Supporting Information for:

Halogen Bonds-enhanced Spin Dynamics: Investigating Co-crystallization Effects on Spin Crossover in Mononuclear Mn(III) Schiff-base Complexes

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Table S1. Selected crystallographic data for complexes **1**–**5**.

	1	**2**	**3**	**4**	**5**
T/K	300	300	300	300	100
CCDC no	2383643	2383640	2383645	2383642	2383644
Empirical formula	$C_{30}H_{32}BrMnN_4O_2$	$C_{15}H_{16}I_{0.5}Mn_{0.5}N_2O$	$C_{36}H_{32}BrF_3I_3MnN_4O_2$	$C_{36}H_{32}F_3I_4MnN_4O_2$	$C_{36}H_{29}BrF_8I_6MnN_5O_2$
Formula weight	615.44	331.22	1125.20	1172.19	1611.89
Crystal system Space group	Monoclinic $P2_1/n$	Orthorhombic $P2_12_12$	Orthorhombic *F*dd2	Orthorhombic *F*dd2	Monoclinic $P2_1/n$
a (Å)	7.8561(4)	7.7479(8)	40.712(3)	41.417(9)	11.168(4)
b (Å)	22.0032(11)	12.2056(13)	15.1137(11)	15.289(3)	18.000(7)
c (Å)	18.1498(10)	15.0826(15)	26.7660(18)	26.888(7)	25.217(9)
α [°]	90	90	90	90	90
β [°]	100.826(2)	90	90	90	90.996(10)
γ [°]	90	90	90	90	90
V [Å³]	3081.5(3)	1426.3(3)	16470(2)	17026(7)	5068(3)
Z	4	4	16	16	4
D_{calc} *[g cm⁻³]*	1.327	1.542	1.815	1.829	2.112
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073

μ [mm^{-1}]	1.756	1.579	3.589	3.258	4.767
F (000)	1264.0	668.0	8608.0	8896.0	2984.0
hkl range	$-9 \le h \le 9$	$-11 \le h \le 12$	$-48 \le h \le 38$	$-54 \le h \le 54$	$-14 \le h \le 14$
	$-26 \le k \le 26$	$-18 \le k \le 15$	$-18 \le k \le 18$	$-20 \le k \le 13$	$-24 \le k \le 23$
	$-21 \le l \le 21$	$-21 \le l \le 23$	$-32 \le l \le 32$	$-35 \le l \le 35$	$-33 \le l \le 31$
Collected	45529	15261	24865	33589	42738
Parameters	343	173	452	440	533
Goodness-of-fit	1.079	1.058	1.152	1.035	1.012
R_1 [$I > 2\sigma(I)$]	0.0474	0.0533	0.0459	0.0513	0.0591
wR_2 [$I > 2\sigma(I)$]	0.1460	0.0841	0.1164	0.1457	0.1096
(Dmap)max./min. [$e \cdot Å^{-3}$]	0.41/-0.90	0.76/-0.89	1.02/-0.67	0.74/-2.77	0.90/-1.04

Table S2. Partial bond lengths, bond angles, and Mn···Mn distances for complexes **1**–**5**.

	1	**2**	**3**	**4**	**5**
T/K	300	300	300	300	100
Mn–N1	2.055(3)	2.013(4)	2.097(5)	1.971(12)	2.067(6)
Mn–N2	2.044(3)	2.013(4)	2.105(5)	2.052(11)	2.137(6)
Mn–N3	1.983(3)	2.076(4)	2.028(5)	2.055(13)	2.163(6)
Mn–N4	1.982(3)	2.076(4)	2.052(5)	1.965(12)	2.238(7)
Mn–Nav	2.016	2.045	2.071	2.011	2.151
Mn–O1	1.880(2)	1.872(3)	1.891(4)	1.893(10)	1.861(5)
Mn–O2	1.880(2)	1.872(3)	1.879(4)	1.896(10)	1.875(5)
Mn–Oav	1.880	1.872	1.885	1.895	1.868
O1–Mn1–N1	86.30(11)	87.23(17)	93.00(19)	94.5(5)	93.9(2)
O1–Mn1–N2	91.13(12)	87.23(17)	85.82(18)	87.0(5)	86.2(2)
O1–Mn1–N3	88.18(11)	92.96(17)	92.65(18)	90.4(6)	91.6(2)
O1–Mn1–N4	94.45(11)	92.96(17)	87.45(17)	88.5(5)	86.2(2)
O2–Mn1–O1	175.95(10)	179.7(2)	179.61(18)	176.8(4)	179.3(2)
O2–Mn1–N1	90.53(12)	91.57(16)	86.68(18)	87.5(5)	86.5(2)

O2–Mn1–N2	86.08(12)	88.22(16)	93.93(19)	90.4(5)	93.3(2)
O2–Mn1–N3	94.70(11)	88.22(16)	87.64(18)	87.4(6)	87.8(2)
O2–Mn1–N4	88.06(11)	91.57(16)	92.74(18)	93.9(5)	94.4(2)
N1–Mn1–N2	85.20(12)	99.3(2)	83.4(2	90.4(5)	80.9(3
N1–Mn1–N3	171.97(11)	171.14(18)	169.4(2)	172.0(5)	164.3(3)
N2–Mn1–N3	89.08(11)	88.53(16)	88.0(2)	83.5(5)	84.9(2)
N4–Mn1–N1	89.90(11)	88.53(16)	86.1(2)	96.4(5)	84.8(3)
N4–Mn1–N2	172.32(12)	171.14(18)	167.23(19)	172.1(5)	163.3(2)
N4–Mn1–N3	96.36(11)	84.0(2)	103.15(19)	90.1(5)	110.2(2)
Mn···Mn (intrachain)	7.86	7.75	9.645/9.871	9.513/9.647	11.168

Table S3. Selected hydrogen bond parameters for complexes **1–5**.

