Supporting Information

Electron transfer coupled spin transition in cyano-bridged mixed-valence {Fe$^{III}_2$Fe$^{II}_2$} molecular squares

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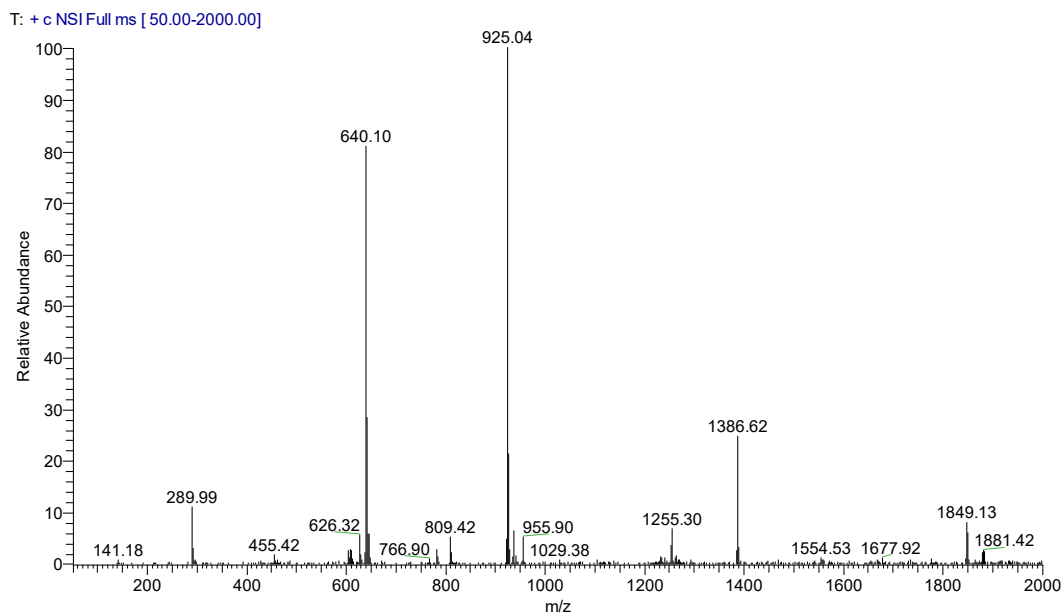
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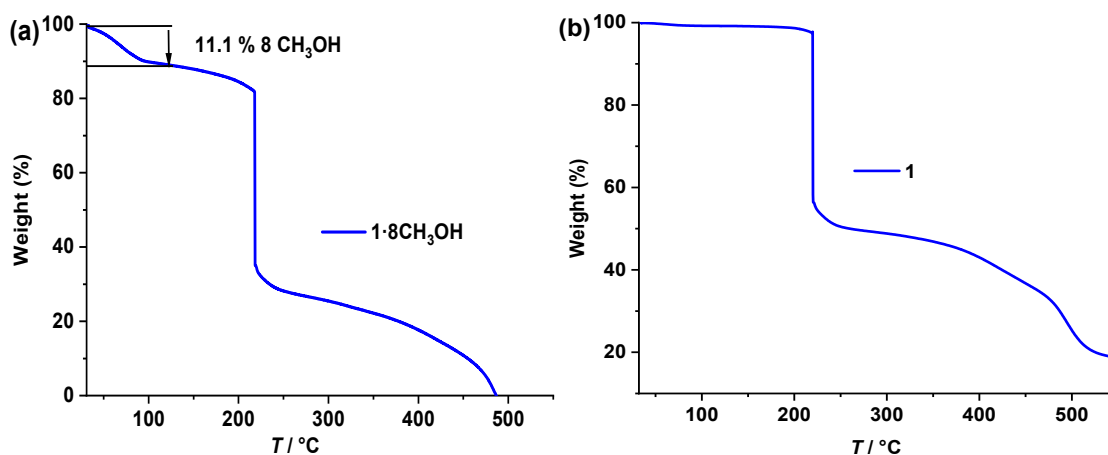
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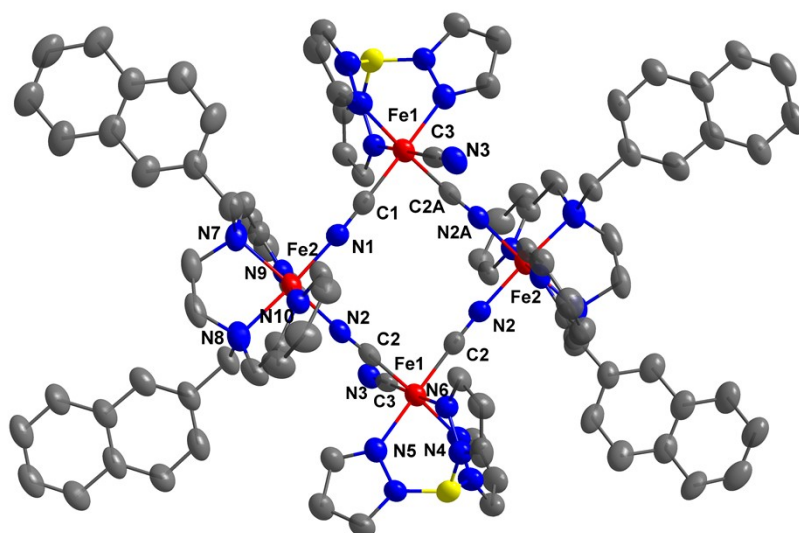
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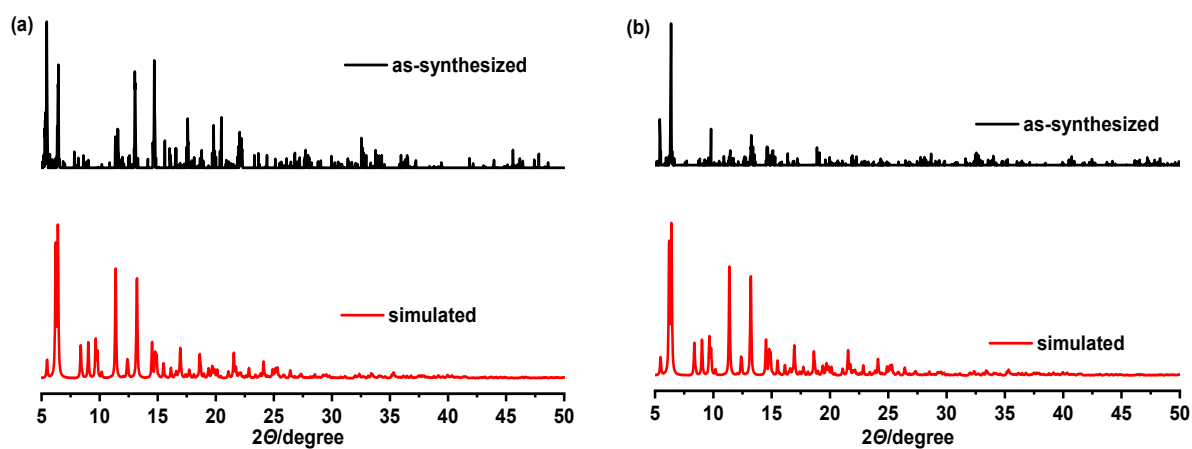
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Table S1. Crystal data and structure refinement for **1**·8CH$_3$OH.

