Supplementary information

Influence of conformational changes on spin crossover properties and superstructure formation in 2D coordination polymers $[Fe(hbtz)_2(RCN)_2](ClO_4)_2$

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Table S1. Crystallographic data for **1**

Temperature/K	260 K	240 K	220 K	200 K	190 K	180 K	170 K	160 K	150 K	140K
Chemical formula	$C_{24}H_{38}Cl_2FeN_{18}O_8$									
Formula Mass	833.47									
Crystal system	Triclinic									
Space group	*P*-1									
Z	1							2		
a/Å	9.806(2)	9.7687(14)	9.7337(9)	9.6999(4)	9.6900(3)	9.6846(3)	9.6826(4)	10.2366(16)	10.1849(11)	10.1557(8)
b/Å	10.085(2)	10.0740(13)	10.0664(9)	10.0480(3)	10.0364(3)	10.0208(3)	10.0049(3)	11.7216(10)	11.6844(7)	11.6792(6)
c/Å	11.9136(16)	11.9033(10)	11.8781(7)	11.8504(4)	11.8284(3)	11.8009(3)	11.7749(4)	16.2866(19)	16.3321(13)	16.3519(10)
α/°	72.577(15)	72.646(10)	72.682(7)	72.774(3)	72.750(3)	72.684(3)	72.597(3)	71.251(7)	70.931(5)	70.681(4)
β/°	67.241(17)	67.387(10)	67.560(7)	67.761(3)	67.838(3)	67.886(3)	67.901(3)	85.263(11)	85.251(8)	85.255(6)
γ/°	63.07(2)	63.069(14)	63.110(9)	63.065(4)	63.027(4)	62.963(4)	62.901(4)	86.212(11)	86.202(8)	86.237(6)
Unit cell volume/Å^3	957.4(4)	953.1(2)	948.32(16)	942.16(7)	938.44(6)	933.87(6)	929.50(7)	1842.6(4)	1829.0(3)	1822.5(2)
No. of reflections measured	7141	7106	7062	7031	7005	6955	6902	13669	13573	13459
No. of independent reflections	3831	3811	3785	3764	3754	3728	3702	7362	7310	7282
R_{int}	0.0235	0.0218	0.0243	0.0231	0.0219	0.0235	0.0212	0.0551	0.0547	0.0450
Final R_1 values ($I > 2\sigma(I)$)	0.0421	0.0391	0.0384	0.0365	0.0362	0.0366	0.0365	0.0963	0.0869	0.0657
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0930	0.0868	0.0841	0.0809	0.0800	0.0810	0.0796	0.2454	0.2151	0.1588
Final R_1 values (all data)[a]	0.0558	0.0516	0.0494	0.0461	0.0450	0.0458	0.0452	0.1487	0.1224	0.0907
Final $wR(F^2)$ values (all data)[b]	0.1003	0.0932	0.0894	0.0863	0.0843	0.0859	0.0839	0.2889	0.2416	0.1757

Continued Table S1

Temperature/K	120K	100K	15K	15K(LIESST)	120 K	140 K	150 K	160 K	170 K	180 K
Chemical formula	$C_{24}H_{38}Cl_2FeN_{18}O_8$									
Formula Mass	833.47									
Crystal system	Triclinic									
Space group	*P*-1									
Z	2								1	
a/Å	10.1301(3)	10.1153(3)	10.0869(3)	10.2326(3)	10.1287(3)	10.1555(8)	10.1820(11)	10.2350(14)	9.6835(3)	9.6861(3)
b/Å	11.6920(2)	11.6862(2)	11.6409(3)	11.7947(6)	11.6897(2)	11.6805(5)	11.6837(8)	11.7152(10)	10.0053(3)	10.0200(3)
c/Å	16.3668(4)	16.3633(4)	16.3369(6)	16.3663(7)	16.3677(4)	16.3542(10)	16.3334(13)	16.2943(17)	11.7750(3)	11.7997(3)
α/°	70.393(2)	70.220(2)	70.019(3)	70.049(4)	70.389(2)	70.680(4)	70.914(5)	71.229(6)	72.587(3)	72.678(3)
β/°	85.284(3)	85.286(2)	85.171(3)	84.367(3)	85.287(3)	85.266(6)	85.251(7)	85.237(9)	67.904(3)	67.891(3)
γ/°	86.322(3)	86.302(3)	86.178(2)	85.390(4)	86.320(3)	86.244(6)	86.224(8)	86.220(10)	62.900(4)	62.963(4)
Unit cell volume/Å^3	1818.54(8)	1812.63(8)	1794.95(10)	1845.42(14)	1817.99(8)	1823.0(2)	1828.4(3)	1841.9(4)	929.61(6)	933.85(6)
No. of reflections measured	13580	13544	12348	9151	13582	13550	13561	13656	6926	6975
No. of independent reflections	7281	7259	6426	6648	7278	7287	7305	7364	3702	3726
R_{int}	0.0240	0.0227	0.0348	0.0147	0.0233	0.0473	0.0609	0.0654	0.0190	0.0205
Final R_1 values ($I > 2\sigma(I)$)	0.0390	0.0363	0.0403	0.0392	0.0390	0.0635	0.0959	0.1143	0.0349	0.0363
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0874	0.0803	0.0988	0.0982	0.0864	0.1543	0.2744	0.3149	0.0751	0.0785
Final R_1 values (all data)[a]	0.0484	0.0446	0.0480	0.0437	0.0476	0.0862	0.1287	0.1605	0.0436	0.0450
Final $wR(F^2)$ values (all data)[b]	0.0927	0.0846	0.1022	0.1009	0.0909	0.1713	0.3044	0.3596	0.0795	0.0828

Continued Table S1.

Temperature/K	190 K	200 K	220 K	240K	260K	280 K	300 K
Chemical formula				$C_{24}H_{38}Cl_2FeN_{18}O_8$			
Formula Mass				833.47			
Crystal system				Triclinic			
Space group				*P*-1			
Z				1			
a/Å	9.6916(4)	9.7013(4)	9.7287(4)	9.7690(11)	9.8066(13)	9.8441(16)	9.8755(18)
b/Å	10.0352(4)	10.0478(4)	10.0623(4)	10.0770(11)	10.0827(13)	10.0890(15)	10.0915(17)
c/Å	11.8275(4)	11.8495(4)	11.8839(4)	11.9043(8)	11.9238(10)	11.9417(11)	11.9545(13)
α/°	72.746(3)	72.777(3)	72.731(3)	72.595(8)	72.502(9)	72.423(11)	72.364(12)
β/°	67.845(3)	67.771(3)	67.580(3)	67.402(8)	67.213(10)	67.060(12)	66.950(13)
γ/°	63.022(4)	63.063(4)	63.103(4)	63.038(11)	62.998(13)	62.951(15)	62.929(18)
Unit cell volume/Å^3	938.40(7)	942.26(7)	948.11(7)	953.1(2)	957.2(2)	961.4(3)	964.8(3)
No. of reflections measured	7018	7038	7082	7108	7159	7185	7206
No. of independent reflections	3752	3764	3786	3809	3833	3844	3856
R_{int}	0.0220	0.0214	0.0211	0.0222	0.0227	0.0226	0.0234
Final R_1 values ($I > 2\sigma(I)$)	0.0362	0.0355	0.0375	0.0390	0.0398	0.0417	0.0446
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0785	0.0787	0.0829	0.0859	0.0904	0.0939	0.0980
Final R_1 values (all data)[a]	0.0453	0.0455	0.0489	0.0521	0.0554	0.0579	0.0623
Final $wR(F^2)$ values (all data)[b]	0.0834	0.0840	0.0887	0.0928	0.0992	0.1027	0.1080

Table S2. Crystallographic data for **2.**

Temperature/K	250(2)	200(2)	160(2)	100(2)
Chemical formula	$C_{22}H_{38}Cl_2FeN_{18}O_8$			
Formula Mass	809.45			
Crystal system	triclinic			
Space group	P-1			
Z	1			
a/Å	9.495(3)	9.454(2)	9.403(3)	9.341(3)
b/Å	9.667(2)	9.637(2)	9.602(2)	9.555(2)
c/Å	11.668(4)	11.621(4)	11.546(4)	11.409(4)
α/°	89.51(3)	89.74(3)	90.08(3)	90.68(3)
β/°	68.43(4)	68.55(4)	68.46(4)	68.74(4)
γ/°	65.88(3)	66.06(3)	66.12(3)	66.37(3)
Unit cell volume/Å^3	896.3(5)	887.7(4)	872.7(4)	854.6(4)
No. of reflections measured	5543	7719	7396	7328
No. of independent reflections	3261	3839	3754	3667
R_{int}	0.0277	0.0255	0.0252	0.0234
Final R_1 values ($I > 2\sigma(I)$)	0.0342	0.0323	0.0313	0.0298
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0794	0.0803	0.0763	0.0780
Final R_1 values (all data) [a]	0.0541	0.0477	0.0447	0.0382
Final $wR(F^2)$ values (all data) [b]	0.0844	0.0851	0.0801	0.0804

[a] $R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [b] $wR^2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

Table S3a. Selected C-H…N and C-H···O interatomic contacts [Å] and angles [°] for **1** in cooling (from 260 to 170 K) and in the heating (from 170 to 300 K) modes.

