe(1)-N(10)	1.997(6)	2.221(2)
Fe(2)-N(13)	2.062(6)	2.170(3)
Fe(2)-N(14)	2.036(6)	2.158(3)
Fe(2)-N(17)	2.082(6)	2.187(3)
Fe(2)-N(18)	2.038(6)	2.134(3)
Fe(2)-N(21)	2.090(6)	2.231(3)
Fe(2)-N(22)	2.041(6)	2.241(3)
N(1)-Fe(1)-N(2)	90.4(2)	86.91(11)
N(1)-Fe(1)-N(5)	88.7(2)	95.15(10)
N(1)-Fe(1)-N(6)	87.0(2)	88.54(11)
N(1)-Fe(1)-N(9)	177.5(2)	173.06(10)
N(1)-Fe(1)-N(10)	98.7(2)	102.54(10)
N(2)-Fe(1)-N(5)	89.9(2)	94.11(11)
N(2)-Fe(1)-N(6)	177.0(2)	174.41(10)
N(2)-Fe(1)-N(9)	87.7(2)	87.72(10)
N(2)-Fe(1)-N(10)	91.7(2)	91.59(10)
N(5)-Fe(1)-N(6)	91.6(2)	89.52(11)
N(5)-Fe(1)-N(9)	93.0(2)	89.62(10)
N(5)-Fe(1)-N(10)	172.4(2)	161.69(11)
N(6)-Fe(1)-N(9)	94.8(2)	96.56(10)
N(6)-Fe(1)-N(10)	87.1(2)	86.23(10)
N(9)-Fe(1)-N(10)	79.7(2)	73.21(9)
N(13)-Fe(2)-N(14)	90.6(2)	89.52(11)
N(13)-Fe(2)-N(17)	175.0(2)	177.20(11)
N(13)-Fe(2)-N(18)	87.0(2)	89.61(11)
N(13)-Fe(2)-N(21)	97.0(2)	94.74(10)
N(13)-Fe(2)-N(22)	87.5(2)	86.15(10)
N(14)-Fe(2)-N(17)	92.3(2)	91.44(10)
N(14)-Fe(2)-N(18)	91.3(2)	94.43(10)
N(14)-Fe(2)-N(21)	89.9(2)	93.62(10)
N(14-Fe(2)-N(22)	167.5(3)	165.93(10)
N(17)-Fe(2)-N(18)	88.9(2)	87.70(10)
N(17)-Fe(2)-N(21)	87.1(2)	87.82(10)
N(17)-Fe(2)-N(22)	90.6(2)	93.53(10)
N(18)-Fe(2)-N(21)	175.9(2)	170.89(10)
N(18)-Fe(2)-N(22)	101.0(2)	98.92(9)
N(21)-Fe(2)-N(22)	78.1(2)	73.45(9)

Table S3. Crystal data for **2**.

Temperature	**120 K**	**240 K**
Empirical formula	$C_{20}H_{28}B_2N_{10}S_2Fe$	
*M*r	550.11	
Crystal system	orthorhombic	
Space group	$Pna2_1$	
a (Å)	17.5600(9)	18.9537(6)
b (Å)	9.3009(3)	9.1407(3)
c (Å)	15.2714(6)	15.2247(4)
V (Å^3)	2494.2(2)	2637.68(14)
Z	4	
D_c (mg cm^{-3})	1.465	1.385
F(000)	1144	
μ (Mo-K_α) (mm^{-1})	0.804	0.760
Crystal size (mm)	0.08x0.10x0.18	
No. of total reflections	4559	4738
No. of reflections [$I>2\sigma(I)$]	3920	3236
R [$I>2\sigma(I)$]	0.0376	0.0493
wR [$I>2\sigma(I)$]	0.0952	0.1021
S	0.786	0.917

Table S4. Selected bond lengths [Å] and angles [°] for **2**.