	D–H···A	D–H	H···A	D···A	Angle
1	N1–H11···Br1	1.00	2.450	3.322(3)	145
	N2–H2···Br2^{vi}	1.00	2.440	3.308(3)	145
2	N2–H2···I1^{vii}	0.98	2.780	3.585(5)	140
	C2–H2A··C5	0.93	2.811	3.379	120
3	N2–H2···Br2^{viii}	0.98	2.720	3.528(10)	140
	N3–H3···Br1	0.98	2.430	3.324(9)	151
	C23–H23··F1	0.93	2.410	3.170(12)	138
4	N2–H2···I1	0.98	2.850	3.667(12)	141
	N3–H3···I2	0.98	2.430	2.298(15)	147
	C23–H23··F3^{ix}	0.93	2.450	3.186(18)	136
5	N1–H1···Br1^{i}	0.98	2.480	3.422(8)	162
	C17–H17··F1^{ii}	0.93	2.410	3.241(11)	149

Symmetry codes: (i) -1+x, y, z; (ii) 1/2-x,1/2+y, 1/2-z; (iii) 2-x, 2-y, -z; (iv) x, 1+y, z; (v) 1-x, 2-y, 1-z (vi) 1+x, y, z; (vii) 1-x,1-y, z; (viii) -1/4+x, 5/4-y, -1/4+z; (ix) 3/4-x,1/4+y,-1/4+z

Table S4. Halogen bond parameters in complexes **3–5**.

	D–Hal···A	D-Hal	Hal···A	D···A	Angle
3	C32–I1··Br2	2.117	3.474	5.586	175
	C34–I3··Br1	2.109	3.413	5.507	171
	C36–I2··Br2	2.100	3.767	5.852	171
	C35–F2··F2	1.333	2.753	3.964	150
4	C31–I4··I1	2.114	3.631	5.735	173
	C33–I3··I	2.091	3.757	5.832	171
	C35–I5··I2	2.090	3.486	5.565	172
	C34–F2··F2	1.304	2.776	3.973	151
5	C23–I1··Br1	2.098	3.475	5.542	167
	C27–I3··Br1	2.092	3.379	5.466	175

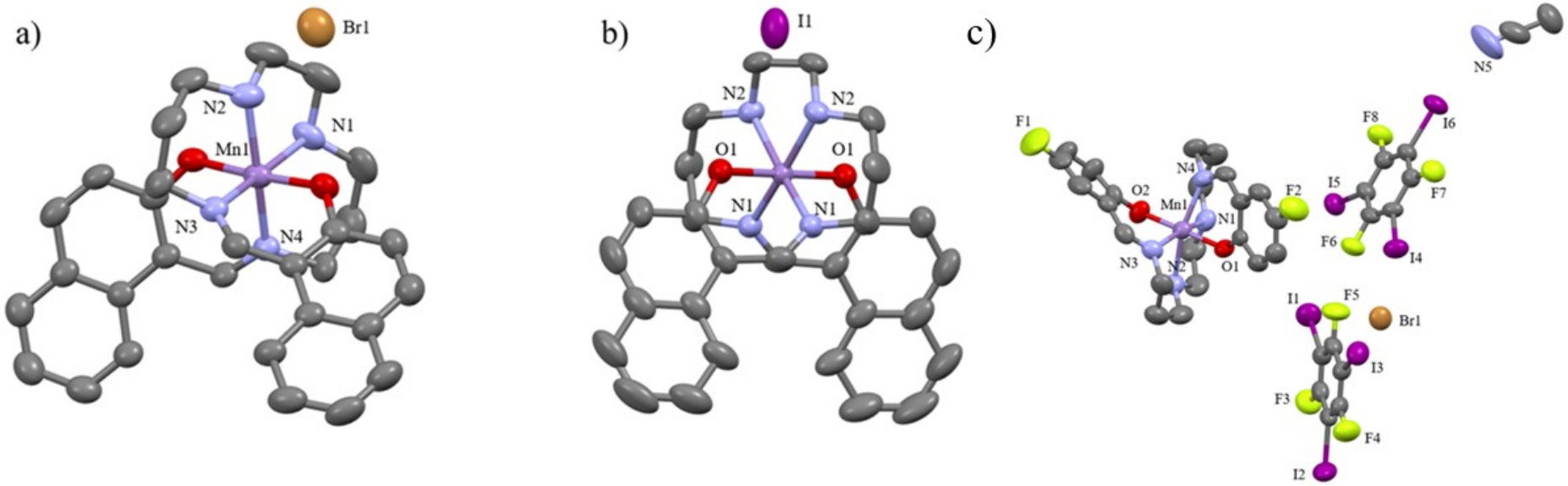


Figure S1. Asymmetric units of complexes **1** (a), **2** (b) and **5** (c). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at 50% probability.