$[Fe(hbtz)_2(AlCN)_2](ClO_4)_2$	**260 K**		**240 K**		**220 K**		**200 K**		**190 K**		**180 K**	
	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)
Nitrile...tz (adjusted layer)												
C22-H22...N11(-1+x,1+y,z)	3.649(7)	131.0	3.627(6)	129.8	3.611(6)	129.0	3.611(5)	128.2	3.635(6)	127.8	3.663(6)	127.9
C231-H23C...N4(-1+x,y,z)	3.35(2)	114.9	3.32(3)	113.9	3.36(4)	105.7	3.30(4)	115.2	3.67(9)	111.5	3.77(9)	118.7
C231-H23D...N13(-x,1-y,1-z)	3.41(4)	166.8	3.33(5)	164.9	3.31(7)	164.0	3.25(7)	164.1	3.32(6)	153.2	3.57(7)	148.3
C231-H23D...N14(-x,1-y,1-z)	3.14(3)	161.3	3.07(4)	159.6	3.12(5)	158.4	2.99(5)	161.1	3.09(5)	171.2	3.32(6)	177.4
C233-H23H...N4(-1+x,y,z)	3.48(4)	142.5	3.49(5)	142.3	3.39(5)	139.7	3.40(6)	139.5	3.41(7)	130.8	3.23(5)	133.1
C233-H23G...N11(-1+x,1+y,z)	3.48(5)	118.6	3.54(6)	111.8	3.56(6)	119.9	3.54(7)	120.0	3.61(8)	129.9	3.63(7)	142.1
C232-H23F…N4(-1+x,y,z)	3.54(3)	142.2	3.45(3)	142.4	3.40(3)	149.4	3.44(3)	149.6	3.35(2)	147.4	3.46(2)	160.5
C231-H23D…N12(-x,1-y,1-z)	3.74(5)	147.6	3.68(6)	142.1	3.76(7)	141.5	3.58(8)	146.3	3.37(7)	131.1	3.56(8)	132.4
C23-H23A...N20	3.536(5)	121.5	3.533(4)	121.7	3.529(4)	122.5	3.531(4)	122.5	3.535(4)	122.5	3.550(4)	122.7
Nitrile…ClO_4^-												
C21-H21B...O1(-x,2-y,1-z)	3.325(15)	167.2	3.403(17)	169.3	3.362(16)	170.4	3.348(14)	170.1	3.339(14)	170.1	3.321(15)	169.2
C21-H21A...O4	3.393(10)	137.2	3.404(9)	138.5	3.416(8)	142.3	3.415(8)	144.6	3.418(8)	144.1	3.424(9)	145.5
C21-H21B...O4(-x,2-y,1-z)	3.459(12)	119.9	3.445(11)	119.4	3.425(10)	119.1	3.417(9)	118.4	3.400(9)	118.0	3.397(11)	117.8
C21-H21A…O41	3.400(12)	153.0	3.405(10)	154.4	3.410(9)	158.3	3.420(8)	160.7	3.405(9)	159.8	3.419(10)	160.8
C23-H23B...O3(x, -1+y,z)	3.622(11)	122.5	3.626(11)	123.5	3.632(10)	125.0	3.627(9)	126.0	3.627(9)	126.7	3.603(9)	127.2
C23-H23B…O31(x,-1+y,z)	3.061(10)	118.0	3.067(8)	119.0	3.084(7)	120.2	3.076(7)	120.9	3.068(7)	121.4	3.042(7)	121.7
C211-H21D...O11	3.80(4)	124.6	3.63(4)	123.5	3.65(5)	124.5	3.65(6)	125.5	3.59(6)	119.4	3.50(7)	122.9
C211-H21D...O41	3.55(4)	172.7	3.53(5)	165.5	3.55(6)	170.5	3.56(7)	174.2	3.48(7)	155.8	3.40(8)	158.5
C212-H21E…O1	3.01(5)	146.1	3.13(5)	148.2	3.13(7)	150.2	3.10(6)	149.7	3.06(7)	144.7	3.08(7)	160.4
C212-H21F…O4	3.27(2)	171.8	3.30(3)	173.4	3.29(3)	174.4	3.27(3)	171.9	3.40(4)	175.5	3.31(4)	168.4
C212-H21F…O41	3.35(3)	155.5	3.37(3)	156.8	3.35(4)	159.6	3.34(4)	156.8	3.45(5)	158.6	3.37(5)	167.2
C212-H21E…O4(-x,2-y,1-z)	3.13(5)	110.2	3.15(5)	109.0	3.17(6)	109.9	3.14(6)	108.9	3.12(6)	109.9	3.14(6)	117.3
C212-H21E…O11(-x,2-y,1-z)	3.46(5)	142.6	3.39(5)	137.3	3.41(7)	139.8	3.38(6)	139.0	3.38(6)	136.0	3.43(6)	151.2
C212-H21E…O31(-x,2-y,1-z)	3.43(5)	144.8	3.45(6)	144.2	3.46(7)	143.2	3.43(7)	143.3	3.36(7)	148.2	3.42(8)	144.2
C213-H21H…O1(-x,2-y,1-z)	3.04(3)	146.7	3.13(4)	150.6	3.14(4)	147.2	3.15(5)	147.9	3.19(6)	140.1	3.20(5)	146.9
C213-H21H…O4(-x,2-y,1-z)	3.22(3)	121.2	3.23(4)	120.7	3.25(4)	119.3	3.27(5)	117.9	3.31(5)	113.2	3.32(5)	116.0
C213-H21H…O11(-x,2-y,1-z)	3.52(3)	145.0	3.45(4)	142.8	3.49(4)	140.2	3.50(5)	140.3	3.57(5)	133.8	3.61(5)	140.7
C213-H21H…O31(-x,2-y,1-z)	3.23(5)	154.8	3.27(6)	153.4	3.25(6)	154.5	3.27(8)	152.7	3.30(8)	152.9	3.30(8)	150.7
C221-H22A…O1(-x,2-y,1-z)	3.19(3)	155.2	3.17(4)	149.4	3.21(5)	160.9	3.18(5)	152.3	3.46(8)	76.0	3.50(8)	77.2
C221_b-H22A_b...O31(-x,2-y,1-z)	3.33(3)	148.2	3.28(4)	153.4	3.34(5)	126.6	3.33(5)	151.7	3.53(8)	108.8	3.65(8)	108.8
Alkyl chain												
C1-H1A...O2	3.417(7)	145.7	3.412(6)	144.8	3.403(6)	144.5	3.398(6)	144.0	3.392(6)	143.9	3.383(5)	143.6
C1-H1A...O21	3.450(8)	161.9	3.421(7)	160.5	3.410(7)	159.7	3.385(6)	158.8	3.381(5)	158.2	3.371(5)	157.9
C1-H1B...O3(-x,-y+2,-z+2)	3.165(6)	117.4	3.155(6)	117.1	3.150(5)	117.1	3.148(5)	117.0	3.146(5)	117.2	3.149(5)	117.2
C2-H2B…O3(-x,-y+2,-z+2)	3.478(6)	120.1	3.472(6)	119.5	3.467(6)	119.3	3.461(5)	119.0	3.461(5)	119.0	3.457(5)	119.2
C3-H3B…O2	3.403(6)	150.3	3.381(6)	150.3	3.370(5)	150.1	3.357(5)	150.2	3.345(5)	150.2	3.333(5)	150.1
C11-H11A…O1(x,-1+y,z)	3.427(19)	135.8	3.231(13)	134.8	3.234(13)	135.2	3.205(11)	135.1	3.205(12)	135.9	3.219(13)	135.9
C11-H11A...O11(x,-1+y,z)	3.430(17)	145.2	3.610(14)	144.7	3.589(14)	145.0	3.573(11)	145.2	3.548(12)	145.6	3.523(12)	145.9

C11-H11A…O21(-x,1-y,2-z)	3.470(7)	115.4	3.461(6)	115.8	3.456(6)	115.8	3.456(5)	115.9	3.456(5)	115.6	3.453(5)	115.6
C12-H12A…O21(-x,1-y,2-z)	3.340(8)	124.7	3.316(7)	123.6	3.300(6)	123.0	3.286(6)	122.2	3.274(6)	122.0	3.268(6)	122.3
C13-H13B…O41(1+x,-1+y,z)	3.405(10)	141.6	3.397(9)	141.7	3.377(9)	141.1	3.364(8)	140.6	3.378(8)	140.7	3.373(8)	140.8
C14-H14...O1(1-x,1-y,1-z)	3.293(15)	156.6	3.285(13)	157.2	3.273(13)	156.9	3.265(11)	156.6	3.244(12)	156.0	3.241(12)	155.4
C14-H14...O11(1-y,-y,2-z)	3.360(17)	168.3	3.350(14)	166.0	3.343(14)	166.4	3.323(12)	167.3	3.330(12)	167.3	3.316(12)	167.6
C4-H4...O4(1+x,-1+y,z)	3.272(8)	170.7	3.260(7)	171.0	3.252(7)	170.8	3.239(6)	170.5	3.228(6)	170.2	3.220(6)	169.7
C4-H4...O31(1+x,-1+y,z)	3.373(9)	139.4	3.354(8)	138.4	3.337(7)	138.5	3.314(6)	137.9	3.305(6)	137.8	3.285(6)	137.7
C4-H4…O3(1+x, -1+y, z)	3.409(8)	135.1	3.397(7)	134.4	3.381(7)	134.1	3.359(6)	133.6	3.349(6)	133.4	3.334(6)	133.1
C4-H4...O41(1+x,-1+y,z)	3.312(10)	159.4	3.306(8)	160.4	3.308(8)	159.9	3.301(7)	159.7	3.300(6)	159.5	3.297(7)	158.6
C1-H1B...N1(1+x,y-1,z)	3.584(3)	149.6	3.572(3)	149.3	3.561(3)	149.3	3.548(3)	149.0	3.550(3)	149.2	3.548(3)	149.4
C14-H14…N11(1-x,-y,1-z)	3.609(4)	87.4	3.607(3)	86.6	3.616(3)	85.7	3.632(3)	84.1	3.647(3)	83.5	3.668(3)	82.9

Continued Table S3a.

$[Fe(hbtz)_2(AlCN)_2](ClO_4)_2$	170 K		170 K		180 K		190 K		200 K		220 K	
	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)
Nitrile...tz (adjusted layer)												
C22-H22...N11(-1+x,1+y,z)	3.682(7)	128.3	3.693(6)	128.1	3.664(6)	127.9	3.641(6)	127.7	3.622(6)	127.8	3.612(5)	128.8
C231-H23C...N4(-1+x,y,z)	3.86(9)	115.2	3.79(8)	113.1	3.86(9)	118.6	3.72(8)	114.3	3.78(8)	116.6	3.26(3)	103.8
C231-H23D...N13(-x,1-y,1-z)	3.50(7)	153.1	3.51(6)	154.2	3.57(7)	148.8	3.48(6)	151.1	3.54 (7)	148.6	3.42(7)	159.0
C231-H23D...N14(-x,1-y,1-z)	3.31(6)	174.1	3.30(5)	172.8	3.34(6)	176.1	3.22(5)	178.4	3.28(6)	177.5	3.17(5)	163.6
C233-H23H...N4(-1+x,y,z)	3.31(4)	136.5	3.34(5)	138.8	3.28(5)	131.8	3.34(6)	133.5	3.36(5)	133.4	3.43(6)	139.7
C233-H23G...N11(-1+x,1+y,z)	3.59(5)	137.6	3.55(6)	134.5	3.57(6)	144.9	3.57(7)	134.5	3.58(6)	130.0	3.56(6)	116.3
C232-H23F…N4(-1+x,y,z)	3.47(2)	158.5	3.470(19)	157.7	3.45(2)	157.5	3.39(3)	152.7	3.39(3)	156.4	3.42(3)	146.9
C231-H23D…N12(-x,1-y,1-z)	3.46(7)	137.3	3.49(6)	138.9	3.52(7)	133.6	3.49(7)	133.4	3.52(7)	132.4	3.86(7)	139.1
C23-H23A...N20	3.560(4)	122.3	3.561(4)	122.2	3.551(4)	122.4	3.539(4)	122.7	3.532(4)	122.8	3.528(4)	122.5
Nitrile…ClO_4^-												
C21-H21B...O1(-x,2-y,1-z)	3.343(14)	170.1	3.349(15)	169.6	3.309(14)	169.2	3.312(14)	169.2	3.344(15)	170.0	3.369(16)	169.9
C21-H21A...O4	3.429(9)	144.7	3.428(8)	145.0	3.420(9)	144.8	3.424(8)	145.2	3.413(9)	144.1	3.411(8)	142.0
C21-H21B...O4(-x,2-y,1-z)	3.390(11)	117.9	3.392(10)	117.8	3.394(10)	117.8	3.407(10)	118.0	3.421(10)	118.1	3.436(10)	118.6
C21-H21A…O41	3.412(10)	159.5	3.420(9)	159.7	3.416(9)	168.9	3.411(9)	160.8	3.420(10)	159.7	3.416(9)	158.0
C23-H23B...O3(x, -1+y,z)	3.591(9)	127.1	3.584(9)	127.0	3.605(9)	126.9	3.618(9)	126.8	3.632(9)	126.2	3.632(10)	125.2
C23-H23B…O31(x,-1+y,z)	3.033(7)	121.6	3.026(7)	121.6	3.046(7)	121.6	3.051(7)	121.5	3.071(7)	121.3	3.070(8)	120.3
C211-H21D...O11	3.54(7)	125.0	3.58(7)	126.1	3.52(7)	123.7	3.57(6)	122.2	3.52(7)	122.3	3.63(5)	124.5
C211-H21D...O41	3.45(8)	164.3	3.49(7)	169.1	3.41(8)	160.0	3.45(7)	160.9	3.44(8)	159.6	3.53(5)	169.6
C212-H21E…O1	3.09(6)	158.5	3.09(5)	156.9	3.04(6)	155.9	3.06(7)	153.2	3.09(8)	155.1	3.06(6)	143.3
C212-H21F…O4	3.33(3)	169.7	3.34(2)	170.8	3.32(4)	171.8	3.35(4)	174.2	3.33(5)	173.7	3.31(3)	170.3
C212-H21F…O41	3.38(4)	165.9	3.39(4)	165.3	3.38(5)	163.9	3.40(5)	163.5	3.40(6)	164.9	3.39(4)	153.2
C212-H21E…O4(-x,2-y,1-z)	3.12(5)	116.0	3.11(5)	116.0	3.11(5)	115.3	3.15(7)	114.5	3.16(7)	114.6	3.11(6)	106.5
C212-H21E…O11(-x,2-y,1-z)	3.42(5)	148.8	3.40(5)	148.3	3.42(6)	147.5	3.44(7)	145.2	3.40(8)	145.4	3.35(6)	133.6
C212-H21E…O31(-x,2-y,1-z)	3.40(7)	145.1	3.38(6)	145.6	3.39(7)	145.8	3.40(8)	146.3	3.42(9)	145.5	3.40(7)	144.7
C213-H21H…O1(-x,2-y,1-z)	3.18(4)	147.1	3.17(5)	150.2	3.18(4)	141.4	3.15(5)	139.5	3.19(5)	142.2	3.14(5)	147.6
C213-H21H…O4(-x,2-y,1-z)	3.28(4)	116.8	3.27(5)	117.8	3.32(4)	113.5	3.29(5)	114.6	3.31(5)	114.8	3.26(5)	118.7
C213-H21H…O11(-x,2-y,1-z)	3.56(4)	141.0	3.54(5)	143.9	3.61(4)	136.2	3.57(5)	135.0	3.56(5)	135.9	3.49(5)	140.7
C213-H21H…O31(-x,2-y,1-z)	3.26(6)	152.0	3.28(7)	150.3	3.30(7)	151.9	3.25(7)	154.5	3.29(7)	152.9	3.27(7)	153.6
C221-H22A…O1(-x,2-y,1-z)	3.47(8)	75.5	3.48(7)	82.2	3.50(7)	72.7	3.48(7)	77.3	3.52(8)	73.9	3.30(4)	159.6
C221_b-H22A_b...O31(-x,2-y,1-z)	3.59(8)	107.4	3.59(7)	113.7	3.67(8)	103.6	3.60(7)	109.9	3.66(8)	105.0	3.43(5)	132.7
Alkyl chain												
C1-H1A...O2	3.381(5)	143.5	3.380(5)	143.4	3.391(5)	143.5	3.391(5)	143.7	3.398(6)	143.6	3.398(6)	144.5
C1-H1A...O21	3.364(5)	157.4	3.368(5)	157.2	3.370(5)	157.7	3.380(5)	158.1	3.383(6)	158.4	3.408(6)	159.7
C1-H1B...O3(-x,-y+2,-z+2)	3.144(5)	117.0	3.149(5)	117.0	3.147(5)	116.9	3.154(5)	117.0	3.151(5)	116.7	3.154(6)	117.1
C2-H2B…O3(-x,-y+2,-z+2)	3.449(5)	119.2	3.455(5)	119.3	3.458(5)	119.2	3.469(5)	119.2	3.467(5)	119.2	3.472(6)	119.3
C3-H3B…O2	3.325(5)	150.4	3.322(5)	150.4	3.335(5)	150.2	3.347(5)	150.1	3.355(5)	150.1	3.370(5)	150.0
C11-H11A…O1(x,-1+y,z)	3.200(12)	136.9	3.209(13)	137.2	3.230(14)	135.9	3.237(14)	135.6	3.215(13)	135.2	3.235(14)	135.2
C11-H11A...O11(x,-1+y,z)	3.531(11)	146.4	3.523(13)	146.3	3.501(13)	146.0	3.518(14)	145.1	3.564(12)	144.7	3.581(15)	144.9
C11-H11A…O21(-x,1-y,2-z)	3.445(5)	115.4	3.442(5)	115.4	3.453(5)	115.7	3.450(5)	115.6	3.453(5)	115.9	3.461(6)	115.7
C12-H12A…O21(-x,1-y,2-z)	3.257(6)	122.2	3.251(5)	122.1	3.270(6)	121.9	3.270(6)	122.3	3.280(6)	122.3	3.299(6)	123.1
C13-H13B…O41(1+x,-1+y,z)	3.375(8)	140.8	3.371(8)	140.3	3.372(8)	140.8	3.366(8)	140.6	3.374(8)	141.1	3.385(9)	141.2