Compound	**1**·8CH$_3$OH		
CCDC	2183791	2215522	2215521
T(K)	298	165	100
Formula		C$_{104}$H$_{120}$B$_2$Fe$_4$N$_{26}$Cl$_2$O$_{16}$	
Formula weight		2306.2	
Crystal system		Triclinic	
Space group		$P\bar{1}$	
Z		1	
a /Å	11.103(7)	11.006(9)	10.964(2)
b /Å	16.132(3)	15.852(4)	15.816(9)
c /Å	17.708(3)	17.6035(16)	17.507(2)
α /°	111.734(7)	111.570(3)	111.488(5)
β /°	93.802(7)	93.521(4)	93.295(5)
γ /°	106.978(6)	106.655(3)	106.620(4)
V / Å^3	2763.0(8)	2687.9(4)	2661.6(5)
d_{calc} (mg/m^3)	1.232	1.266	1.279
μ / mm^{-1}	3.48	3.58	3.61
F(000)	1058	1058	1058
Collected reflections	48878	39555	45600
Unique reflections	9293	8821	8737
R_{int}	0.078	0.069	0.059
Goodness-of-fit on F^2	1.06	1.06	1.06
R_1 [I >2σ (I)]	0.062	0.054	0.038
wR_2 [I >2σ (I)]	0.185	0.156	0.107

$R_1 = \Sigma$ (|F_o|−|F_c|) / Σ |F_o|; $wR_2 = [\Sigma$ w (|F_o|−|F_c|)^2 / Σ w F_o^2]$^{1/2}$.

Table S2. Selected bond lengths (Å) of **1**·8CH$_3$OH at different temperatures.

	1·8CH$_3$OH $^{298\ K}$	**1**·8CH$_3$OH $^{165\ K}$	**1**·8CH$_3$OH $^{100\ K}$
Fe1−C1	1.933(3)	1.876(3)	1.865(2)
Fe1−C2	1.912(4)	1.867(3)	1.862(2)
Fe1−C3	1.936(4)	1.930(4)	1.922(3)
Fe1−N4	1.997(3)	2.002(3)	2.003(2)
Fe1−N5	1.997(3)	2.007(3)	2.011(2)
Fe1−N6	1.984(3)	1.994(3)	1.995(2)
Fe2−N1	2.121(3)	2.022(3)	1.993(2)
Fe2−N2	2.121(3)	2.024(3)	1.994(2)
Fe2−N7	2.282(3)	2.240(3)	2.225(2)
Fe2−N8	2.286(3)	2.246(3)	2.232(2)
Fe2−N9	2.193(3)	2.150(3)	2.132(2)
Fe2−N10	2.201(3)	2.164(3)	2.144(2)
Fe1−C$_{C≡N}$	1.927(4)	1.891(4)	1.883(3)
Fe1−N$_{Tp}$	1.993(3)	2.001(3)	2.003(2)
Fe2−N$_{C≡N}$	2.121(3)	2.023(3)	1.994(2)
Fe2-N$_{bnbpen}$	2.241(3)	2.200(3)	2.183(2)
π-π distances	3.400(2)-3.444(2)	3.360(2)-3.399(3)	3.338(3)-3.377(4)

Table S3. Selected bond angles (°) of **1**·8CH$_3$OH at different temperatures.

