Supporting Information

Halogen substitution effects on crystal structures and magnetic properties in nickel dithiolate molecular crystals

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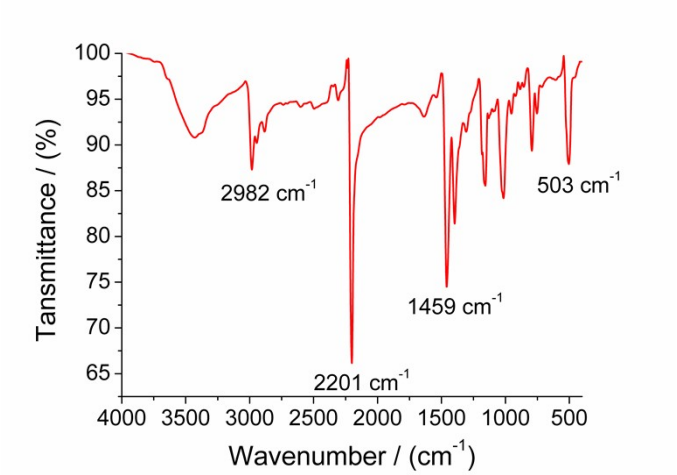

Fig.S1 IR spectrum of **1**.

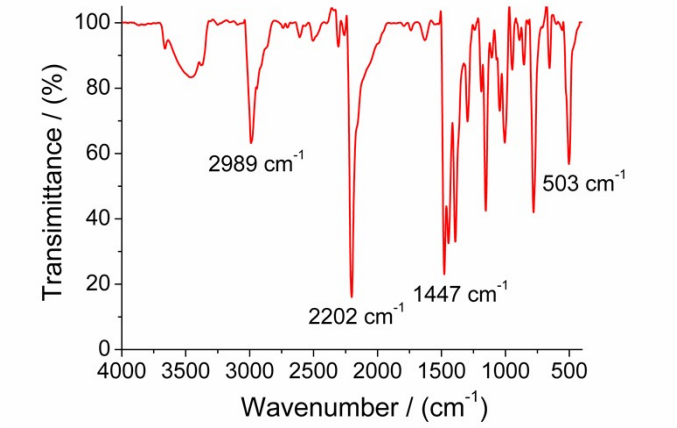

Fig.S2 IR spectrum of **2**.

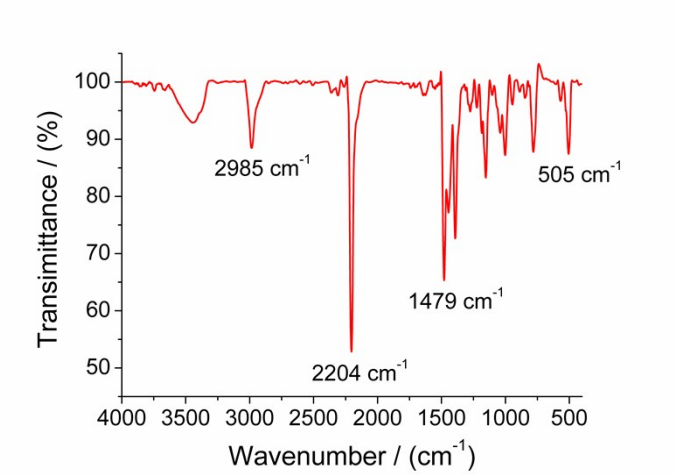

Fig.S3 IR spectrum of **3**.

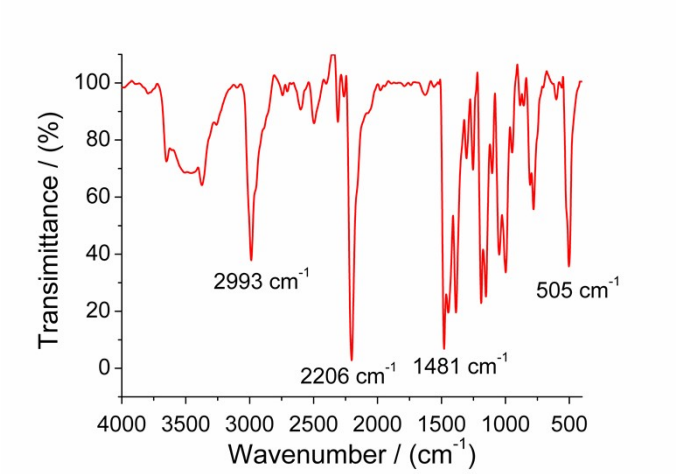

Fig.S4 IR spectrum of **4**.

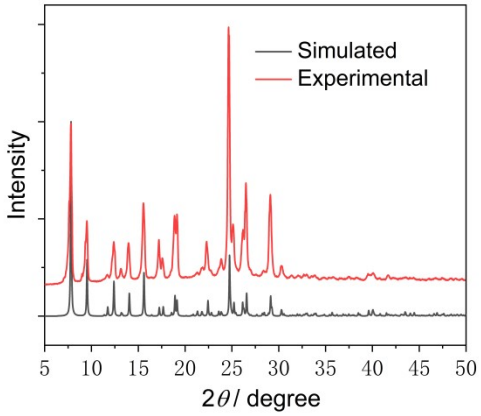

Fig.S5 PXRD patterns of **1**.