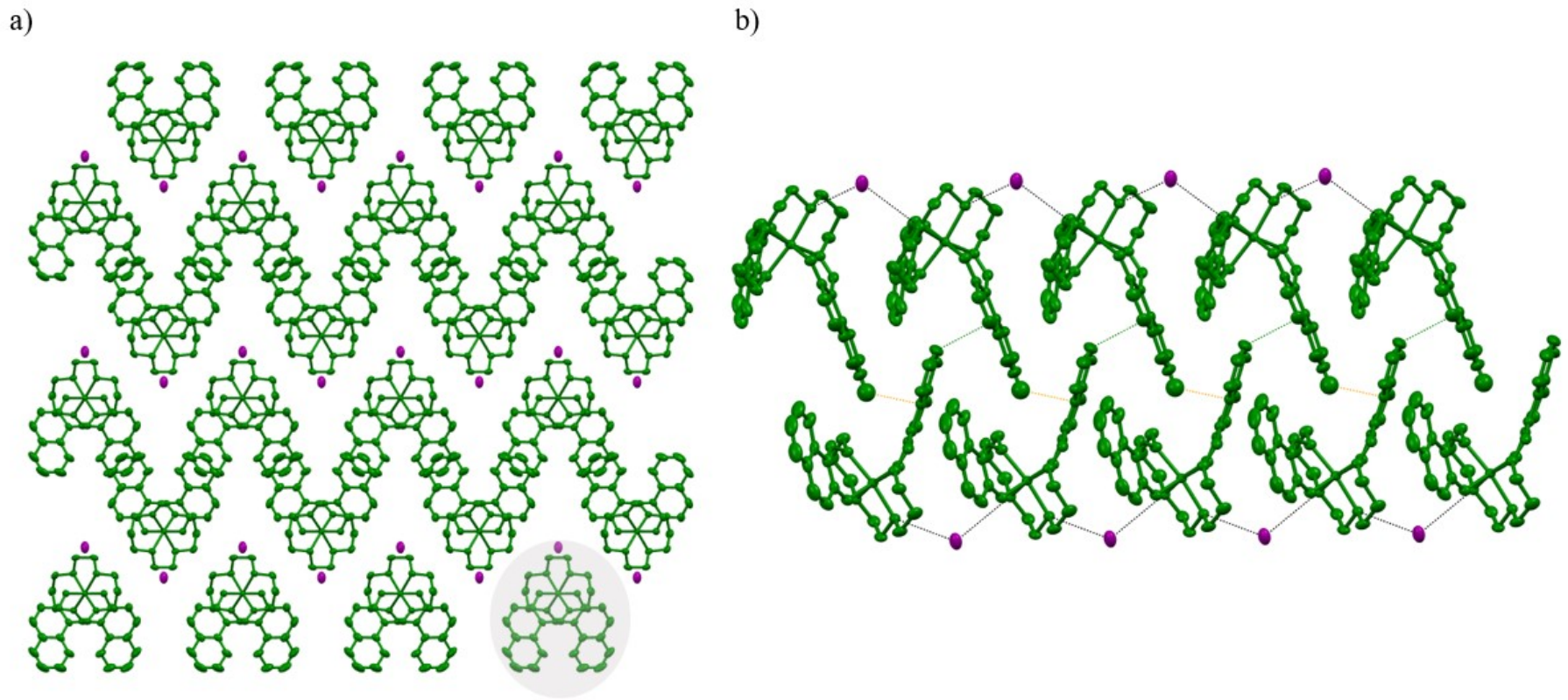


Figure S2. (a) Crystal packing of complex **2** at 300 K, viewed along the *a* axis. The chain is shown in a light grey background. (b) The details of the layer formed by the [Mn(naphth-sal-N-1,5,8,12)]$^{+}$ chains, viewed along the *b* axis. The dashed black, green and orange lines, indicate the N_{amine}–H···I hydrogen bonds, C···C contacts and C–H···π interactions, respectively. The cations are shown in green and the anions are shown in purple, hiding unnecessary hydrogen atoms for clarity.

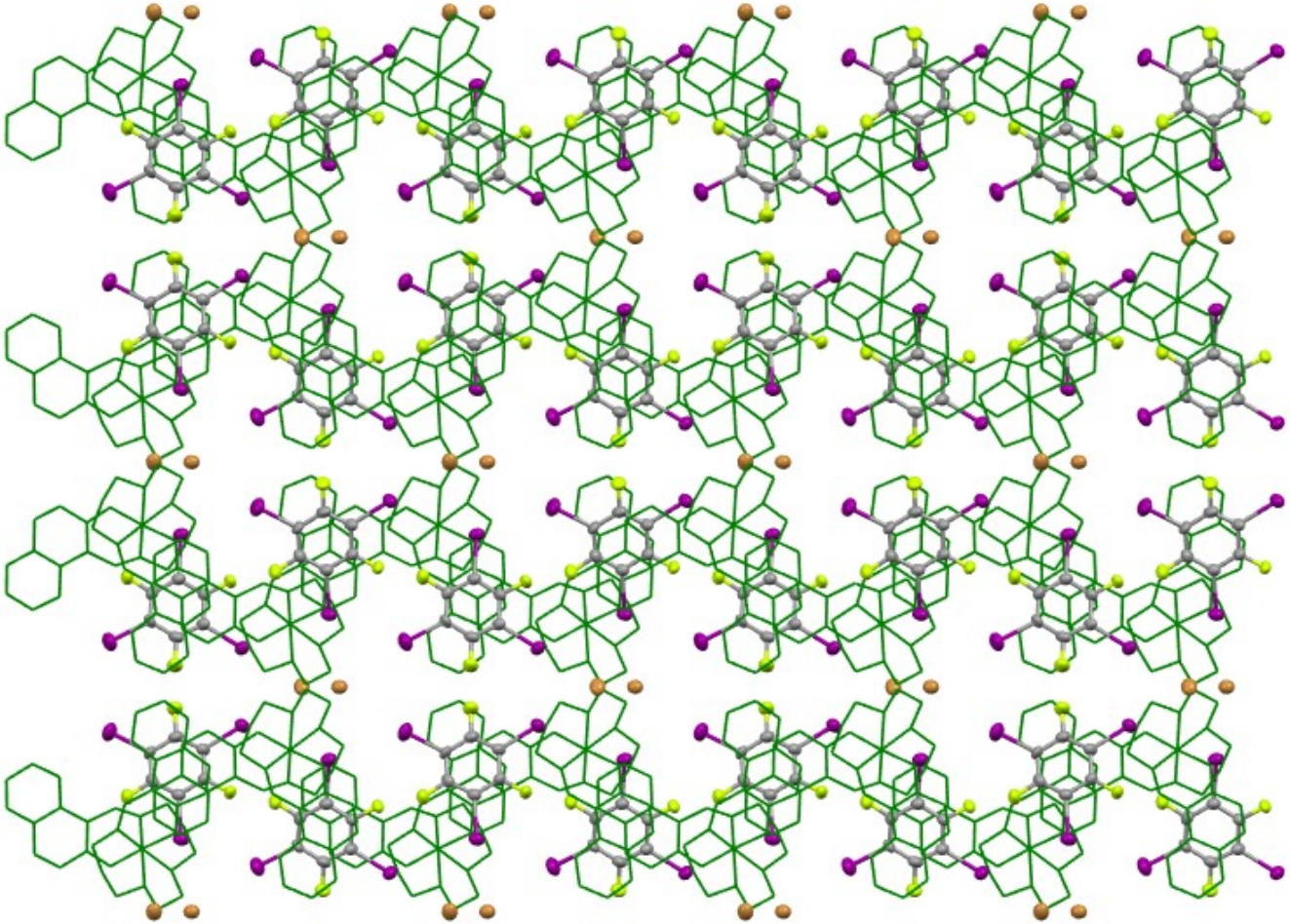


Figure S3. (a) Crystal packing of complex **3** at 300 K, viewed along the *b* axis.