C14-H14...O1(1-x,1-y,1-z)	3.229(11)	154.9	3.230(13)	155.3	3.238(12)	155.2	3.230(12)	155.9	3.243(12)	156.5	3.271(13)	157.0
C14-H14...O11(1-y,-y,2-z)	3.310(11)	167.0	3.306(13)	166.9	3.316(11)	167.8	3.346(12)	167.9	3.341(12)	167.3	3.346(15)	166.6
C4-H4...O4(1+x,-1+y,z)	3.204(6)	169.3	3.209(6)	169.6	3.222(6)	169.7	3.228(6)	170.0	3.239(6)	170.3	3.247(7)	170.6
C4-H4...O31(1+x,-1+y,z)	3.277(5)	137.6	3.274(5)	137.4	3.285(6)	137.8	3.297(6)	138.0	3.305(6)	137.9	3.335(7)	138.1
C4-H4…O3(1+x, -1+y, z)	3.323(6)	132.7	3.327(6)	132.6	3.341(6)	133.2	3.352(6)	133.8	3.370(6)	133.8	3.384(7)	134.2
C4-H4...O41(1+x,-1+y,z)	3.299(7)	158.0	3.294(7)	158.0	3.296(7)	158.6	3.304(7)	158.8	3.299(7)	159.8	3.308(8)	160.2
C1-H1B...N1(1+x,y-1,z)	3.548(3)	149.7	3.549(3)	149.7	3.547(3)	149.5	3.546(3)	149.3	3.551(3)	149.3	3.558(3)	149.2
C14-H14…N11(1-x,-y,1-z)	3.689(3)	82.1	3.689(3)	82.2	3.667(3)	82.8	3.645(3)	83.6	3.629(3)	84.2	3.614(3)	85.5

Continued Table S3a.

$[Fe(hbtz)_2(AlCN)_2](ClO_4)_2$	240 K		260 K		280 K		300 K	
	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)
Nitrile...tz (adjusted layer)								
C22-H22...N11(-1+x,1+y,z)	3.626(6)	129.8	3.642(7)	131.0	3.669(8)	131.5	3.715(11)	132.1
C231-H23C...N4(-1+x,y,z)	3.29(2)	112.0	3.31(2)	111.3	3.356(17)	111.7	3.381(17)	111.9
C231-H23D...N13(-x,1-y,1-z)	3.39(5)	163.5	3.47(4)	164.1	3.53(3)	166.0	3.58(3)	167.2
C231-H23D...N14(-x,1-y,1-z)	3.10(4)	163.1	3.16(3)	163.9	3.24(2)	162.9	3.28(3)	158.4
C233-H23H...N4(-1+x,y,z)	3.47(5)	144.6	3.47(4)	141.4	3.51(4)	141.5	3.60(4)	133.6
C233-H23G...N11(-1+x,1+y,z)	3.51(5)	111.9	3.51(5)	118.3	3.50(4)	118.3	3.46(5)	127.8
C232-H23F…N4(-1+x,y,z)	3.49(3)	141.9	3.51(2)	143.5	3.64(2)	138.7	3.61(2)	136.8
C231-H23D…N12(-x,1-y,1-z)	3.73(5)	142.9	3.79(5)	143.9	3.86(3)	145.9	3.89(3)	144.0
C23-H23A...N20	3.529(4)	122.0	3.539(5)	121.3	3.533(6)	121.0	3.549(7)	119.6
Nitrile…ClO_4^-								
C21-H21B...O1(-x,2-y,1-z)	3.395(17)	169.5	3.40(2)	168.2	3.326(14)	167.0	3.343(18)	165.9
C21-H21A...O4	3.391(9)	139.7	3.388(10)	136.9	3.390(11)	136.3	3.384(14)	134.4
C21-H21B...O4(-x,2-y,1-z)	3.441(11)	119.4	3.452(12)	119.8	3.459(12)	120.2	3.463(14)	120.0
C21-H21A…O41	3.421(10)	155.7	3.411(11)	152.6	3.416(12)	152.3	3.398(15)	150.0
C23-H23B...O3(x, -1+y,z)	3.639(11)	124.1	3.629(11)	122.5	3.601(12)	121.9	3.608(14)	120.0
C23-H23B…O31(x,-1+y,z)	3.068(8)	119.1	3.062(9)	117.9	3.045(10)	117.5	3.034(12)	115.4
C211-H21D...O11	3.63(4)	123.9	3.64(4)	124.3	3.75(3)	124.5	3.73(3)	122.3
C211-H21D...O41	3.55(4)	169.0	3.54(4)	168.6	3.52(3)	168.6	3.49(3)	163.3
C212-H21E…O1	3.11(6)	148.2	3.10(5)	150.0	2.98(4)	146.2	3.00(4)	152.4
C212-H21F…O4	3.28(3)	172.6	3.28(2)	173.8	3.27(2)	170.6	3.29(2)	173.9
C212-H21F…O41	3.38(3)	155.8	3.38(3)	157.7	3.38(3)	154.2	3.39(3)	159.6
C212-H21E…O4(-x,2-y,1-z)	3.14(5)	109.1	3.13(5)	110.4	3.10(4)	110.8	3.11(4)	115.7
C212-H21E…O11(-x,2-y,1-z)	3.36(6)	137.2	3.40(5)	139.9	3.46(4)	142.7	3.47(4)	148.1
C212-H21E…O31(-x,2-y,1-z)	3.45(6)	144.9	3.45(5)	145.1	3.40(4)	146.0	3.42(4)	147.7
C213-H21H…O1(-x,2-y,1-z)	3.11(4)	150.1	3.11(4)	149.5	3.03(3)	147.3	3.03(4)	137.8
C213-H21H…O4(-x,2-y,1-z)	3.21(4)	121.7	3.22(4)	120.9	3.20(3)	121.9	3.19(4)	116.6
C213-H21H…O11(-x,2-y,1-z)	3.43(4)	144.2	3.47(4)	142.8	3.53(3)	145.9	3.52(4)	136.3
C213-H21H…O31(-x,2-y,1-z)	3.26(6)	153.1	3.26(5)	154.5	3.23(5)	154.8	3.23(5)	158.4
C221-H22A…O1(-x,2-y,1-z)	3.23(4)	150.0	3.23(3)	148.5	3.22(3)	153.5	3.27(3)	142.9
C221_b-H22A_b...O31(-x,2-y,1-z)	3.35(3)	154.0	3.36(3)	156.4	3.36(3)	149.7	3.39(3)	162.3
Alkyl chain								
C1-H1A...O2	3.406(6)	144.9	3.410(7)	145.6	3.418(7)	145.6	3.429(8)	145.9
C1-H1A...O21	3.425(7)	160.5	3.444(8)	161.7	3.466(9)	162.3	3.489(9)	163.1
C1-H1B...O3(-x,-y+2,-z+2)	3.163(6)	117.3	3.164(6)	117.3	3.167(6)	117.1	3.174(7)	117.3
C2-H2B…O3(-x,-y+2,-z+2)	3.486(6)	119.4	3.484(7)	119.9	3.481(7)	120.2	3.492(8)	120.3
C3-H3B…O2	3.386(6)	150.0	3.397(6)	150.3	3.410(6)	150.2	3.414(7)	150.4
C11-H11A…O1(x,-1+y,z)	3.234(14)	134.8	3.273(18)	134.9	3.451(19)	135.7	3.46(2)	135.4
C11-H11A...O11(x,-1+y,z)	3.607(14)	144.9	3.60(2)	145.0	3.446(18)	145.3	3.46(2)	145.3
C11-H11A…O21(-x,1-y,2-z)	3.458(6)	115.6	3.470(7)	115.5	3.475(7)	115.1	3.489(8)	114.7
C12-H12A…O21(-x,1-y,2-z)	3.313(7)	123.7	3.335(7)	124.7	3.354(8)	125.1	3.371(9)	126.0
C13-H13B…O41(1+x,-1+y,z)	3.390(9)	141.8	3.418(10)	142.0	3.420(10)	142.0	3.456(12)	142.1

C14-H14...O1(1-x,1-y,1-z)	3.295(13)	157.1	3.287(16)	156.9	3.294(15)	156.1	3.308(17)	156.1
C14-H14...O11(1-y,-y,2-z)	3.340(15)	166.4	3.366(18)	166.4	3.385(17)	168.3	3.379(19)	168.1
C4-H4...O4(1+x,-1+y,z)	3.273(7)	170.6	3.276(8)	170.8	3.277(8)	170.6	3.277(10)	170.7
C4-H4...O31(1+x,-1+y,z)	3.355(8)	138.5	3.373(9)	139.0	3.387(10)	139.8	3.401(11)	139.6
C4-H4…O3(1+x, -1+y, z)	3.392(7)	134.7	3.409(8)	134.9	3.419(8)	135.3	3.432(10)	135.5
C4-H4...O41(1+x,-1+y,z)	3.295(8)	159.9	3.306(9)	160.0	3.310(10)	159.2	3.320(13)	159.6
C1-H1B...N1(1+x,y-1,z)	3.570(3)	149.5	3.583(3)	149.8	3.599(3)	150.2	3.614(3)	150.2
C14-H14…N11(1-x,-y,1-z)	3.614(3)	86.2	3.611(4)	87.3	3.616(4)	87.9	3.620(4)	88.4

Table S3b. Selected C-H…N and C-H···O interatomic contacts [Å] and angles [°] for **1** (superstructure) in cooling (from 160 to 15 K) mode and after LIESST experiment (15 K).