	1·8CH$_3$OH $^{298\ K}$	**1**·8CH$_3$OH $^{165\ K}$	**1**·8CH$_3$OH $^{100\ K}$
C1A−Fe1−C3	89.42(14)	91.91(13)	91.97(10)
C1A−Fe1−N4	177.46(13)	176.41(12)	176.29(9)
C1A−Fe1−N5	92.48(13)	91.65(12)	91.40(9)
C1A−Fe1−N6	89.58(13)	89.18(12)	89.34(9)
C2−Fe1−C1A	88.32(13)	90.25(13)	90.79(10)
C2−Fe1−C3	87.05(14)	88.31(13)	88.55(10)
C2−Fe1−N4	90.80(12)	90.76(12)	90.64(9)
C2−Fe1−N5	176.75(14)	176.72(12)	176.57(9)
C2−Fe1−N6	94.35(14)	94.20(13)	94.15(9)
C3−Fe1−N4	92.92(13)	91.57(12)	91.49(9)
C3−Fe1−N5	89.80(14)	88.95(13)	88.74(9)
C3−Fe1−N6	178.25(14)	177.26(13)	176.99(9)
N10−Fe2−N7	95.06(10)	93.33(10)	93.12(7)
N10−Fe2−N8	76.06(10)	76.46(10)	76.81(7)
N1−Fe2−N10	94.75(11)	95.94(11)	95.90(8)
N1−Fe2−N2	95.02(11)	96.86(11)	97.53(8)
N1−Fe2−N7	165.24(10)	165.28(11)	165.47(8)
N1−Fe2−N8	91.52(11)	90.41(10)	90.09(8)
N1−Fe2−N9	94.14(11)	93.71(11)	93.87(8)
N2−Fe2−N10	91.11(11)	91.22(10)	91.39(8)
N2−Fe2−N7	95.79(11)	94.35(10)	93.60(7)
N2−Fe2−N8	166.06(11)	166.32(10)	166.59(8)
N2−Fe2−N9	92.24(11)	93.03(11)	92.93(8)
N4−Fe1−N5	88.53(11)	87.50(11)	87.33(8)
N6−Fe1−N4	88.11(12)	87.32(11)	87.15(8)
N6−Fe1−N5	88.80(13)	88.49(12)	88.52(9)
N7−Fe2−N8	80.20(11)	80.64(10)	80.89(7)
N9−Fe2−N10	170.19(10)	168.92(10)	168.70(7)
N9−Fe2−N7	75.43(10)	76.16(10)	76.20(7)
N9−Fe2−N8	99.57(10)	98.06(10)	97.56(7)

Symmetry code: A = -x+1, -y+1, -z.

Table S4. Crystal data and structure refinement for **1**.

	1		
CCDC	2220543	2220544	2183792
T /K	298	200	100
Formula		$C_{96}H_{88}B_2Fe_4N_{26}Cl_2O_8$	
Formula weight		2049.8	
Crystal system		Triclinic	
Space group		$P\bar{1}$	
a /Å	11.646(2)	11.684(2)	10.998(3)
b /Å	14.444(3)	14.378(3)	15.766(5)
c /Å	16.283(3)	16.243(3)	16.541(5)
α /°	107.241(8)	107.075(9)	110.445(4)
β /°	94.910(8)	94.534(10)	93.745(5)
γ /°	104.543(8)	104.418(9)	108.936(4)
V / Å^3	2494.0(8)	2492.0(9)	2489.8(12)
d_{calc} (mg/m^3)	1.365	1.366	1.367
μ / mm^{-1}	3.85	3.86	3.92
F(000)	1058	1058	1058
Collected reflections	37304	29759	16395
Unique reflections	8204	8127	8090
R_{int}	0.095	0.095	0.047
Goodness-of-fit on F^2	1.02	1.04	1.03
R_1 [$I > 2\sigma(I)$]	0.072	0.079	0.089
wR_2 [$I > 2\sigma(I)$]	0.229	0.229	0.273

$R_1 = \Sigma \, (|F_o|-|F_c|) \, / \, \Sigma \, |F_o|$; $wR_2 = [\Sigma \, w \, (|F_o|-|F_c|)^2 \, / \, \Sigma \, w \, F_o^2]^{1/2}$.

Table S5. Selected bond lengths (Å) of **1** at different temperatures.