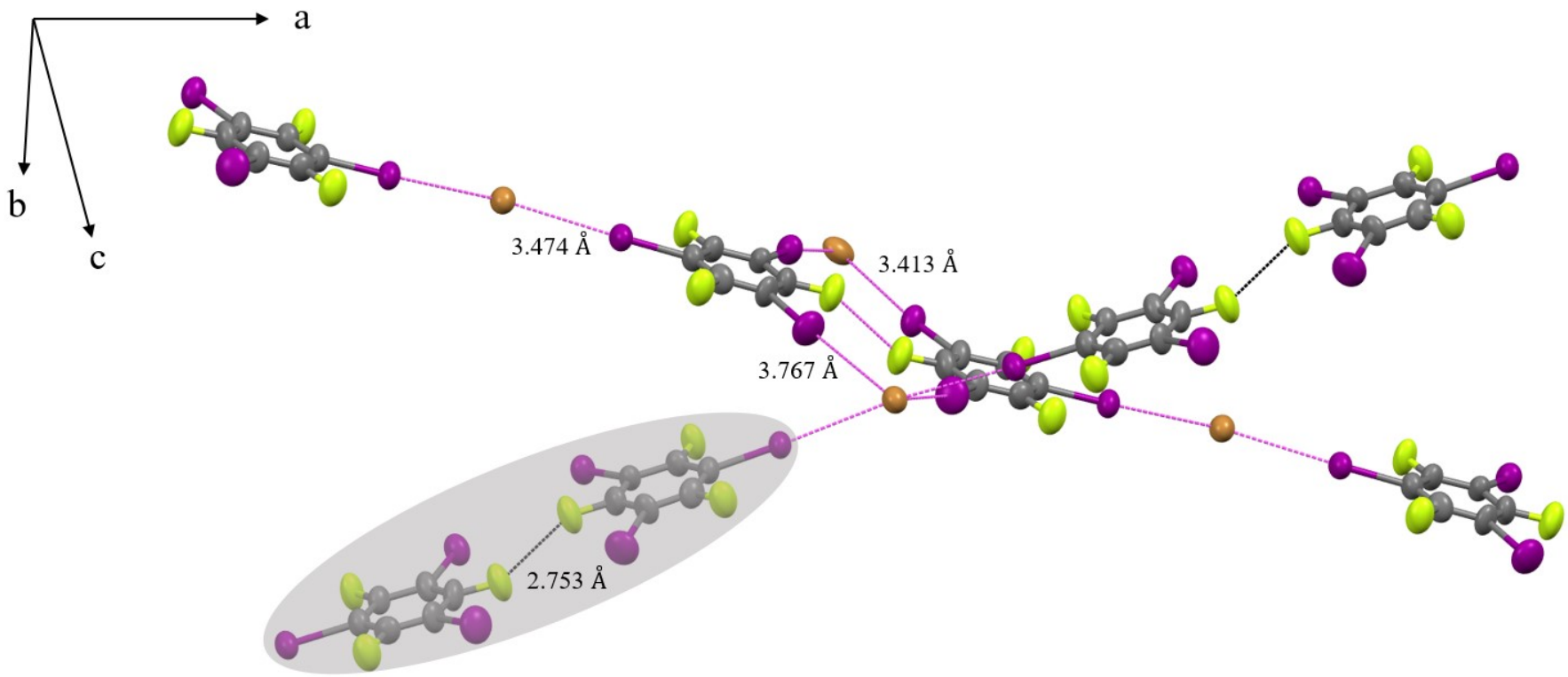


Figure S4. In the stacking of complex **3**, the shaded region represents a unit formed by two TFTIB molecules, connected by black C−F···F–C halogen bonds. A three-dimensional halogen-bonded network is constructed through magenta C−I···Br halogen bonds.

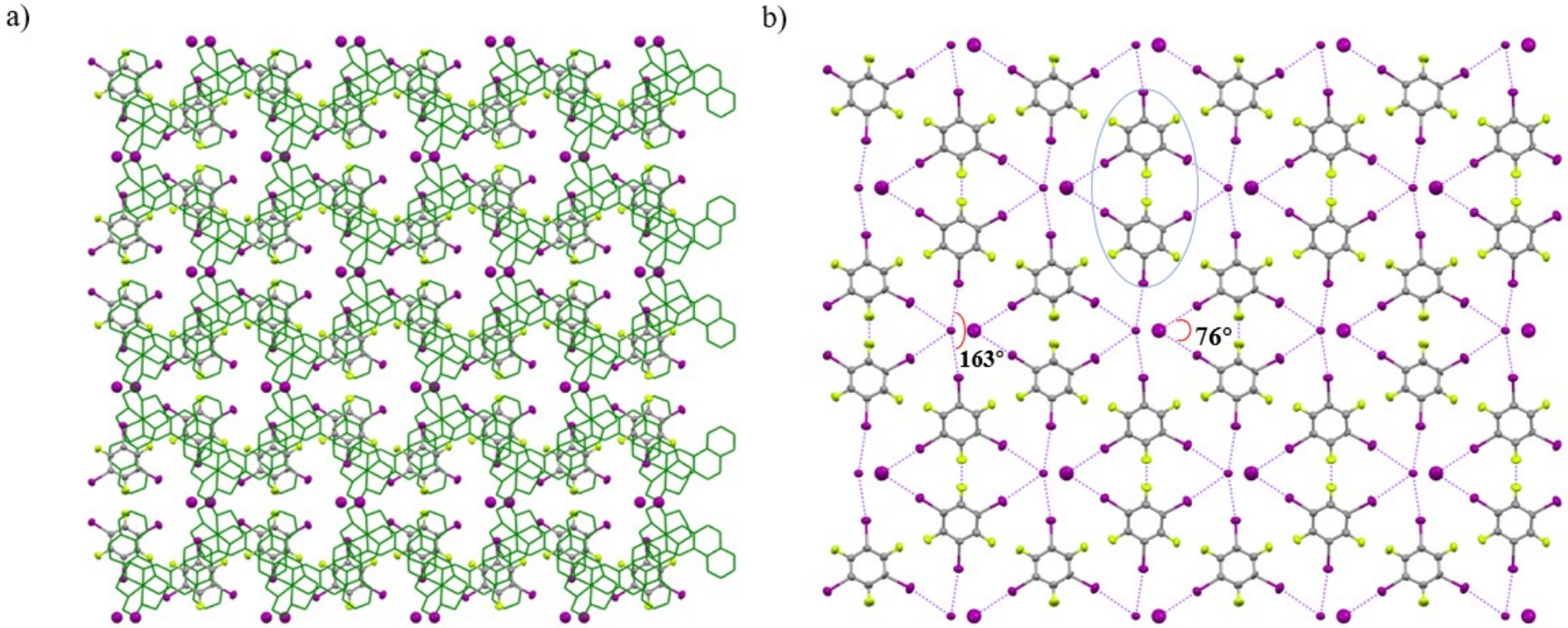


Figure S5. (a) Crystal packing of complex **4** at 300 K, viewed along the *b* axis. (b) Three-dimensional halogen network constructed by TFTIB molecule and I^- anion, viewed along the *b* axis.