$[Fe(hbtz)_2(AlCN)_2](ClO_4)_2$	**160 K**		**150 K**		**140 K**		**120 K**		**100 K**		**15 K**		**15 K (LIESST)**	
	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)	D...A	<(DHA)
C22-H22...N11(-1+x, y, z)	3.671(10)	125.9	3.649(9)	122.7	3.640(6)	122.0	3.618(4)	121.5	3.605(3)	121.2	3.574(3)	120.3	3.526(4)	120.2
C122-H122...N41(1+x, y, z)	3.634(10)	127.6	3.626(9)	126.1	3.605(6)	124.9	3.588(3)	123.2	3.575(3)	122.3	3.538(3)	120.6	3.459(4)	119.2
C23-H23B...N34(1-x, 1-y, 1-z)	4.210(10)	131.5	4.317(9)	125.6	4.358(6)	124.8	4.388(3)	123.7	4.395(3)	123.5	4.389(3)	122.9	4.144(4)	123.3
C123-H23D...N4(2-x, 2-y, -z)	4.088(11)	145.4	4.080(11)	145.8	4.060(7)	143.3	4.027(3)	141.9	4.002(3)	141.3	3.953(3)	140.7	3.774(4)	142.1
C23 - H23B - N13(1-x, 1-y, 1-z)	5.143(11)	84.5	5.283(9)	81.3	5.329(6)	81.3	5.351(3)	80.6	5.358(3)	80.6	5.362(3)	80.1	5.313(4)	78.4
C123 - H23D - N43(2-x, 2-y, -z)	4.833(13)	92.1	4.768(11)	90.8	4.755(7)	88.3	4.750(3)	86.9	4.744(3)	86.2	4.708(3)	85.2	4.755(4)	85.0
C23 - H23B - N14(1-x, 1-y, 1-z)	4.985(11)	96.6	5.155(9)	93.2	5.207(6)	93.2	5.239(3)	92.6	5.248(3)	92.6	5.251(3)	92.1	5.150(4)	89.6
C123 - H23D - N44(2-x, 2-y, -z)	4.647(13)	105.3	4.595(11)	104.7	4.577(7)	102.2	4.557(3)	100.9	4.543(3)	100.3	4.497(3)	99.3	4.470(4)	97.8
C23 - H23B - N11(1-x, 1-y, 1-z)	6.000(12)	82.1	6.251(9)	79.9	6.321(6)	80.2	6.365(3)	80.0	6.378(3)	79.9	6.400(4)	79.6	6.383(4)	76.6
C123 - H23D - N41(2-x, 2-y, -z)	5.415(14)	87.4	5.334(12)	87.0	5.315(8)	85.2	5.309(4)	84.0	5.308(3)	83.5	5.293(3)	82.7	5.333(4)	80.5
C23 - H23B - N12(1-x, 1-y, 1-z)	5.733(11)	77.2	5.926(9)	74.6	5.988(6)	74.9	6.018(3)	74.3	6.028(3)	74.4	6.037(3)	74.0	6.043(4)	72.0
C123 - H23D - N42(2-x, 2-y, -z)	5.253(13)	83.1	5.176(12)	82.0	5.166(7)	79.8	5.170(3)	78.7	5.170(3)	78.1	5.147(3)	77.2	5.230(4)	76.5
C23-H23B...N20(1-x, 1-y, 1-z)	3.873(10)	109.8	3.864(9)	105.1	3.867(6)	104.4	3.859(3)	103.3	3.856(3)	103.2	3.845(3)	102.6	3.774(4)	103.8
C123-H23D...N120(2-x, 2-y, -z)	3.953(12)	119.6	3.924(11)	117.0	3.900(7)	114.0	3.874(3)	112.2	3.853(3)	111.7	3.809(3)	111.0	3.853(3)	114.6
C21-H21A...O1	3.432(10)	161.9	3.430(9)	160.7	3.454(6)	161.4	3.465(3)	160.9	3.469(3)	161.1	3.463(3)	161.2	3.360(3)	160.8
C121-H21D...O1A(1+x, 1+y, z)	3.551(11)	164.9	3.596(9)	158.4	3.627(6)	153.9	3.627(3)	151.2	3.633(3)	149.7	3.638(3)	148.3	3.613(3)	152.2
C21-H21A...O4	3.499(11)	115.8	3.369(8)	113.0	3.337(6)	112.0	3.310(3)	111.4	3.300(3)	111.2	3.277(3)	110.8	3.475(3)	111.8
C121-H21D...O4A(1+x, 1+y, z)	3.841(12)	123.7	3.906(10)	123.6	3.954(6)	121.8	3.986(3)	120.8	4.017(3)	120.4	4.103(3)	120.7	4.246(3)	123.0
C21-H21B...O1A(x, 1+y, z)	3.739(10)	134.1	3.780(9)	136.3	3.767(6)	136.9	3.755(3)	137.3	3.732(3)	137.3	3.692(3)	137.3	3.635(3)	130.5
C121-H21C...O1(1+x, y, z)	3.932(11)	130.5	4.173(10)	132.7	4.270(6)	134.0	4.315(3)	134.4	4.339(3)	134.3	4.371(3)	134.2	4.311(3)	123.2
C21-H21B...O4A(x, 1+y, z)	3.441(9)	161.1	3.506(8)	166.8	3.497(6)	166.8	3.510(3)	168.7	3.504(3)	168.9	3.523(3)	170.0	3.467(3)	170.3
C121-H21C...O4(1+x, y, z)	3.410(9)	149.9	3.470(8)	154.1	3.493(5)	156.9	3.501(3)	158.8	3.501(3)	159.4	3.490(3)	159.1	3.417(3)	151.1
C23-H23B...O3(1-x, 1-y, 1-z)	3.366(14)	134.7	3.490(9)	144.8	3.517(6)	146.9	3.538(3)	149.1	3.546(3)	149.8	3.544(3)	151.1	3.515(3)	144.4
C123-H23D...O2A(1-x, 1-y, -z)	3.296(15)	121.0	3.289(12)	120.0	3.283(7)	120.7	3.291(3)	121.1	3.288(3)	121.2	3.264(3)	121.4	3.289(3)	121.5
C1-H1B...O3(x, 1+y, z)	3.203(9)	117.1	3.122(7)	119.1	3.125(5)	120.3	3.136(3)	121.0	3.130(2)	121.3	3.100(3)	122.1	3.074(3)	121.2
C31-H31B...O2(1+x, y, z)	3.394(9)	144.7	3.434(8)	141.8	3.431(5)	141.5	3.432(3)	141.1	3.435(3)	140.5	3.424(3)	140.6	3.531(3)	139.5
C1-H1A...O1A(x, 1+y, z)	3.720(9)	145.9	3.572(8)	146.3	3.501(5)	146.7	3.465(3)	147.2	3.456(3)	146.9	3.441(3)	146.6	3.627(3)	147.0
C31-H31B...O1(1+x, y, z)	4.020(9)	144.7	4.047(8)	145.6	4.018(5)	145.8	3.984(3)	145.9	3.971(3)	145.8	3.960(3)	146.2	4.335(3)	144.7
C1-H1A...O3A(x, 1+y, z)	3.352(9)	152.3	3.378(8)	149.7	3.372(6)	148.6	3.368(3)	148.0	3.355(3)	147.9	3.323(3)	147.0	3.341(3)	151.6
C31-H31B...O3A(1+x, y, z)	3.906(11)	111.5	3.701(9)	110.3	3.646(6)	111.4	3.612(3)	111.9	3.595(3)	111.7	3.506(3)	111.3	3.502(3)	112.1
C2-H2B...O3(x, 1+y, z)	3.452(9)	121.4	3.482(9)	116.7	3.504(6)	116.0	3.512(3)	116.2	3.514(3)	116.0	3.505(3)	114.6	3.422(3)	115.6
C32-H32B...O2A(1+x, y, z)	3.564(8)	126.6	3.555(7)	125.3	3.556(5)	125.4	3.549(3)	125.3	3.540(3)	125.1	3.510(3)	124.1	3.601(3)	122.0
C3-H3B...O3A(x, 1+y, z)	3.743(12)	136.1	3.809(11)	132.9	3.800(7)	132.1	3.774(4)	132.3	3.753(3)	132.4	3.760(4)	130.4	3.877(4)	131.2
C33-H33B...O2(1+x, y, z)	3.386(8)	149.9	3.359(7)	152.8	3.357(5)	152.8	3.359(3)	151.9	3.357(2)	151.9	3.356(3)	151.9	3.405(3)	153.2
C11-H11A...O1(1-x, 1-y, 1-z)	3.232(10)	127.2	3.140(9)	114.6	3.128(6)	110.3	3.123(3)	107.9	3.121(3)	107.0	3.107(3)	105.9	3.113(3)	110.7
C41-H41A...O1A(1-x, 1-y, -z)	3.443(9)	150.5	3.448(9)	153.6	3.463(6)	154.8	3.456(3)	154.5	3.454(3)	153.9	3.446(3)	152.3	3.484(3)	110.0
C11 - H11A…O2(1-x, 1-y, 1-z)	4.467(11)	127.1	4.655(9)	123.7	4.724(6)	122.6	4.765(3)	121.4	4.782(3)	121.3	4.784(3)	119.8	4.517(3)	126.8
C41-H41B...O2A(1-x, 1-y, -z)	3.554(9)	112.1	3.528(9)	111.5	3.510(6)	111.1	3.472(3)	111.3	3.462(3)	111.8	3.457(3)	112.9	3.499(3)	151.1
C12-H12A...O3A(1-x, 1-y, 1-z)	3.375(11)	115.9	3.463(9)	113.6	3.486(6)	111.9	3.526(3)	110.1	3.541(3)	109.0	3.582(3)	106.7	3.459(3)	113.0