	1[298K]	**1**[200K]	**1**[100K]
Fe1−C1	1.906(6)	1.920(5)	1.877(7)
Fe1−C2	1.913(6)	1.924(6)	1.862(7)
Fe1−C3	1.921(6)	1.926(6)	1.921(10)
Fe1−N4	1.976(4)	1.992(4)	1.989(5)
Fe1−N5	1.983(4)	1.986(4)	1.984(6)
Fe1−N6	1.956(5)	1.974(5)	1.970(7)
Fe2−N1	2.121(5)	2.104(4)	1.972(6)
Fe2−N2	2.102(5)	2.105(5)	1.983(6)
Fe2−N7	2.265(4)	2.268(4)	2.169(6)
Fe2−N8	2.259(4)	2.256(4)	2.185(6)
Fe2−N9	2.198(5)	2.194(5)	2.090(6)
Fe2−N10	2.203(5)	2.208(5)	2.101(6)
Fe1−C$_{C\equiv N}$	1.913(6)	1.923(5)	1.887(8)
Fe1−N$_{Tp}$	1.972(4)	1.984(4)	1.981(6)
Fe2−N$_{C\equiv N}$	2.112(5)	2.105(4)	1.978(6)
Fe2−N$_{bnbpen}$	2.231(5)	2.232(5)	2.136(6)
π-π distances [Å]	3.322(4)-3.390(4)	3.180(5)-3.396(6)	3.155(4)-3.391(4)

**Table S6.** Selected bond angles (°) of **1** at different temperatures.

|	**1**[298 K]	**1**[200 K]	**1**[100 K]
C1−Fe1−C3	88.0(2)	87.7(2)	90.4(3)
C1−Fe1−N4	178.89(2)	179.3(2)	177.7(3)
C1−Fe1−N5	94.0(2)	93.90(2)	92.3(3)
C1−Fe1−N6	91.4(2)	91.4(2)	90.2(3)
C2−Fe1−C1	87.0(2)	87.3(2)	90.3(3)
C2−Fe1−C3	88.8(2)	89.1(2)	87.8(3)
C2−Fe1−N4	91.88(2)	92.03(2)	90.9(2)
C2−Fe1−N5	178.66(2)	178.78(2)	176.8(3)
C2−Fe1−N6	91.3(2)	91.2(3)	92.9(3)
C3−Fe1−N4	91.9(2)	92.36(2)	91.5(3)
C3−Fe1−N5	90.4(2)	90.7(2)	90.2(3)
C3−Fe1−N6	179.4(2)	179.13(3)	179.1(3)
N4−Fe1−N5	87.12(2)	86.79(2)	86.6(2)
N6−Fe1−N4	88.62(3)	88.47(2)	87.8(2)
N6−Fe1−N5	89.59(2)	89.12(3)	89.1(3)
N10−Fe2−N7	98.81(2)	98.86(2)	95.7(2)
N10−Fe2−N8	76.26(2)	76.00(2)	77.2(2)
N1−Fe2−N10	90.93(3)	90.33(2)	92.3(3)
N1−Fe2−N2A	99.16(2)	98.91(2)	95.7(2)
N1−Fe2−N7	165.38(2)	165.91(2)	167.4(2)
N1−Fe2−N8	91.31(2)	91.36(3)	90.2(3)
N1−Fe2−N9	93.80(3)	94.21(17)	94.0(3)
N2A−Fe2−N10	90.59(3)	90.74(2)	90.8(2)
N2A−Fe2−N7	91.66(2)	91.66(3)	94.0(2)
N2A−Fe2−N8	163.37(3)	163.31(2)	166.9(2)
N2A−Fe2−N9	94.09(3)	94.58(2)	92.5(2)
N7−Fe2−N8	80.55(2)	80.64(2)	82.1(3)
N9−Fe2−N10	172.73(2)	172.39(2)	172.6(2)
N9−Fe2−N7	75.52(2)	75.58(2)	77.4(2)
N9−Fe2−N8	98.10(2)	97.77(3)	98.8(2)

Symmetry code: A = -*x*+2, -*y*+1, -*z*+2.

Table S7. Structural parameters for **1**·8CH$_3$OH and **1** at high and low temperature.

Compd.		$\Sigma_{Fe}(°)$	ζ_{Fe}	$\Theta_{Fe}(°)$	
1·8CH$_3$OH 298 (100) K	Fe1	20.94 (20.81)	0.19 (0.36)	70.67 (60.71)	[FeC3N3]
	Fe2	77.52 (72.11)	0.33 (0.51)	223.37 (203.21)	[FeN6]
1 298 (100) K	Fe1	21.72 (17.46)	0.18 (0.28)	60.44 (53.81)	[FeC3N3]
	Fe2	76.12 (67.12)	0.32 (0.43)	242.79 (202.39)	[FeN6]