	120 K	**240 K**
Fe-N(1)	1.955(4)	2.199(5)
Fe-N(2)	1.980(3)	2.247(5)
Fe-N(3)	2.002(4)	2.124(5)
Fe-N(4)	2.001(3)	2.180(5)
Fe-N(5)	1.977(3)	2.154(5)
Fe-N(6)	1.994(3)	2.128(4)
<Fe-N>	1.985	2.172
N(1)-Fe-N(2)	80.75(14)	73.1(2)
N(1)-Fe-N(3)	168.92(14)	162.61(18)
N(1)-Fe-N(4)	93.95(15)	93.28(19)
N(1)-Fe-N(5)	85.98(14)	84.94(19)
N(1)-Fe-N(6)	93.84(15)	93.6(2)
N(2)-Fe-N(3)	91.51(14)	90.7(2)
N(2)-Fe-N(4)	84.72(13)	82.9(2)
N(2)-Fe-N(5)	96.03(13)	96.34(19)
N(2)-Fe-N(6)	170.95(16)	165.1(2)
N(3)-Fe-N(4)	93.21(15)	90.8(2)
N(3)-Fe-N(5)	86.98(14)	90.86(19)
N(3)-Fe-N(6)	94.80(15)	103.2(2)
N(4)-Fe-N(5)	179.21(14)	178.2(2)
N(4)-Fe-N(6)	88.44(13)	91.33(19)
N(5)-Fe-N(6)	90.78(13)	89.04(18)

Table S5. Crystal data for **3·1/2CH_2Cl_2** and **3**.

	3·1/2CH_2Cl_2		**3**
Temperature	**120 K**	**220 K**	**120 K**
Empirical formula	$C_{18.5}H_{25}B_2Cl_1N_{10}S_2Fe$		$C_{18}H_{24}B_2N_{10}S_2Fe$
*M*r	546.52		522.06
Crystal system	monoclinic		triclinic
Space group	$P2_1/c$		P-1
a (Å)	8.3943(3)	8.5966(3)	10.6049(11)
b (Å)	16.3890(7)	16.4233(4)	11.4786(12)
c (Å)	18.3407(7)	18.4914(5)	11.8227(14)
α(°)			80.328(9)
β(°)	100.121(4)	101.100(3)	64.876(11)
γ(°)			65.734(10)
V (Å^3)	2483.9(2)	2561.86(13)	1187.9(3)
Z	4		2
D_c (mg cm^{-3})	1.510	1.464	1.460
F(000)	1164		540
μ (Mo-K_α) (mm^{-1})	0.913	0.885	0.839
Crystal size (mm)	0.03x0.04x0.08		0.06x0.15x0.15
No. of total reflections	6428	6780	5899
No. of reflections [$I>2\sigma(I)$]	3735	3914	3625
R [$I>2\sigma(I)$]	0.0644	0.0654	0.0864
wR [$I>2\sigma(I)$]	0.1474	0.1973	0.2046
S	0.884	0.857	0.902

$R_1 = \Sigma\ ||Fo| - |Fc|| / \Sigma\ |Fo|$; $wR = [\ \Sigma\ [w(Fo^2 - Fc^2)^2] / \Sigma\ [w(Fo^2)^2]]^{1/2}$.
$w = 1/\ [\sigma^2(Fo^2) + (m\ P)^2 + n\ P]$ where $P = (Fo^2 + 2Fc^2) / 3$;
m = 0.1008 (**1**), 0.2000 (**2**) and 0.1451 (**3**);
n = 6.1831 (**1**), 0.0000 (**2**) and 0.0000 (**3**)

Table S6. Selected bond lengths [Å] and angles [°].

	3·1/2CH_2Cl_2		**3**
	120 K	**220 K**	**120 K**
Fe-N(1)	2.127(4)	2.237(4)	2.213(3)
Fe-N(2)	2.152(4)	2.262(4)	2.220(3)
Fe-N(3)	2.116(4)	2.182(4)	2.182(4)
Fe-N(4)	2.074(4)	2.127(4)	2.160(3)
Fe-N(5)	2.069(4)	2.124(4)	2.159(3)
Fe-N(6)	2.081(4)	2.157(4)	2.173(4)
N(1)-Fe-N(2)	75.95(14)	73.46(14)	74.55(13)
N(1)-Fe-N(3)	92.75(14)	92.54(13)	90.92(13)
N(1)-Fe-N(4)	90.64(15)	90.65(13)	98.05(12)
N(1)-Fe-N(5)	168.71(15)	165.08(15)	172.32(13)
N(1)-Fe-N(6)	90.15(14)	88.89(14)	91.57(13)
N(2)-Fe-N(3)	88.42(14)	87.59(13)	89.68(13)
N(2)-Fe-N(4)	166.22(15)	163.27(14)	172.59(12)
N(2)-Fe-N(5)	93.31(15)	92.56(15)	97.93(13)
N(2)-Fe-N(6)	91.84(14)	91.92(13)	92.61(13)
N(3)-Fe-N(4)	89.14(15)	87.92(14)	90.32(13)
N(3)-Fe-N(5)	90.37(15)	92.02(14)	87.45(13)
N(3)-Fe-N(6)	177.06(15)	178.29(14)	176.98(12)
N(4)-Fe-N(5)	100.26(15)	103.70(14)	89.48(13)
N(4)-Fe-N(6)	91.30(15)	93.00(14)	87.66(13)
N(5)-Fe-N(6)	86.69(15)	86.36(15)	90.30(13)