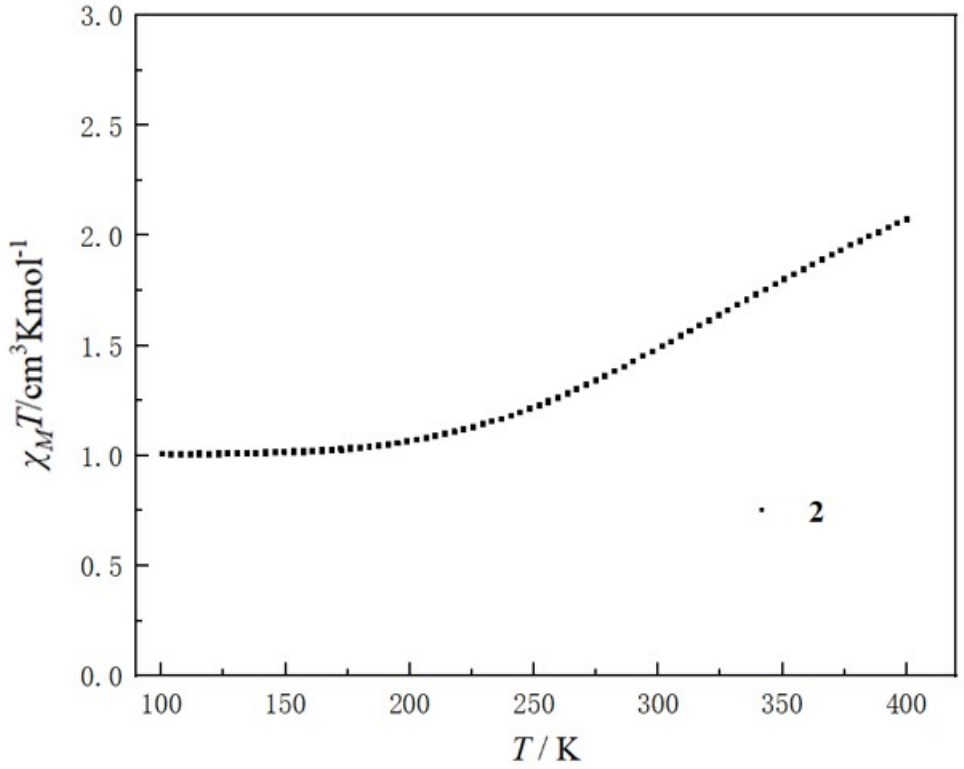
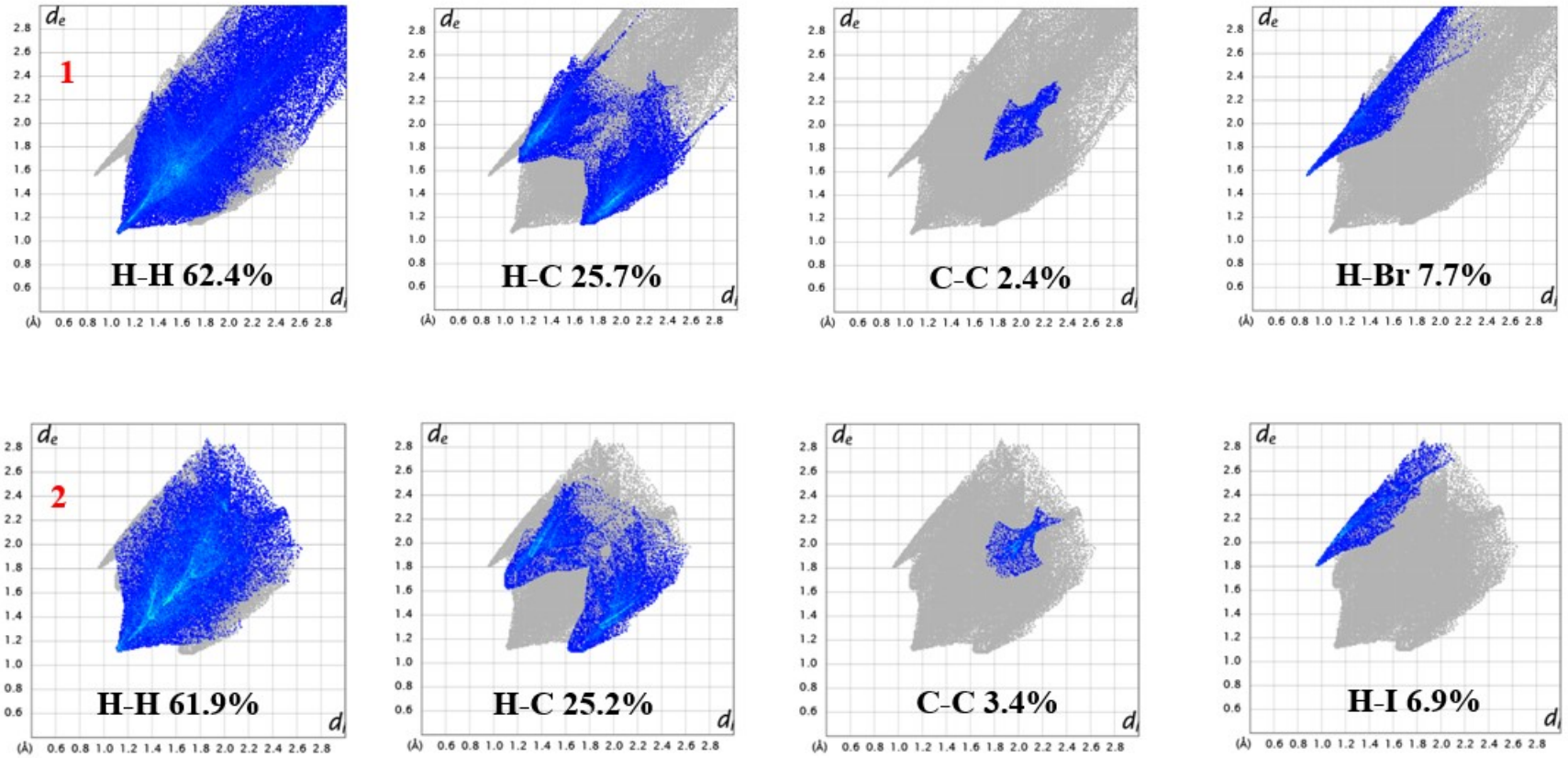


Figure S6. Thermal dependence of the $\chi_M T$ for complex **2** in the temperature ranges of 400 K →100 K and 100 K → 400 K at a cooling and heating rate of 3 K min^{-1}.