[a] Σ_{Fe}: the sum of |90-a| for the 12 cis-N-Fe-N angles around the iron atom; [b] ζ_{Fe}: the average of the sum of the deviation of 6 unique metal-ligand bond lengths around the central metal atom(Fe)from the average value. [c] Θ_{Fe}: the sum of the deviation of 24 unique torsional angles between the ligand atoms on opposite triangular faces of the octahedron viewed along the pseudo-threefold axis (θi) from 60°. All of these data are obtained through the OctaDist software.[1]
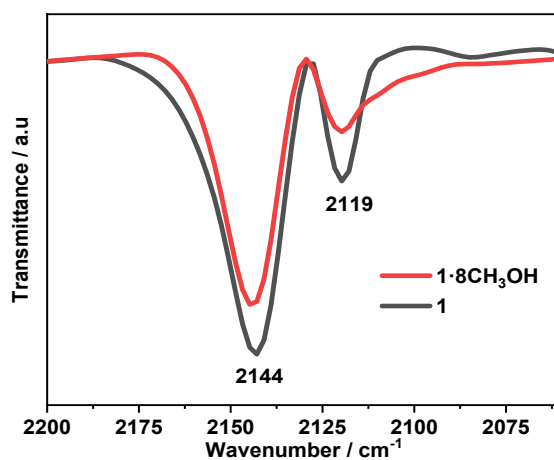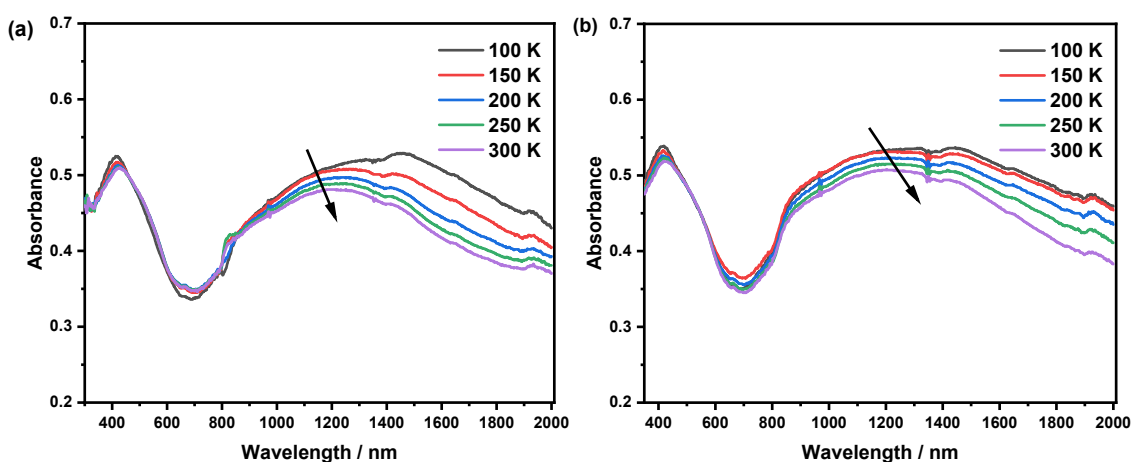

Figure S7. IR spectra for **1**·8CH$_3$OH and **1** at room temperature.
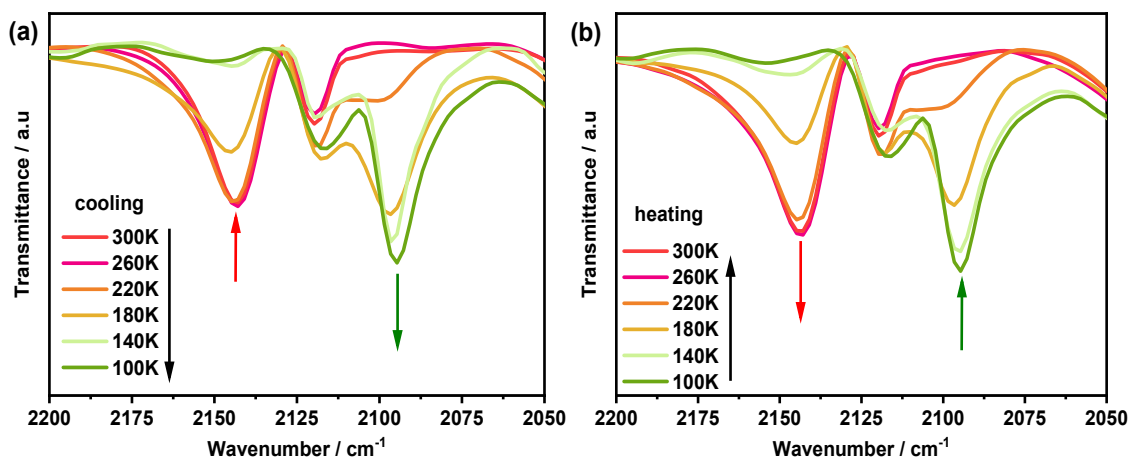
Figure S8. Variable temperature solid state FT–IR spectra for **1**·8CH$_3$OH: (a) in cooling (300 → 100 K) and (b) heating modes (100 → 300 K)
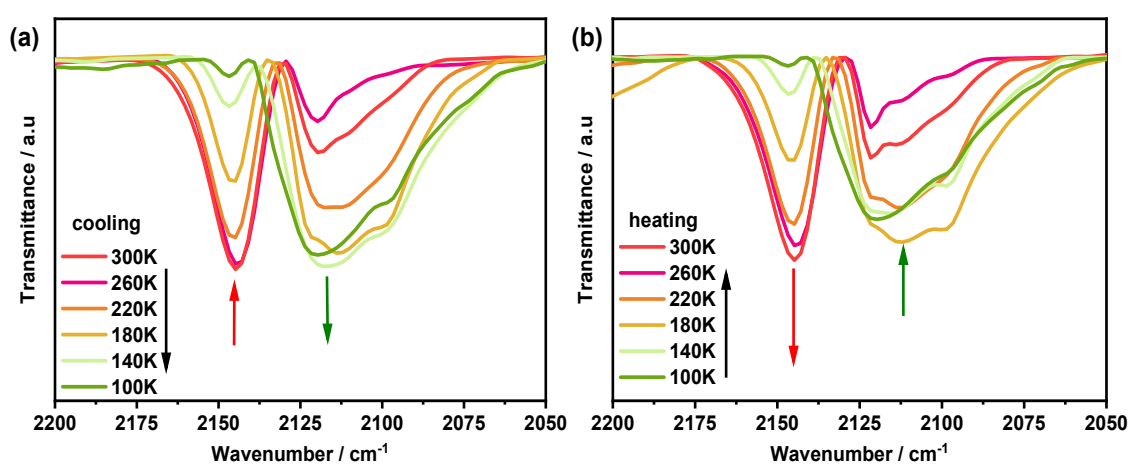
Figure S9. Variable temperature solid state FT–IR spectra for **1**: (a) in cooling (300 → 100 K) and (b) heating modes (100 → 300 K).