Table S7. Intermolecular interactions for **1·CH_3CN** (see also **Figure 4**).

110 K		**250 K**	
$py^{(Fe2)}$…$tzpy^{(Fe1)}$		**$py^{(Fe2)}$…$tzpy^{(Fe1)}$**	
C37···C18	3.380	C37···C18	3.582
C38···C19	3.283	C38···C18	3.577
C39···C19	3.523	C38···C19	3.414
C39···C20	3.485	C39···C19	3.595
C38···C18	3.424	C39···C19	3.595
C37···C19	3.491	C40···C22	3.569
C40···C21	3.508		
C40···C22	3.467		
$py^{(Fe1)}$…$tzpy^{(Fe2)}$		**$tzpy^{(Fe2)}$… $py^{(Fe1)}$**	
C41···C14	3.560		
C41···C15	3.486	C41···C14	3.460
C42···C15	3.326	C41···C15	3.526
C43···C15	3.475	C42···C14	3.593
C42···C16	3.524	C42···C15	3.401
C43···C16	3.514	C43···C15	3.461
C44···C16	3.593	C43···C16	3. 523
C44···C17	3.580	C45···C17	3.564
C45···C17	3.504	C45·····C17	3.564
$pz^{(Fe1)}$…$pz^{(Fe1)}$		**$pz^{(Fe1)}$…$pz^{(Fe1)}$**	
C11···C11	3.582	C7···C7	3.474
$pz^{(Fe1)}$… $pz^{(Fe2)}$		**$pz^{(Fe1)}$…$pz^{(Fe2)}$**	
C9···C33	3.346	C2···C27	3.497
C9···C34	3.530	C3···C27	3.405
C7···C31	3.570	C5···C33	3.380
C3···C31	3.381		
$pz^{(Fe2)}$…$pz^{(Fe2)}$		**pz···CH_3CN**	
C28···C32	3.511	C3···C50	3.483
C29···C29	3.394	C33···C48	3.403
C25···C26	3.597		
$py^{(Fe1)}$…$py^{(Fe2)}$			
C17···C35	3.551		
$tzpy^{(Fe1)}$···CH_3CN			
C23···C49	3.568		
$pz^{(Fe1)}$···CH_3CN			
C2···C50	3.543		
C3···C50	3.324		
$pz^{(Fe2)}$···CH_3CN			
C33···C48	3.363		
C34···C48	3.576		

Table S8. Intermolecular interactions for **2**, **3·1/2CH$_2$Cl$_2$** and **3** (see also **Figure S5a,b**).

Intermolecular Contacts for 2	**120 K**	**240 K**
C12···C6	3.506	---
C2···C11	3.507	---
C12···C6’	3.698	---

Intermolecular Contacts for 3·1/2CH$_2$Cl$_2$	**120 K**	**220 K**
S1···S1	3.365	3.356
C1···C15	3.396	3.437
C2···C15	3.562	---
C2···C18	3.439	3.485
C5···C12	3.458	3.558
C6···C11	3.569	---
C6···C12	3.570	---
C19···C9	3.450	3.524
C19···C13	3.393	3.552
C19···C17	3.430	3.586

Intermolecular Contacts for 3	**120 K**
C12···C12	3.480
C7···C2	3.539
C16···C5	3.485
S1···C7	3.552
S1···C8	3.457
S1···C9	3.397
S2···C16	3.517
S2···C17	3.504
S2···C18	3.453