1
H-H 62.4%
H-C 25.7%
C-C 2.4%
H-Br 7.7%
2
H-H 61.9%
H-C 25.2%
C-C 3.4%
H-I 6.9%
d_e
d_i
(Å) 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8

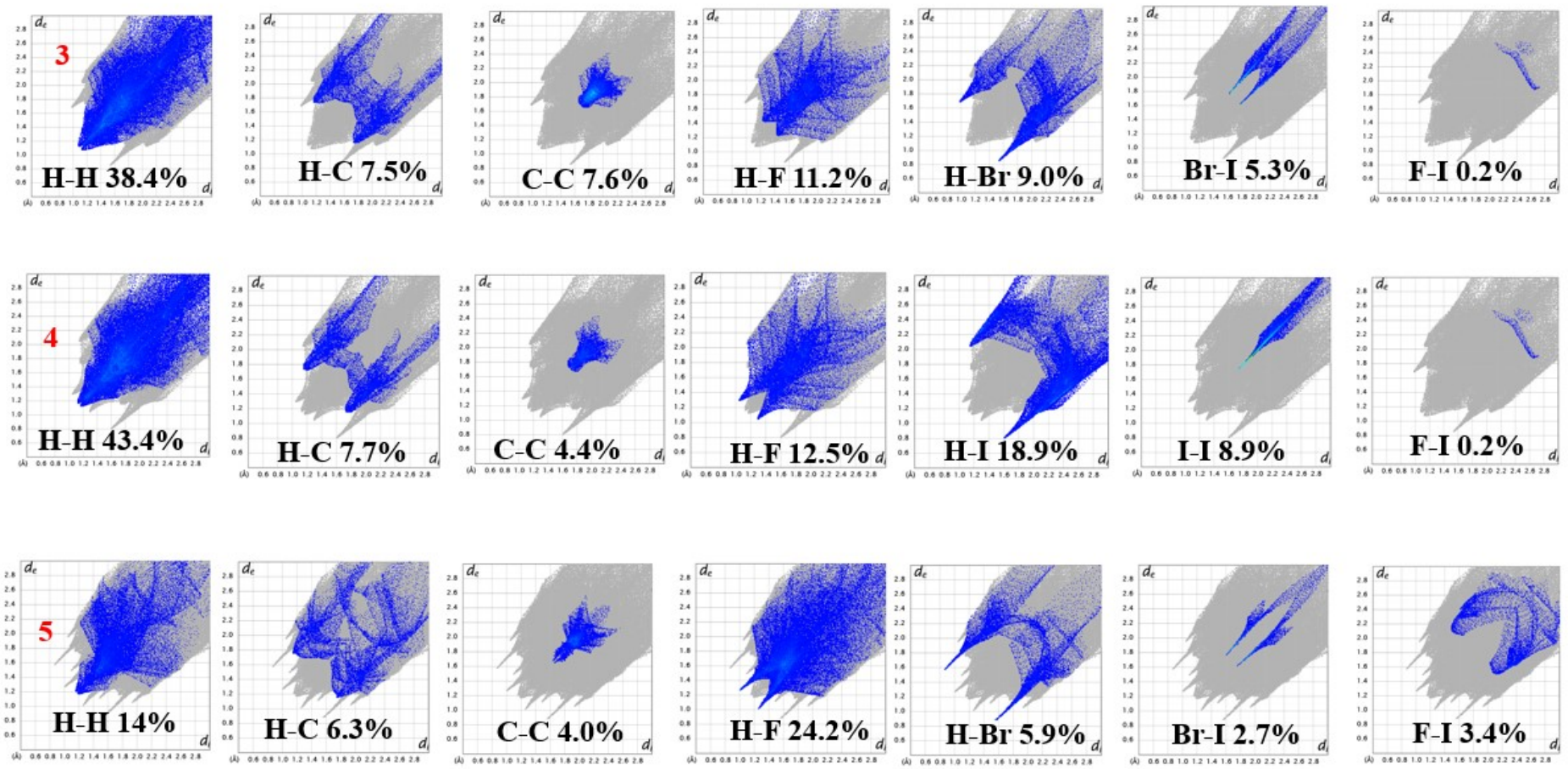


Figure S7. The 2D fingerprint plots of contacts: H··· H, H···C, C···C, H···F, H···X, X···I, F···I(X =Br，I) for complex **1**–**5** at 300 K.