C42-H42B...O2(1-x, 1-y, -z)	3.534(12)	114.6	3.727(10)	113.1	3.806(6)	112.3	3.867(3)	110.7	3.891(3)	110.2	3.930(3)	109.4	3.857(3)	111.8
C42-H42B...O3(1-x, 1-y, -z)	3.907(13)	159.2	3.647(9)	157.8	3.598(6)	156.5	3.568(3)	154.1	3.553(3)	153.2	3.527(3)	152.0	3.523(3)	155.6
C13-H13A...O4A(1-x, 1-y, 1-z)	3.923(11)	109.0	3.832(9)	113.4	3.800(6)	114.5	3.769(3)	115.3	3.745(3)	115.9	3.627(3)	118.8	3.568(3)	117.3
C43-H43A...O4	3.815(10)	152.0	3.933(8)	153.3	3.972(6)	153.1	4.001(3)	151.7	4.010(3)	151.0	4.020(3)	150.6	3.946(3)	154.2
C14-H14...O1(1+x, y, z)	3.192(8)	157.8	3.203(8)	151.9	3.206(5)	150.4	3.207(3)	149.9	3.200(3)	149.6	3.177(3)	148.1	3.186(3)	155.4
C44-H44...O1A(x, 1+y, z)	3.259(8)	162.6	3.264(7)	163.1	3.276(5)	163.1	3.279(3)	163.4	3.280(3)	163.7	3.265(3)	164.2	3.335(3)	165.8
C4-H4...O2A(1+x, 1+y, z)	3.234(8)	134.7	3.193(7)	135.5	3.179(5)	133.8	3.164(3)	133.3	3.156(3)	132.7	3.140(3)	131.7	3.222(3)	131.4
C34-H34...O4	3.228(7)	166.0	3.224(7)	163.7	3.230(5)	163.5	3.236(3)	164.3	3.237(3)	163.9	3.231(3)	164.5	3.254(3)	167.4
C4-H4...O4A(1+x, 1+y, z)	3.240(7)	162.5	3.241(7)	158.5	3.234(5)	158.9	3.219(3)	158.1	3.212(3)	157.9	3.201(3)	157.4	3.239(3)	163.8
C34-H34...O3	3.298(8)	134.4	3.265(8)	132.7	3.255(5)	132.2	3.248(3)	131.6	3.234(3)	131.7	3.208(3)	131.3	3.282(3)	133.7
C1-H1B...N31(x, 1+y, z)	3.536(8)	149.7	3.550(8)	150.3	3.561(6)	149.2	3.552(3)	147.8	3.542(3)	147.2	3.520(3)	147.0	3.496(4)	143.9
C31-H31A...N1(x, y-1, z)	3.535(8)	150.2	3.554(7)	148.7	3.573(5)	147.4	3.571(3)	146.6	3.567(3)	146.4	3.559(3)	144.7	3.521(3)	145.3
C14 - H14 - N11(2-x, 1-y, 1-z)	3.580(8)	75.9	3.569(8)	71.2	3.567(5)	69.4	3.578(3)	68.7	3.575(3)	67.9	3.561(3)	66.7	3.404(3)	73.8
C44 - H44 - N41(1-x, 2-y, -z)	3.851(8)	81.9	3.966(8)	81.0	3.997(5)	79.9	3.991(3)	79.5	3.973(3)	79.2	3.932(3)	78.3	3.761(3)	83.2

Table S4. Selected C-H…N and C-H···O interatomic contacts [Å] and angles [°] for **2**.

	250 K		**200 K**		**160 K**		**100 K**	
C3-H3B···N3	3.426(4)	112.6	3.417(3)	112.4	3.413(3)	112.1	3.406(3)	111.0
C4-H4···N13	3.674(4)	121.6	3.649(3)	121.5	3.513(3)	120.6	3.360(3)	120.0
C11-H11B···N11[j]	3.550(3)	138.9	3.524(3)	139.1	3.517(3)	139.3	3.518(3)	139.9
C13-H13A···N13	3.466(3)	114.3	3.458(3)	114.4	3.448(3)	115.0	3.430(2)	115.6
C22-H22A···N1[k]	3.563(4)	138.7	3.575(3)	138.8	3.636(3)	140.0	3.708(3)	141.4
C1-H1A···O4_$1	3.605(13)	125.5	3.552(10)	124.7	3.527(8)	124.3	3.479(10)	123.7
C1-H1B···O1_$2	3.236(11)	120.4	3.257(8)	120.6	3.241(7)	121.5	3.209(9)	121.4
C1-H1A···O3_$2	3.504(12)	114.4	3.477(8)	112.9	3.441(6)	112.9	3.406(11)	112.3
C2-H2A···O4_$1	3.455(12)	111.7	3.401(8)	112.2	3.363(7)	112.2	3.304(10)	112.4
C3-H3A···O4_$1	3.488(12)	127.0	3.465(7)	125.4	3.428(6)	124.8	3.382(10)	123.0
C4-H4···O1_$3	3.123(9)	149.6	3.111(5)	148.9	3.095(5)	146.5	3.079(8)	142.6
C11-H11A···O4_$3	3.518(10)	167.7	3.527(6)	167.9	3.499(5)	169.0	3.506(9)	168.9
C11-H11B···O3_$4	3.169(10)	119.5	3.197(8)	119.3	3.210(7)	118.3	3.197(11)	116.7
C12-H12A···O3_$4	3.423(10)	120.3	3.454(8)	120.0	3.440(6)	121.2	3.402(12)	122.1
C13-H13B···O4_$5	3.532(9)	152.9	3.532(6)	152.5	3.491(6)	152.5	3.446(9)	152.4
C14-H14···O2_$6	3.337(10)	152.7	3.328(6)	152.7	3.285(5)	151.4	3.242(7)	152.5
C14-H14···O3_$6	3.331(12)	137.6	3.317(8)	137.7	3.282(6)	136.0	3.249(11)	132.9
C21-H21A···O2_$3	3.374(10)	115.2	3.346(5)	114.8	3.345(5)	117.2	3.338(7)	119.6
C21-H21A···O1_$7	3.333(10)	134.2	3.301(6)	134.1	3.272(5)	132.6	3.259(7)	130.5
C21-H21A···O2_$7	3.502(13)	117.5	3.519(12)	117.5	3.471(9)	117.6	3.384(12)	118.3
C1-H1A···O14_$1	3.271(18)	119.8	3.210(15)	119.3	3.235(15)	120.3	3.29(3)	122.3
C1-H1B···O11_$2	3.65(2)	131.3	3.67(2)	131.2	3.608(16)	131.8	3.47(3)	128.9
C1-H1B···O14_$2	3.351(18)	123.4	3.323(17)	123.7	3.329(15)	126.2	3.37(2)	131.4
C2-H2B···O14_$1	3.202(18)	116.6	3.140(17)	116.0	3.153(15)	115.4	3.19(3)	114.2
C3-H3B···O12_$7	3.319(18)	140.6	3.269(19)	141.0	3.279(15)	141.3	3.37(3)	144.3
C3-H3A···O14_$1	3.515(17)	116.5	3.467(16)	115.6	3.450(14)	116.5	3.43(2)	118.0
C4-H4···O11_$3	3.195(16)	154.7	3.189(15)	153.2	3.146(13)	152.1	3.07(2)	146.7
C11-H11A···O14_$3	3.601(19)	170.4	3.589(19)	171.2	3.520(14)	172.6	3.45(2)	173.9
C11-H11B···O13_$4	3.641(19)	119.8	3.57(3)	118.0	3.577(18)	117.7	3.47(3)	117.7
C14-H14···O12_$6	3.322(19)	142.0	3.278(14)	141.5	3.270(12)	141.0	3.239(19)	144.5
C14-H14···O13_$6	3.38(2)	148.1	3.36(2)	145.7	3.302(16)	144.1	3.24(3)	139.1
C21-H21A···O11_$7	3.466(19)	144.7	3.429(16)	144.6	3.404(13)	143.0	3.31(2)	138.5
C21-H21B···O12_$3	3.384(18)	113.1	3.376(15)	112.4	3.356(13)	110.4	3.32(2)	112.8

[j] -1-x,1-y,1-z; [k] 1-x,-y,-z; $1 x, y-1, z-1; $2 -x, -y+1, -z; $3 x, y-1, z; $4 -x, -y+1, -z+1; $5 -x, -y+2, -z+1; $6 x-1, y, z; $7 -x+1, -y+1, -z;

Table S5. Selected Fe-N distances (Å), N-Fe-N and Fe-N-C angles (°), torsion angles (°), Fe···Fe interatomic distances and distances between nitrogen donor atoms (Å) for **1** in cooling mode.

	260 K	240 K	220 K	200 K	190 K	180 K	170 K	160 K	150 K	140K	120K
Fe-N4	2.1589(19)	2.1543(18)	2.1410(18)	2.1194(17)	2.0973(17)	2.0683(18)	2.0409(17)	2.0073(49)	1.9883(44)	1.9770(33)	1.9720(18)
Fe-N14	2.1846(20)	2.1788(18)	2.1668(18)	2.1408(17)	2.1190(17)	2.0876(18)	2.0588(17)	2.0406(50)	2.0123(46)	2.0028(32)	1.9911(18)
Fe-N20	2.1510(22)	2.1450(19)	2.1331(19)	2.1043(19)	2.0794(19)	2.0430(19)	2.0092(18)	1.9874(52)	1.9594(47)	1.9387(34)	1.9339(18)
Fe-N34								2.0150(50)	1.9865(46)	1.9771(33)	1.9754(18)
Fe-N44								2.0406(50)	2.0121(45)	2.0066(32)	1.9928(18)
Fe-N120								1.9813(54)	1.9531(48)	1.9492(34)	1.9418(18)
Fe-N20-C20	176.26 (22)	176.50(20)	176.62(19)	176.54(19)	176.28(18)	176.04(19)	175.83(18)	175.39(55)	175.05(49)	174.15(34)	173.55(18)
Fe-N120-C120								176.52(51)	176.65(46)	175.90(33)	175.42(17)
N4-Fe-N4[a]	180.0	180.0	180.0	180.0	180.0	180.0	180.0	179.74(19)	179.32(18)	179.32(13)	179.33(7)
N14-Fe-N14	180.0	180.0	180.0	180.0	180.0	180.0	180.0	179.35(19)	179.35(18)	179.76(13)	179.87(8)
N4-Fe-N14	87.69(7)	87.70(7)	87.78(7)	87.79(6)	87.77(6)	87.79(7)	87.72(7)	87.39(19)	87.34(18)	87.75(13)	87.84(7)
N4-Fe-N44								91.97(19)	92.00(18)	92.03(13)	92.06(7)
N4-Fe-N20	89.83(7)	89.90(7)	89.89(7)	89.79(7)	89.86(6)	89.79(7)	89.82(7)	89.3(2)	88.91(19)	88.80(13)	88.77(7)
N4-Fe-N120								90.0(2)	90.20(18)	90.23(13)	90.10(7)
N14-Fe-N20	91.84(8)	91.90(7)	91.98(7)	91.90(7)	91.81(7)	91.67(7)	91.65(7)	91.4(2)	92.02(19)	91.82(13)	91.81(7)
N14-Fe-N120								88.38(19)	88.00(19)	88.06(13)	88.12(7)
N11-N12-C11-C12	70.82(33)	70.88(31)	70.42(30)	70.66(28)	70.24(28)	70.35(28)	70.24(28)	71.76(81)	73.67(71)	74.55(50)	75.14(27)
N12-C11-C12-C13	65.84(34)	65.62(31)	66.00(30)	65.93(29)	66.16(28)	65.76(29)	65.80(28)	67.21(86)	69.10(76)	70.09(52)	71.03(27)
C11-C12-C13-C13[b]	175.82(30)	175.77 (28)	175.93(27)	175.94(26)	176.08(25)	175.93(25)	175.80(25)	174.83(74)	176.63(66)	176.66(46)	176.42(24)
N41-N42-C41-C42								-69.18(78)	-68.84(74)	-68.87(53)	-69.57(28)
N42-C41-C42-C43								-65.52(80)	-66.18(73)	-66.80(52)	-67.77(27)
C41-C42-C43-C43[c]								-174.35(75)	-174.15(66)	-174.12(46)	-173.82(25)
N1-N2-C1-C2	-67.43(28)	-67.29(26)	-66.79(25)	-66.71(24)	-66.75(24)	-67.25(24)	-67.87(24)	-70.59(73)	-72.77(72)	-72.86(50)	-71.73(27)
N2-C1-C2-C3	-58.10(29)	-57.89(26)	-57.63(26)	-57.40(24)	-57.51(24)	-57.56(24)	-57.56(23)	-56.39(78)	-54.21(86)	-54.69(59)	-56.41(30)
C1-C2-C3-C3[d]	-178.89(28)	-179.27(25)	-179.15(25)	-178.76(23)	-178.65(23)	-178.48(23)	-178.07(23)	-177.64(71)	-179.27(78)	-178.16(54)	-178.15(28)
N31-N32-C31-C32								68.69(68)	67.59(63)	66.87(46)	66.85(25)
N32-C31-C32-C33								57.70(64)	56.95(60)	57.27(44)	57.00(24)
C31-C32-C33-C33[e]								176.32(59)	176.23(54)	176.10(39)	176.73(22)
Fe-Fe[f]	13.1029(28)	13.1011(18)	13.0857(12)	13.0717(6)	13.0473(5)	13.0109(5)	12.9721(6)	12.8874(19)	12.8196(17)	12.7937(12)	12.7904(6)
Fe-Fe[g]								13.0718(20)	13.1774(17)	13.2338(12)	13.2746(7)
Fe-Fe[h]	12.1531(30)	12.1530(18)	12.1477(13)	12.1454(6)	12.1381(5)	12.1246(5)	12.1085(6)	12.2151(20)	12.2969(17)	12.3439(13)	12.4026(7)
Fe-Fe[i]								12.0149(20)	11.9776(17)	11.9749(13)	11.9802(7)
N4···N4[h]	9.6097(44)	9.6063(37)	9.5975(34)	9.5933(32)	9.5987(32)	9.5954(33)	9.5944(32)	9.6685(94)	9.7069(86)	9.7527(65)	9.8087(35)
N34…N34[i]								9.5244(96)	9.5002(88)	9.4843(63)	9.4739(35)
N14···N14[f]	10.0884(41)	10.0948(36)	10.0993(35)	10.1190(33)	10.1192(33)	10.1257(33)	10.1217(33)	10.1097(97)	10.1157(88)	10.1315(63)	10.1590(34)
N44…N44[g]								10.2027(100)	10.3119(86)	10.3606(64)	10.4216(34)
Pl…Fe1	8.0302	8.0090	7.9860	7.9603	7.9501	7.9416	7.9353	8.0717(22)	8.1103(19)	8.0935(14)	8.0601(7)
Pl…Fe1[a]								7.8868(15)	7.8494(11)	7.8272(8)	7.8080(4)