Figure S10. Variable–temperature solid–state UV–vis spectra for **1**·8CH$_3$OH (a) and **1** (b) in heating mode.
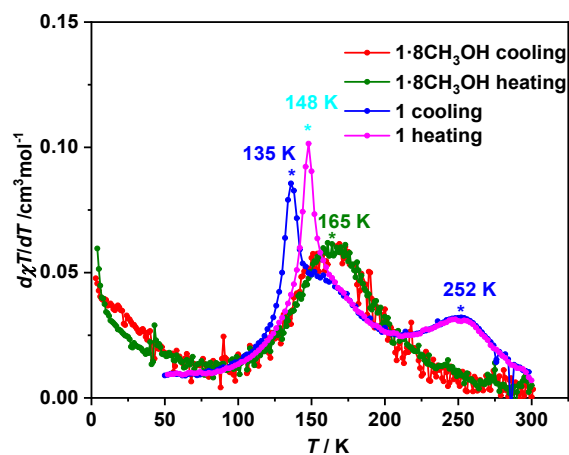
Figure S11. Plots of $d\chi T/dT$ vs. temperature for **1**·8CH$_3$OH and **1**.
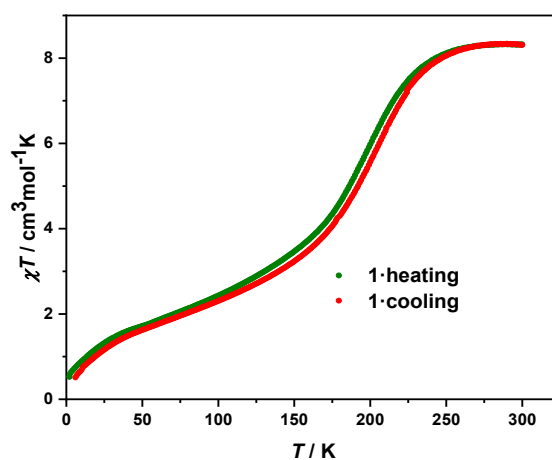
Figure S12. Plots of $\chi_M T$ vs. temperature for **1**·8CH$_3$OH and **1** (3 K·min^{-1} from 2 to 300 K)

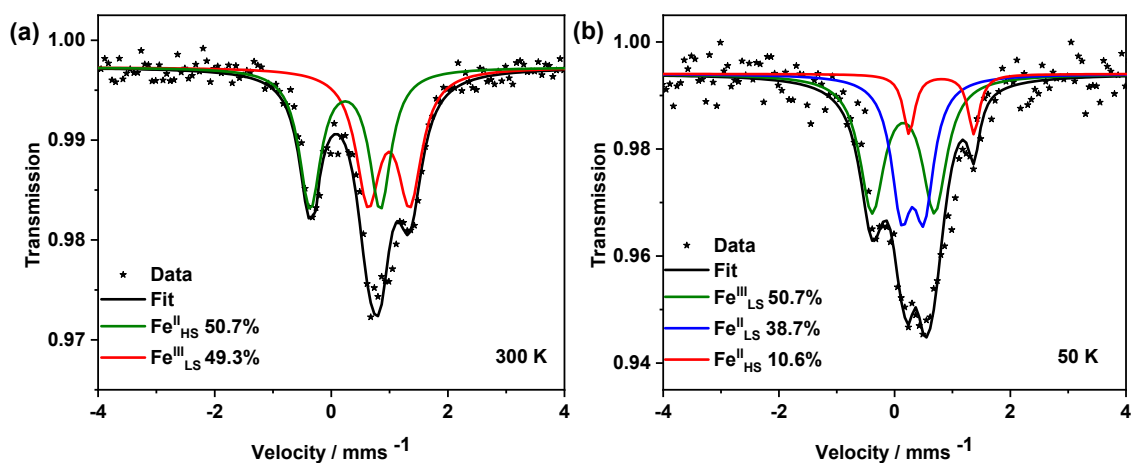**Figure S13.** ^{57}Fe Mössbauer spectra of **1**·8CH$_3$OH at 300 K (a) and 50 K (b).