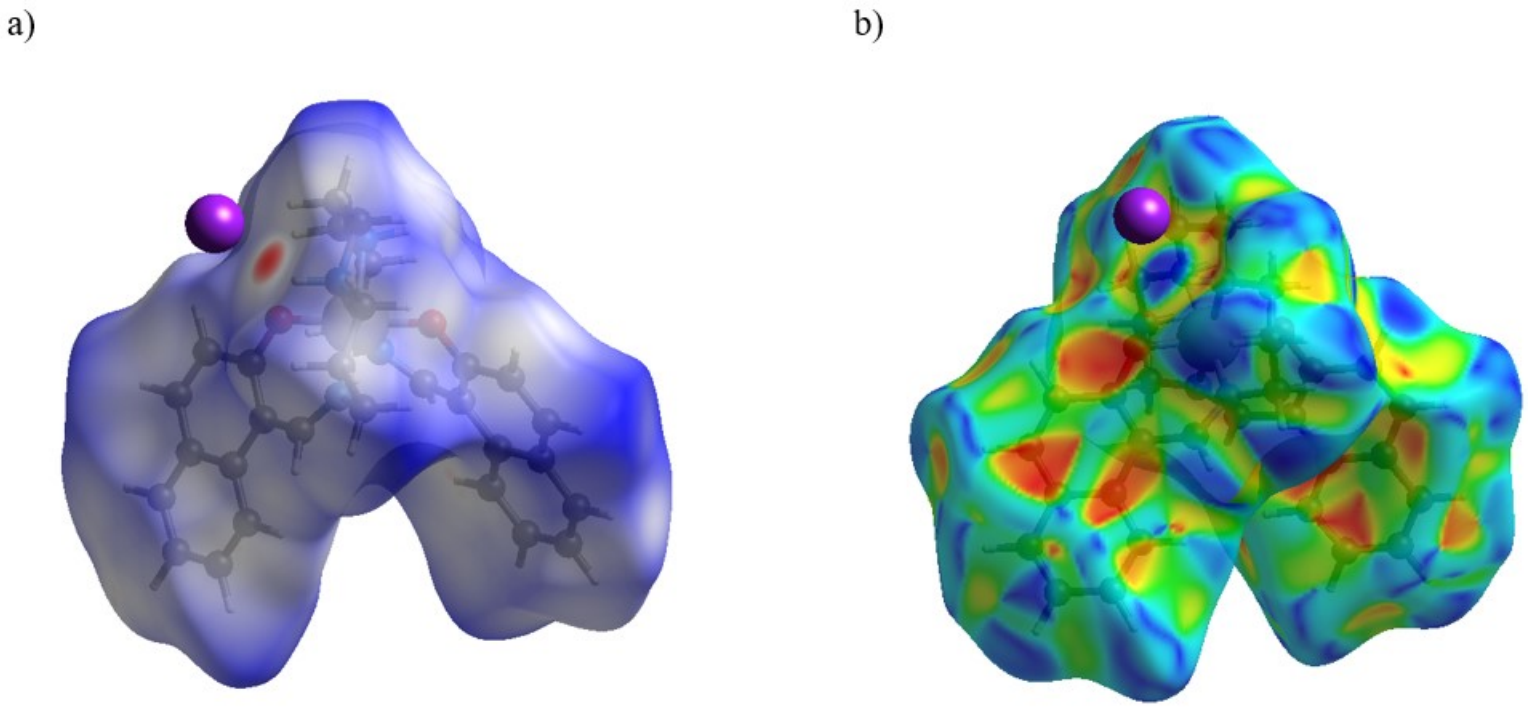


Figure S8. (a) The Hirshfeld surface mapped with d_{norm} for complex **2**. (b) The Hirshfeld surface mapped with shape index for complex **2**.

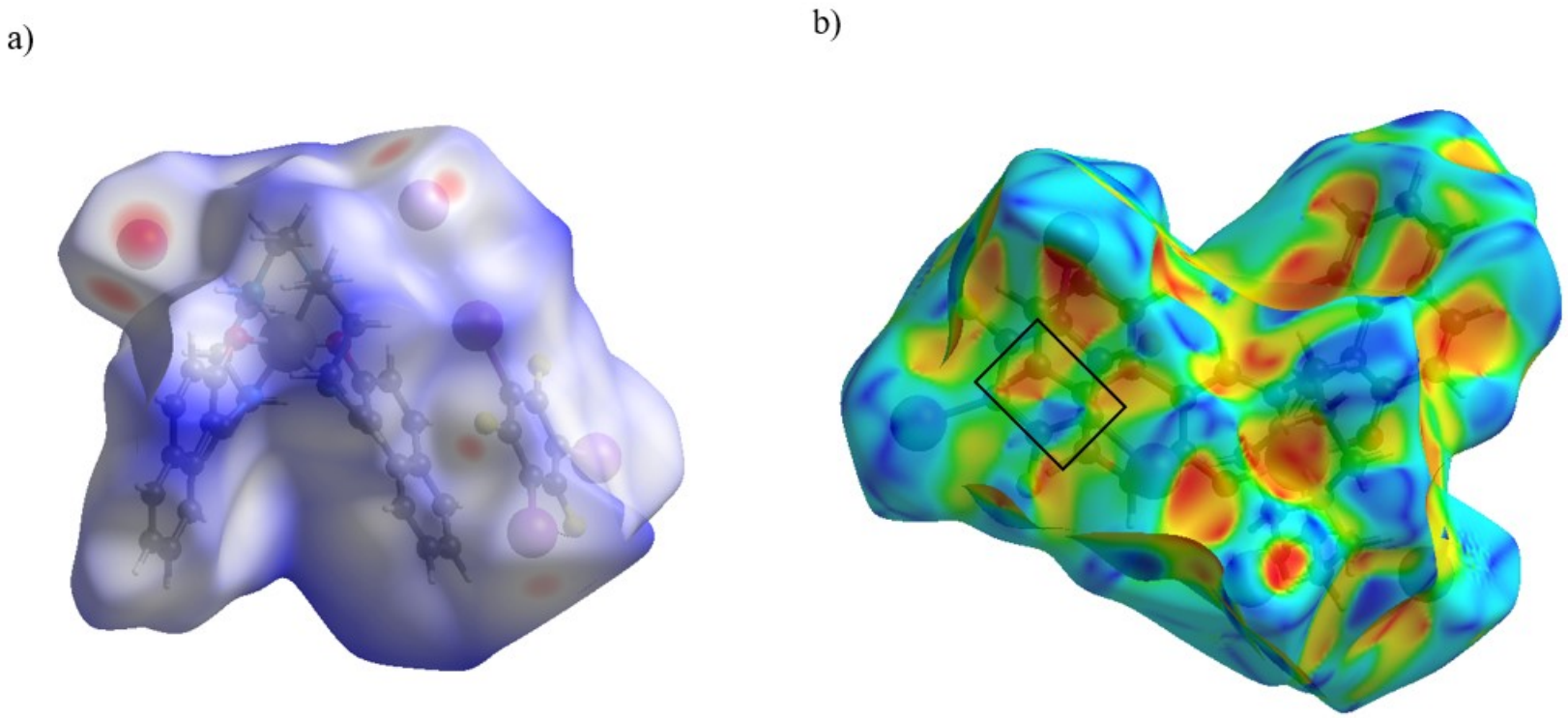


Figure S9. (a) The Hirshfeld surface mapped with d_{norm} for complex **4**. (b) The Hirshfeld surface mapped with shape index for complex **4**. The π···π stacking based on the adjacent blue and red triangles have been marked with a black box.