[a] 1-x,1-y,1-z; [b] 1-x, -y, 2-z (average) / 2-x, 2-y, 1-z (superstructure); [c] 1-x, 1-y, -z; [d] -x, 1-y, 2-z (average) / 1-x, 2-y, 1-z (superstructure); [e] 2-x,1-y,-z; [f] 1-x, -y, 2-z (average) / 2-x, 2-y, 1-z (superstructure); [g] 1-x, 1-y, -z; [h] -x, 1-y, 2-z (average) / 1-x, 2-y, 1-z (superstructure); [i] 2-x,1-y,-z

Continued Table S5 (cooling mode)

	100K	15K	15K(LIESST)
Fe-N4	1.9725(17)	1.9730(19)	2.1610(21)
Fe-N14	1.9901(17)	1.9906(20)	2.1882(21)
Fe-N20	1.9330(17)	1.9333(22)	2.1453(26)
Fe-N34	1.9709(17)	1.9745(19)	2.1630(21)
Fe-N44	1.9923(17)	1.9924(19)	2.1919(21)
Fe-N120	1.9399(17)	1.9417(23)	2.1594(27)
Fe-N20-C20	173.44(16)	173.69(18)	176.83(21)
Fe-N120-C120	175.32(16)	175.40(18)	176.28(20)
N4-Fe-N4[a]	179.30(7)	179.17(8)	178.50(9)
N14-Fe-N14	179.91(7)	179.93(9)	178.50(8)
N4-Fe-N14	87.86(7)	87.83(8)	87.06(8)
N4-Fe-N44	92.05(7)	92.14(8)	91.76(8)
N4-Fe-N20	88.71(7)	88.65(8)	88.37(8)
N4-Fe-N120	90.03(7)	90.14(8)	89.65(8)
N14-Fe-N20	91.74(7)	91.79(8)	91.36(8)
N14-Fe-N120	88.11(7)	88.11(8)	87.75(8)
N11-N12-C11-C12	75.29(24)	75.31(26)	71.63(29)
N12-C11-C12-C13	71.76(24)	73.46(25)	70.77(28)
C11-C12-C13-C13[b]	176.48(22)	177.97(23)	-179.42(26)
N41-N42-C41-C42	-69.79(25)	-69.78(27)	-70.63(30)
N42-C41-C42-C43	-68.01(25)	-67.95(25)	-64.72(29)
C41-C42-C43-C43[c]	-174.00(22)	-173.71(24)	-173.90(26)
N1-N2-C1-C2	-70.98(24)	-70.41(29)	-62.20(31)
N2-C1-C2-C3	-57.11(25)	-56.14(33)	-57.09(33)
C1-C2-C3-C3[d]	-177.74(23)	-178.86(29)	179.74(30)
N31-N32-C31-C32	66.71(23)	65.45(27)	62.33(29)
N32-C31-C32-C33	56.61(22)	56.14(26)	55.60(29)
C31-C32-C33-C33[e]	176.86(20)	176.63(24)	178.16(27)
Fe-Fe[f]	12.7908(6)	12.7741(7)	13.0546(8)
Fe-Fe[g]	13.2839(6)	13.2825(7)	13.3520(8)
Fe-Fe[h]	12.4192(6)	12.4000(7)	12.4895(9)
Fe-Fe[i]	11.9740(6)	11.9350(7)	11.8504(9)
N4···N4[h]	9.8230(32)	9.8009(38)	9.8150(43)
N34…N34[i]	9.4650(32)	9.4165(38)	9.3499(42)
N14···N14[f]	10.1656(32)	10.1610(39)	10.1378(41)
N44…N44[g]	10.4354(32)	10.4440(39)	10.2420(41)
Pl…Fe1	8.0292(7)	7.9692(7)	8.0977(9)
Pl…Fe1[a]	7.7886(4)	7.7461(4)	7.8177(5)

[a] 1-x,1-y,1-z; [b] 1-x, -y, 2-z (average) / 2-x, 2-y, 1-z (superstructure); [c] 1-x, 1-y, -z; [d] -x, 1-y, 2-z (average) / 1-x, 2-y, 1-z (superstructure); [e] 2-x,1-y,-z; [f] 1-x, -y, 2-z (average) / 2-x, 2-y, 1-z (superstructure); [g] 1-x, 1-y, -z; [h] -x, 1-y, 2-z (average) / 1-x, 2-y, 1-z (superstructure); [i] 2-x,1-y,-z

Table S5. Selected Fe-N distances (Å), N-Fe-N and Fe-N-C angles (°), torsion angles (°), Fe···Fe interatomic distances and distances between nitrogen donor atoms (Å) for **1** in heating mode.

Table 1	120 K	140 K	150 K	160 K	170 K	180 K	190 K	200 K	220 K	240K
Fe-N4	1.9718(18)	1.9771(31)	1.9908(51)	2.0155(55)	2.0414(17)	2.0693(17)	2.0958(17)	2.1204(17)	2.1459(17)	2.1557(18)
Fe-N14	1.9913(18)	1.9993(31)	2.0158(52)	2.0474(55)	2.0574(17)	2.0887(17)	2.1168(17)	2.1416(17)	2.1669(17)	2.1781(18)
Fe-N20	1.9347(18)	1.9402(31)	1.9543(52)	1.9765(56)	2.0107(18)	2.0443(19)	2.0784(19)	2.1018(19)	2.1303(19)	2.1442(19)
Fe-N34	1.9739(18)	1.9832(31)	1.9909(51)	2.0107(56)						
Fe-N44	1.9915(18)	2.0017(31)	2.0095(52)	2.0412(58)						
Fe-N120	1.9424(18)	1.9458(32)	1.9514(55)	1.9748(58)						
Fe-N20-C20	173.53(18)	173.79(32)	174.47(53)	175.00(60)	175.81(18)	176.12(19)	176.41(19)	176.49(18)	176.76(19)	176.35(20)
Fe-N120-C120	175.51(17)	175.89(30)	177.01(54)	176.43(56)						
N4-Fe-N4[a]	179.23(7)	179.29(12)	179.34(19)	179.2(2)	180.0	180.0	180.0	180.0	180.0	180.0
N14-Fe-N14	179.95(8)	179.69(13)	179.47(19)	179.2(2)	180.0	180.0	180.0	180.0	180.0	180.0
N4-Fe-N14	87.89(7)	87.68(12)	87.4(2)	86.9(2)	87.78(6)	87.76(6)	87.73(6)	87.82(6)	87.77(6)	87.78(7)
N4-Fe-N44	92.07(7)	92.01(13)	92.1(2)	92.4(2)						
N4-Fe-N20	88.68(7)	88.85(13)	89.0(2)	89.4(2)	89.77(6)	89.73(7)	89.79(6)	89.82(6)	89.84(7)	89.80(7)
N4-Fe-N120	90.18(7)	90.19(13)	90.4(2)	90.2(2)						
N14-Fe-N20	91.70(7)	91.76(12)	91.9(2)	91.3(2)	91.64(7)	91.69(7)	91.79(7)	91.83(6)	91.95(7)	91.85(7)
N14-Fe-N120	88.17(7)	88.13(12)	87.9(2)	88.5(2)						
N11-N12-C11-C12	74.92(26)	74.08(47)	73.46(80)	73.23(91)	69.76(27)	70.36(28)	70.59(28)	70.62(28)	70.48(29)	70.71(31)
N12-C11-C12-C13	71.43(27)	70.98(48)	69.22(85)	65.88(1.00)	65.99(27)	65.94(28)	65.80(29)	65.69(29)	65.99(30)	65.84(31)
C11-C12-C13-C13[b]	176.57(24)	176.58(43)	176.54(73)	174.70(84)	176.12(24)	175.75(25)	176.15(25)	175.97(25)	176.06(27)	175.77(28)
N41-N42-C41-C42	-69.79(28)	-69.30(50)	-68.56(85)	-69.22(89)						
N42-C41-C42-C43	-67.64(27)	-66.77(50)	-66.30(85)	-64.56(92)						
C41-C42-C43-C43[c]	-174.04(24)	-173.88(45)	-173.38(75)	-174.00(81)						
N1-N2-C1-C2	-71.39(27)	-72.60(48)	-72.41(82)	-71.44(82)	-67.96(23)	-67.47(24)	-67.08(24)	-66.78(24)	-66.77(25)	-67.39(26)
N2-C1-C2-C3	-56.70(29)	-54.92(57)	-54.45(96)	-54.95(89)	-57.76(23)	-57.58(24)	-57.49(24)	-57.27(24)	-57.60(25)	-57.69(27)
C1-C2-C3-C3[d]	-178.01(27)	-177.76(52)	-178.45(86)	-177.68(84)	-178.14(22)	-178.50(22)	-178.55(23)	-178.97(23)	-179.04(24)	-179.03(25)
N31-N32-C31-C32	66.69(25)	66.71(43)	66.52(71)	68.72(75)						
N32-C31-C32-C33	57.31(23)	57.64(41)	57.24(67)	56.62(72)						
C31-C32-C33-C33[e]	176.99(22)	176.53(38)	176.41(62)	176.72(66)						
Fe-Fe[f]	12.7892(6)	12.7913(12)	12.8177(18)	12.8931(19)	12.9709(5)	13.0088(5)	13.0455(6)	13.0715(5)	13.0951(6)	13.0955(14)
Fe-Fe[g]	13.2745(7)	13.2377(12)	13.1792(18)	13.0721(20)						
Fe-Fe[h]	12.4017(7)	12.3480(12)	12.3007(18)	12.2177(20)	12.1095(5)	12.1252(5)	12.1393(6)	12.1470(5)	12.1525(6)	12.1561(15)
Fe-Fe[i]	11.9805(7)	11.9761(12)	11.9780(18)	12.0139(19)						
N4···N4[h]	9.8030(34)	9.7552(61)	9.7091(98)	9.6480(106)	9.5923(31)	9.5953(32)	9.5966(32)	9.5964(32)	9.5930(33)	9.6032(36)
N34…N34[i]	9.4768(34)	9.4788(60)	9.4873(99)	9.5651(106)						
N14···N14[f]	10.1609(34)	10.1318(60)	10.1012(99)	10.0904(108)	10.1238(32)	10.1221(33)	10.1215(32)	10.1167(32)	10.1089(34)	10.0949(36)
N44…N44[g]	10.4217(34)	10.3709(61)	10.2958(101)	10.1870(111)						
Pl…Fe1	8.0582 (7)	8.0974(13)	8.1135(20)	8.0710(22)	7.9360	7.9416	7.9502	7.9603	7.9828	8.0118
Pl…Fe1[a]	7.8068 (4)	7.8281(8)	7.8477(11)	7.8835(14)						