Table S8. Mössbauer spectrum data of **1**·8CH$_3$OH and **1**.

|	T (K)	Fe site	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Aera (%)
1·8CH$_3$OH	300	Fe$^{II}_{HS}$	0.99	0.72	50.7
		Fe$^{III}_{LS}$	0.24	1.20	49.3
	50	Fe$^{II}_{HS}$	0.81	1.12	10.6
		Fe$^{II}_{LS}$	0.31	0.39	38.7
		Fe$^{III}_{LS}$	0.15	1.08	50.7
1	300	Fe$^{II}_{HS}$	1.10	0.89	49.4
		Fe$^{III}_{LS}$	0.19	1.24	50.6
	200	Fe$^{II}_{HS}$	0.91	1.34	24.7
		Fe$^{II}_{LS}$	0.31	0.30	25.4
		Fe$^{III}_{LS}$	0.12	0.90	50.0
	30	Fe$^{II}_{LS}$	0.46	0.45	50.8
		Fe$^{III}_{LS}$	0.01	1.02	49.2
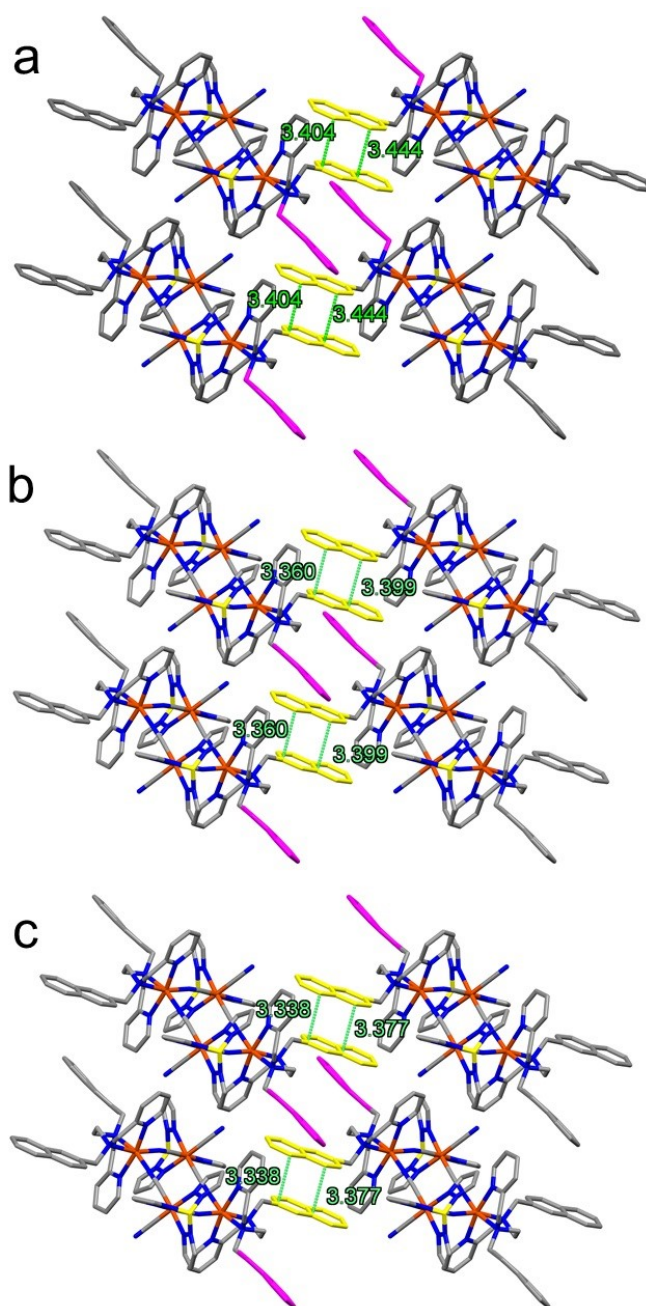
Figure S14. Packing diagrams of **1**·8CH$_3$OH (a: 298 K, b: 165 K, c: 100 K) illustrating intermolecular π-π interactions between adjacent bnbpen ligands along the b-axis. All hydrogen atoms are omitted for clarity.
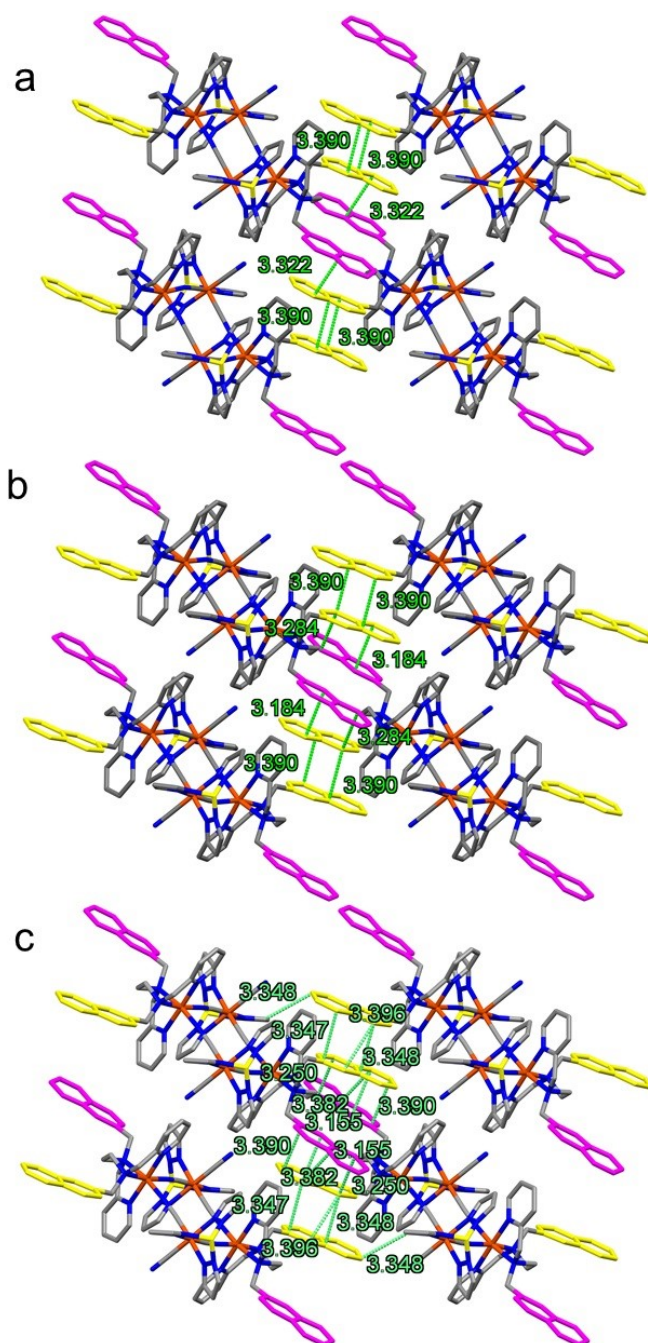
Figure S15. Packing diagrams of **1** (a: 298 K, c: 200 K, e: 100 K) illustrating intermolecular π-π interactions between adjacent bnbpen ligands along the b-axis. All hydrogen atoms are omitted for clarity.