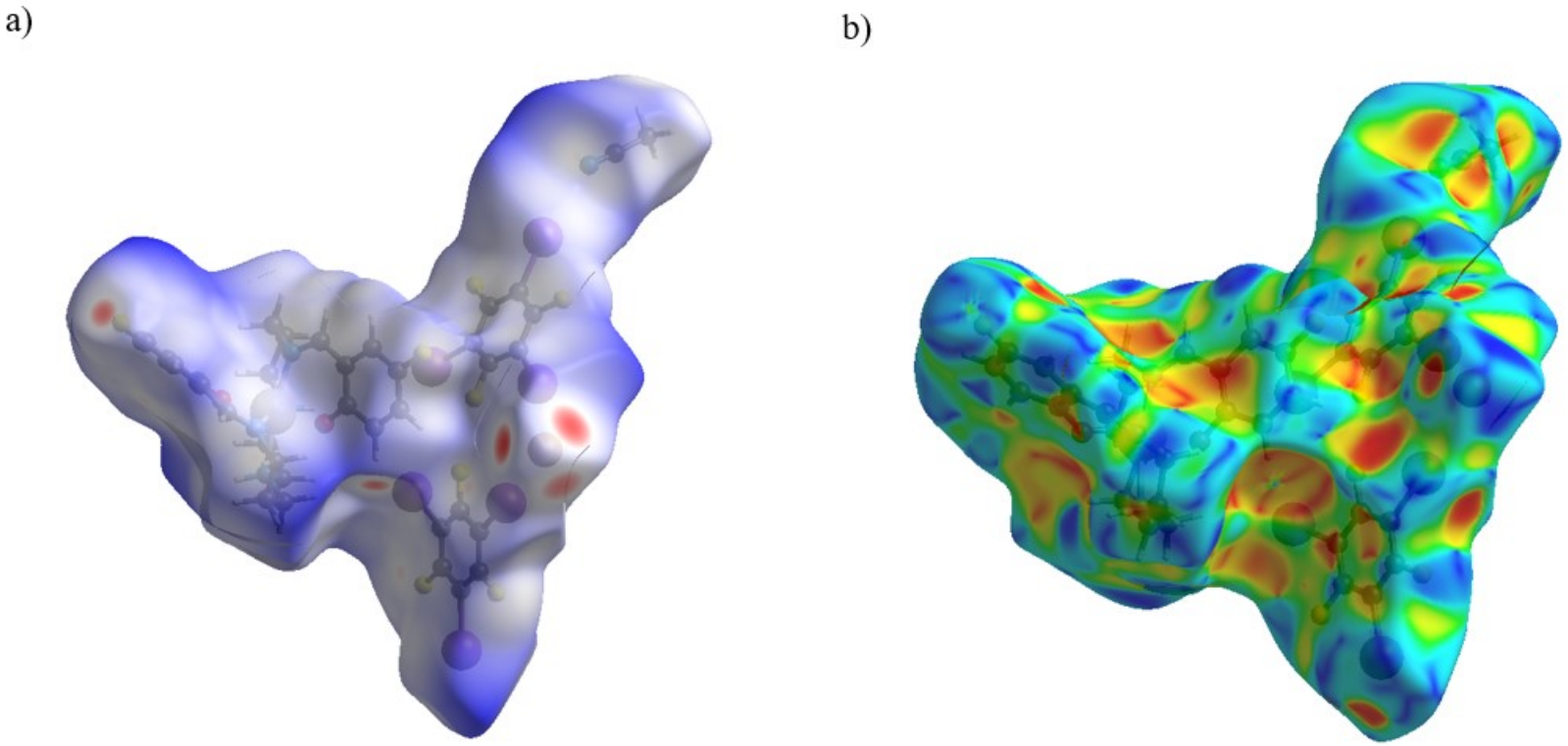


Figure S10. (a) The Hirshfeld surface mapped with d_{norm} for complex **5**. (b) The Hirshfeld surface mapped with shape index for complex **5**.

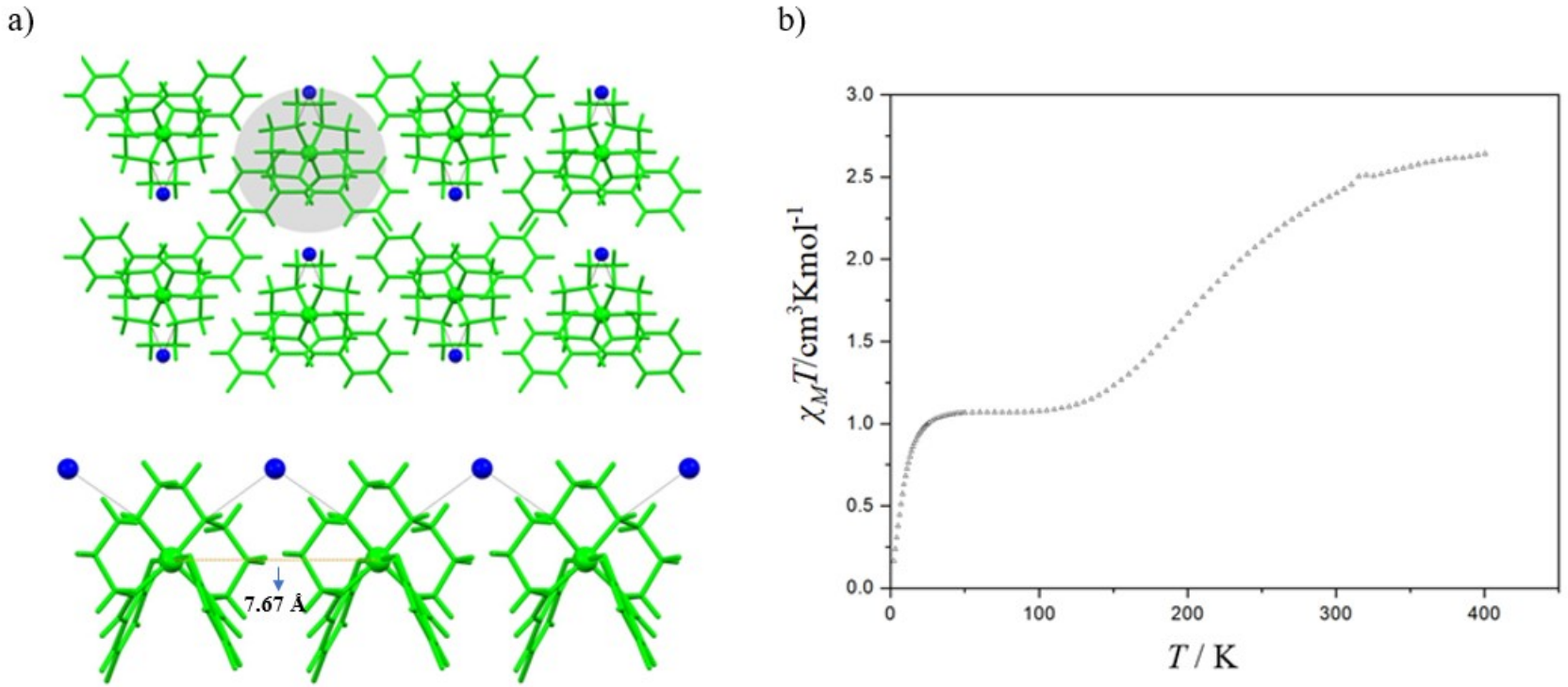


Figure S11. (a) The crystal packing and cation-anion chains of complex [Mn(5-F-sal-N-1,5,8,12)] $Cl_{0.28}Br_{0.72}$. (b) Thermal dependence of the $\chi_M T$ for complex [Mn(5-F-sal-N-1,5,8,12)] $Cl_{0.28}Br_{0.72}$ between 2 K and 400 K.[1]

References

1. C. Y. Qin, S. Z. Zhao, H. Y. Wu, Y. H. Li, Z. K. Wang, Z. Wang and S. Wang, *Dalton Trans*, 2021, **50**, 5899-5910.