[a] 1-x,1-y,1-z; [b] 1-x, -y, 2-z (average) / 2-x, 2-y, 1-z (superstructure); [c] 1-x, 1-y, -z; [d] -x, 1-y, 2-z (average) / 1-x, 2-y, 1-z (superstructure); [e] 2-x,1-y,-z; [f] 1-x, -y, 2-z (average) / 2-x, 2-y, 1-z (superstructure); [g] 1-x, 1-y, -z; [h] -x, 1-y, 2-z (average) / 1-x, 2-y, 1-z (superstructure); [i] 2-x,1-y,-z

Continued Table S5 (heating mode)

Table 1	260K	280 K	300 K
Fe-N4	2.1632(18)	2.1671(19)	2.1677(20)
Fe-N14	2.1852(19)	2.1884(19)	2.1902(21)
Fe-N20	2.1485(20)	2.1539(21)	2.1542(22)
Fe-N34			
Fe-N44			
Fe-N120			
Fe-N20-C20	176.40(21)	176.13(22)	175.91(24)
Fe-N120-C120			
N4-Fe-N4[a]	180.0	180.0	180.0
N14-Fe-N14	180.0	180.0	180.0
N4-Fe-N14	87.76(7)	87.68(7)	87.69(8)
N4-Fe-N44			
N4-Fe-N20	89.81(7)	89.79(7)	89.82(8)
N4-Fe-N120			
N14-Fe-N20	91.75(7)	91.71(8)	91.71(8)
N14-Fe-N120			
N11-N12-C11-C12	70.82(32)	70.48(34)	70.56(37)
N12-C11-C12-C13	65.78(33)	66.02(34)	66.08(38)
C11-C12-C13-C13[b]	175.82(29)	175.45(31)	175.53(34)
N41-N42-C41-C42			
N42-C41-C42-C43			
C41-C42-C43-C43[c]			
N1-N2-C1-C2	-67.82(27)	-68.59(28)	-68.90(30)
N2-C1-C2-C3	-58.07(28)	-58.02(29)	-58.59(32)
C1-C2-C3-C3[d]	-178.97(27)	-178.90(29)	-179.30(31)
N31-N32-C31-C32			
N32-C31-C32-C33			
C31-C32-C33-C33[e]			
Fe-Fe[f]	13.0974(17)	13.1006(19)	13.1014(22)
Fe-Fe[g]			
Fe-Fe[h]	12.1561(18)	12.1603(21)	12.1650(24)
Fe-Fe[i]			
N4···N4[h]	9.6056(39)	9.6128(40)	9.6202(44)
N34…N34[i]			
N14···N14[f]	10.0891(37)	10.0832(39)	10.0818(42)
N44…N44[g]			
Pl…Fe1	8.0357	8.0584	8.0752
Pl…Fe1[a]			

[a] 1-x,1-y,1-z; [b] 1-x, -y, 2-z (average) / 2-x, 2-y, 1-z (superstructure); [c] 1-x, 1-y, -z; [d] -x, 1-y, 2-z (average) / 1-x, 2-y, 1-z (superstructure); [e] 2-x,1-y,-z; [f] 1-x, -y, 2-z (average) / 2-x, 2-y, 1-z (superstructure); [g] 1-x, 1-y, -z; [h] -x, 1-y, 2-z (average) / 1-x, 2-y, 1-z (superstructure); [i] 2-x,1-y,-z

Intermolecular contacts involving =CH- and -CH_2- groups of allyl cyanide in 1.

There is only one very distant contact C22-H22...N11(1+x,-1+y,z) established between =CH– group of bent conformer and tetrazole ring of neighboring layer which remains in the range 3.6–3.75Å (280–170 K). Both types of conformers interact with perchlorate anions through –CH_2– groups. Finally perchlorate anions form C4-H4…O4(ClO_4^-) contacts with tetrazole rings. Unfortunately, because of severe disordering of both allyl cyanide molecules and perchlorate anions more detailed discussion of intermolecular contacts is not possible.

Intramolecular contact within polymeric layer in 2.

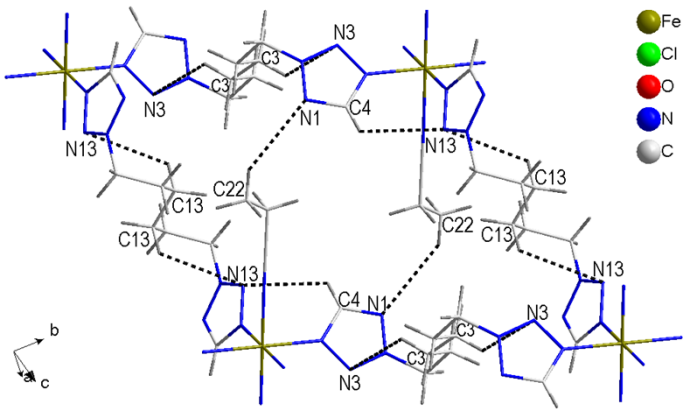
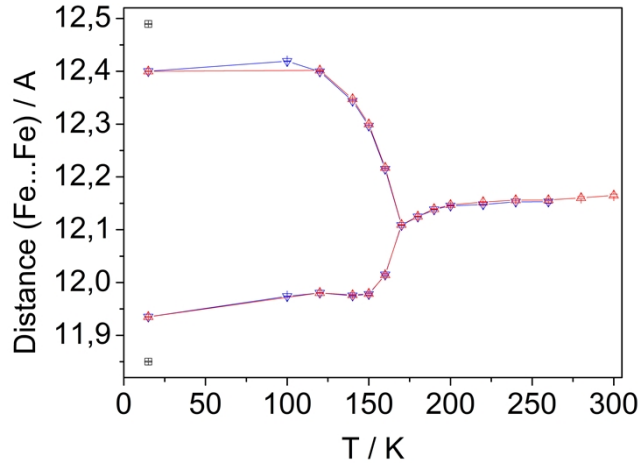


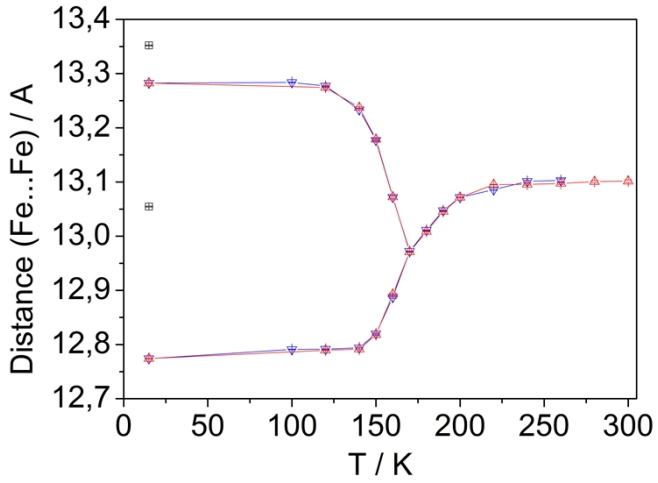
Figure S1. Drawing showing C-H...N contacts established within polymeric layer (black dotted lines) in **2**.

A comparison of changes of rhombic windows dimensions in 1 and 2.

In **2**, SCO involves shrinkage of the rhombic window formed within polymeric layer. In the temperature range 250 and 150 K, the smaller diagonal (established between the corner iron atoms) decreases from 10.42 to 10.34 Å whereas the larger one decreases from 22.23 to 21.63 Å. These alterations are very similar to those noticed in acetonitrile analog, in which corresponding diagonals are reduced from 10.32 to 10.22 and 22.37 to 21.82 Å, in the same temperature range. A presence of larger allyl cyanide molecules in **1** causes that the deformation of rhombic window does not correspond to the one observed in acetonitrile and propionitrile analogs. Thus, the smaller diagonal is reduced at the similar extent (10.36 at 260 K, 10.24 at 160 K, 10.18 at 150 K and 10.13 at 120 K) but the longer diagonal slightly increases at lower temperatures (23.02 at 260K, 22.91 K at 160 K, 22.97 at 150 K and 23.09 at 120 K).



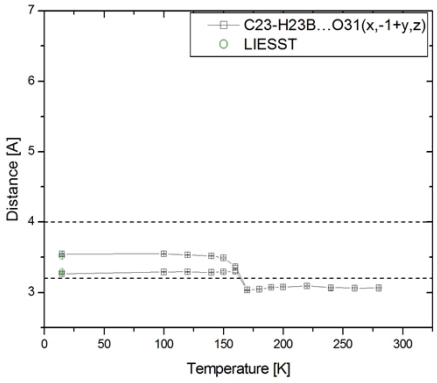
a)

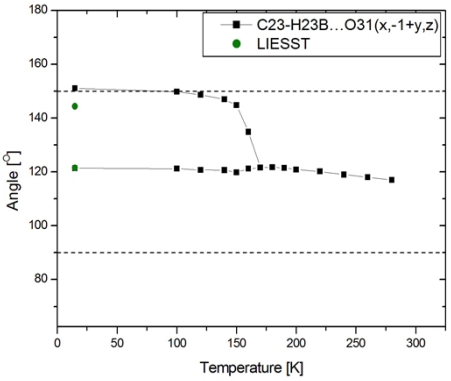


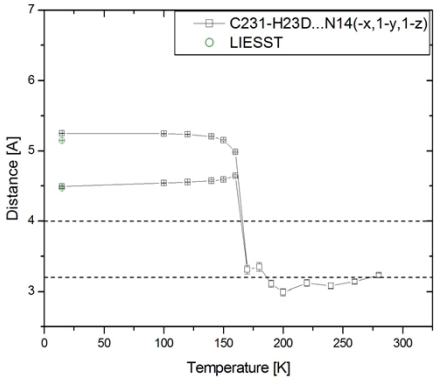
b)

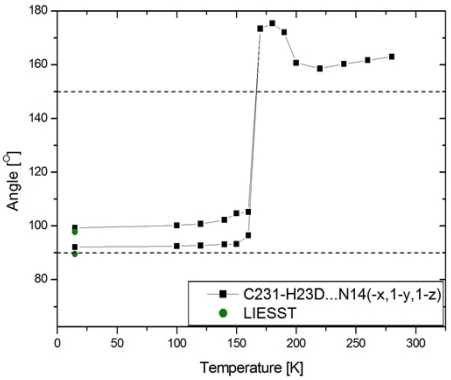
Figure S2. Temperature dependence of distances between Fe(II) ions bridged in [1-11] (a) and [001] (b) directions in **1**.

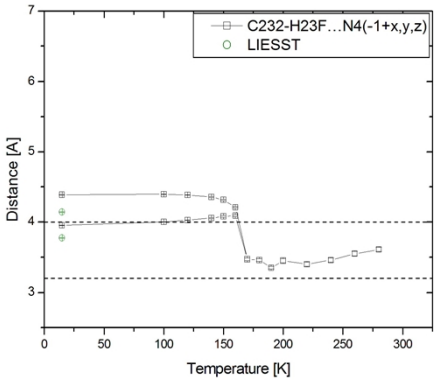
Selected intermolecular distances in 1.