The amount of solvent molecules within the crystal structure affects how they pack as well as intermolecular π-π interactions between adjacent naphthyl groups of bnbpen, the intermolecular π-π interactions continued to decrease during the cooling process from 298 K to 100 K.
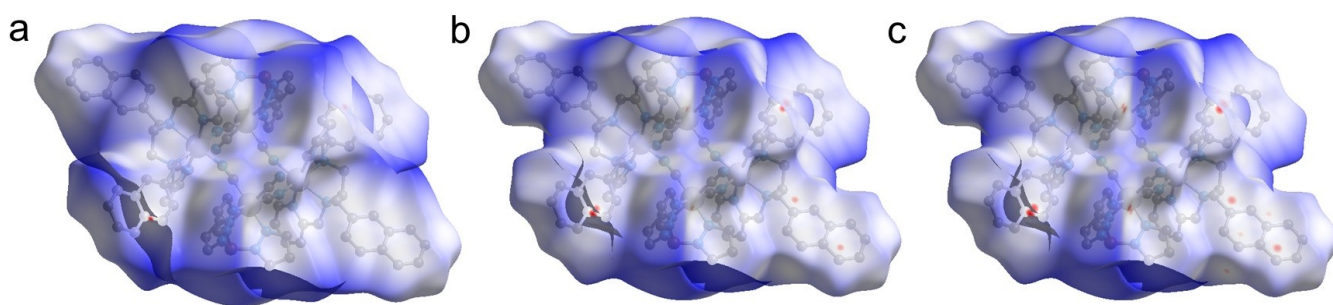
Figure S16. Hirshfeld surface of **1**·8CH$_3$OH (a: 298 K, b: 165 K, c: 100 K) mapped with d_{norm} function.
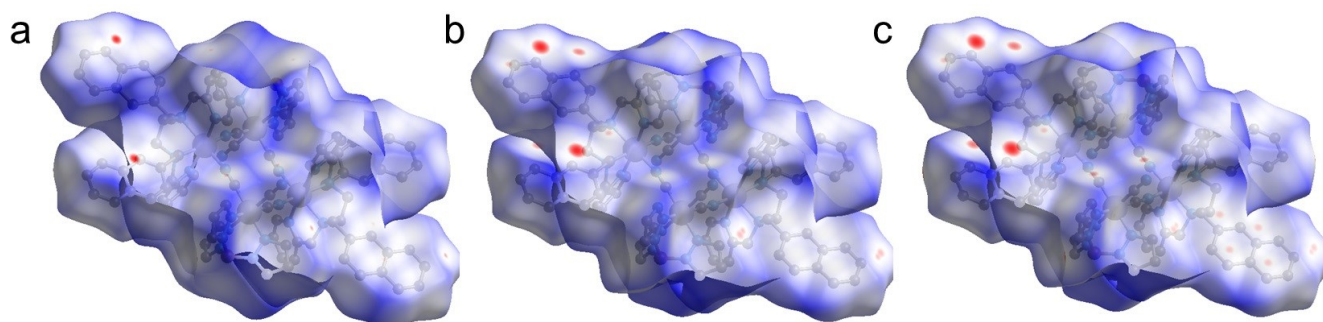
Figure S17. Hirshfeld surface of **1** (a: 298 K, b: 200 K, c: 100 K) mapped with d_{norm} function.

The Hirshfield surface map also showed that the intermolecular interaction force is very weak at 298 K between the naphthalene rings, while the intermolecular interaction force near the naphthalene ring was strong at 100 K. It was clear that low temperature stabilized the LS state of the complex.

1. R. Ketkaew, Y. Tantirungrotechai, P. Harding, G. Chastanet, P. Guionneau, M. Marchivie and D. J. Harding, *Dalton Trans.*, 2021, **50**, 1086-1096.