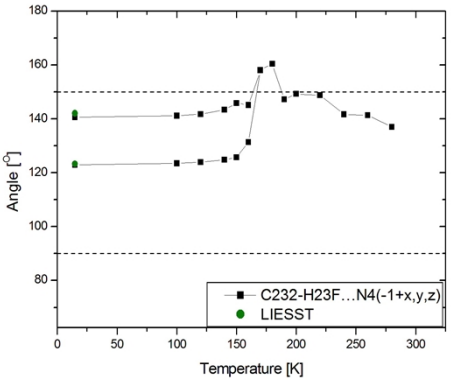


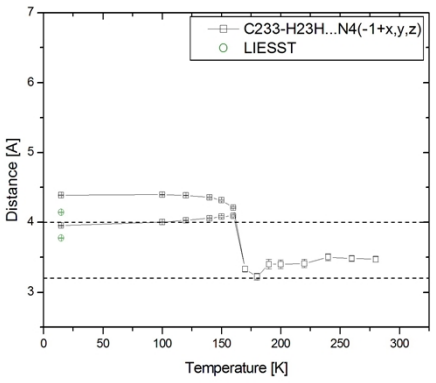


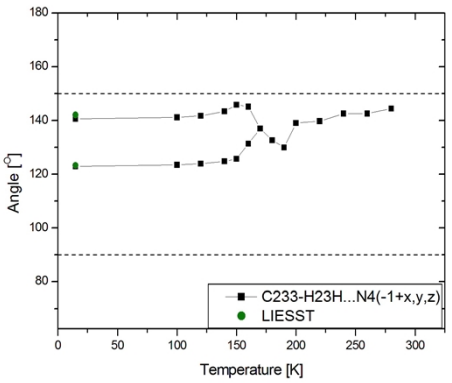












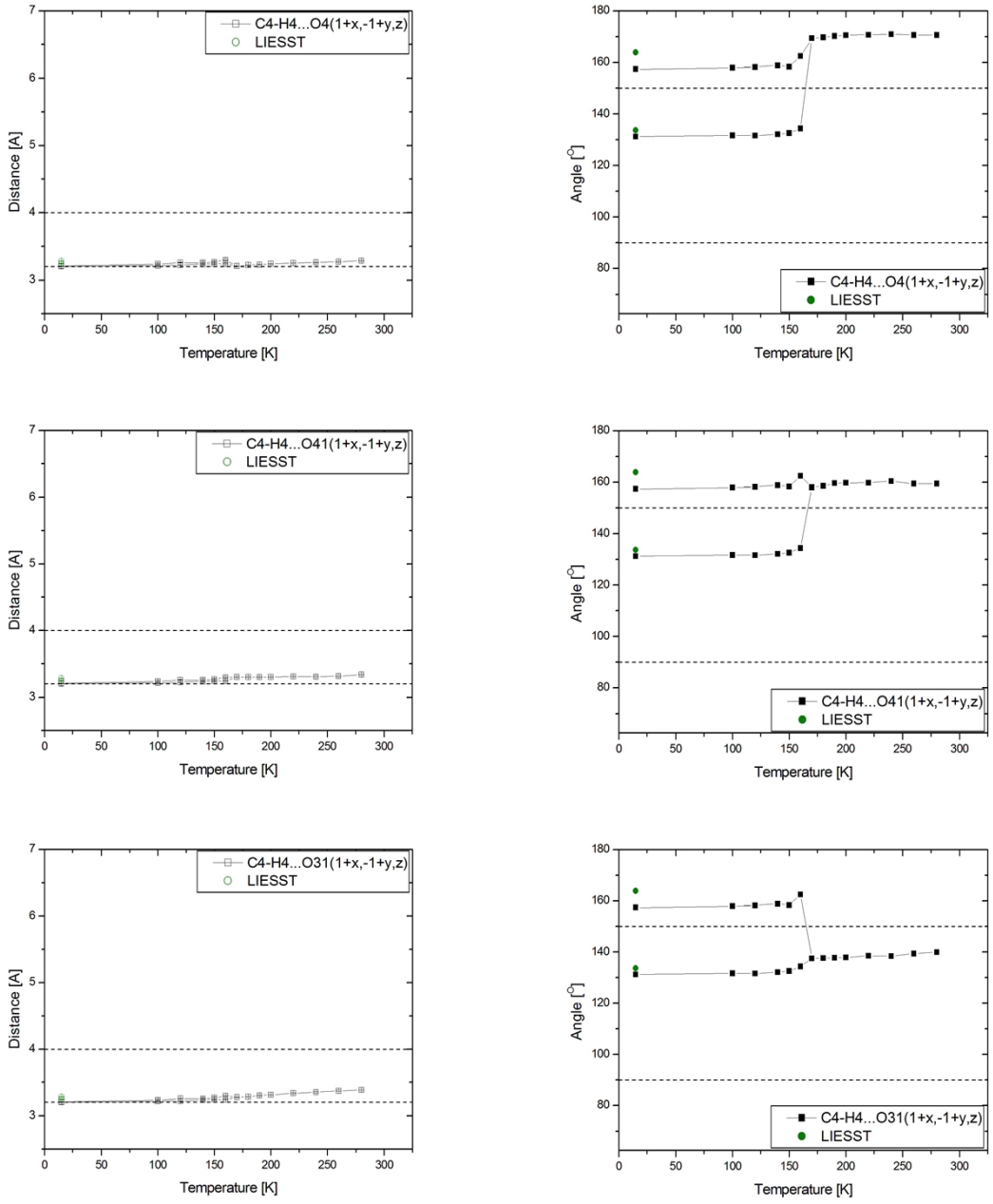


Figure S3. Alteration of selected intermolecular distances related to formation of superstructure in **1**.

The temperature dependence of the lattice parameters.

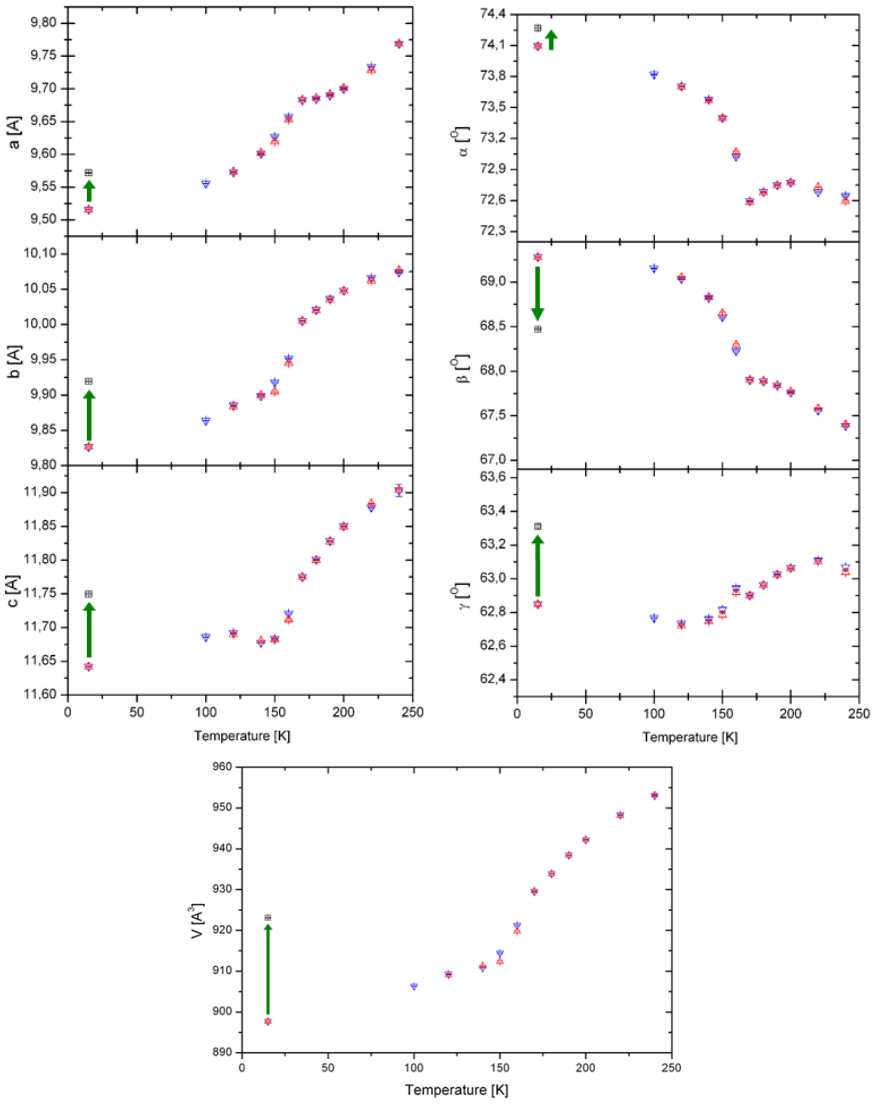


Figure S4. Temperature dependence of the lattice parameters for complex **1** (blue upside-down triangle: on cooling; red triangle: on heating; black square: after laser irradiation).

The intensity of the superstructure reflections.

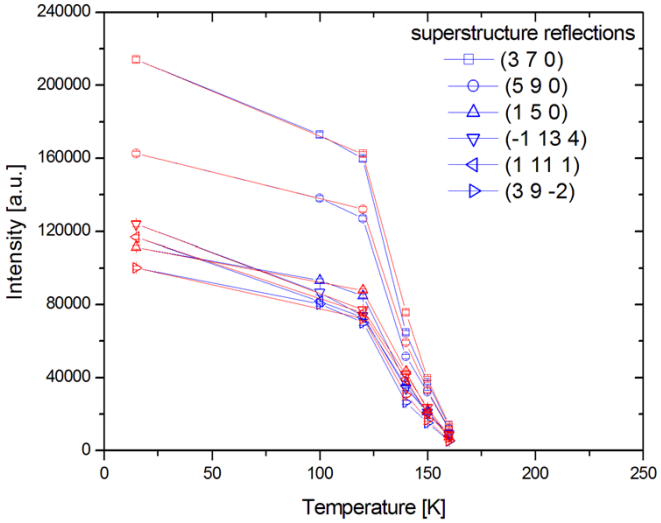
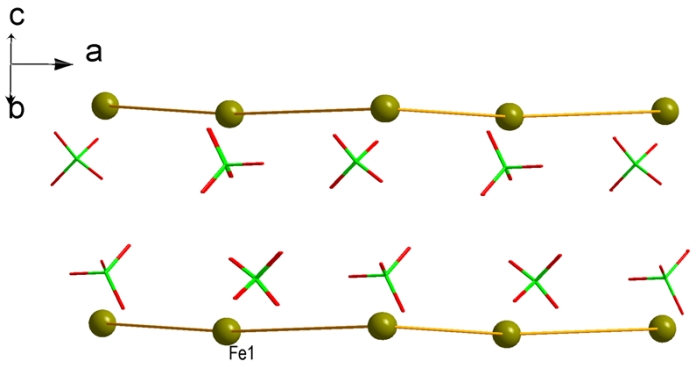
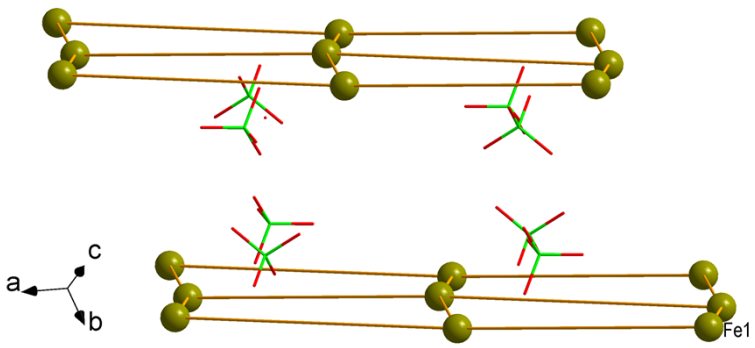


Figure S5. Temperature dependence of the intensity of the selected superstructure reflections for compound **1** (upside-down triangle: on cooling; triangle: on heating).

Corrugation of the polymeric layers in 1.



a)



b)

Figure S6. Corrugation of the polymeric layers in **1.**