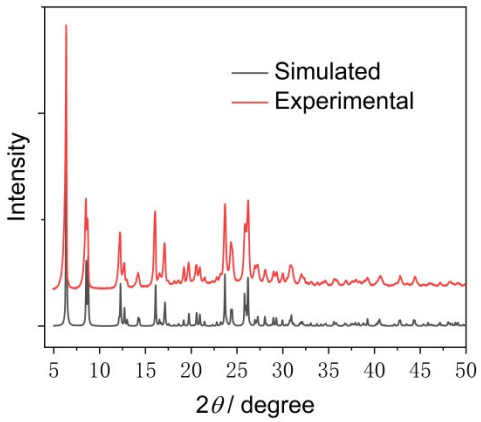

Fig.S6 PXRD patterns of **2**.

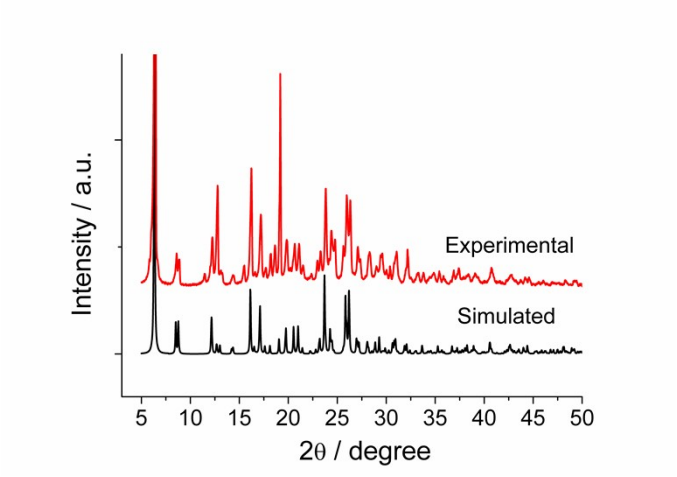

Fig.S7 PXRD patterns of **3**.

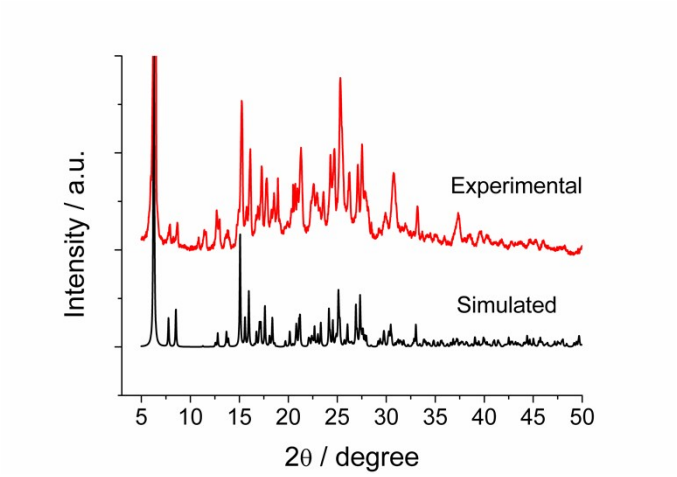

Fig.S8 PXRD patterns of **4**.

Table S1: Bond lengths and bond angles in both anions and cations in **1** at 293 K.

		1	
Ni(1)-S(1)	2.1407(13)	Ni(1)-S(2)	2.1408(13)
Ni(1)-S(3)	2.1395(13)	Ni(1)-S(4)	2.1427(12)
S(1)-C(2)	1.712(5)	S(2)-C(3)	1.718(5)
S(3)-C(6)	1.715(5)	S(4)-C(7)	1.711(5)
C(1)-C(2)	1.435(7)	C(2)-C(3)	1.359(7)
C(3)-C(4)	1.413(7)	C(5)-C(6)	1.416(7)
C(6)-C(7)	1.358(6)	C(7)-C(8)	1.436(7)
N(1)-C(1)	1.137(7)	N(2)-C(4)	1.148(7)
N(3)-C(5)	1.148(7)	N(4)-C(8)	1.138(6)
C(9)-C(10)	1.497(10)	N(5)-C(9)	1.547(8)
C(11)-C(12)	1.432(10)	N(5)-C(11)	1.482(8)

C(13)-C(14)	1.516(9)	N(5)-C(13)	1.520(8)
C(15)-C(16)	1.474(9)	C(16)-C(17)	1.357(11)
N(5)-C(15)	1.498(8)		
S(3)-Ni(1)-S(1)	87.10(5)	S(3)-Ni(1)-S(2)	177.05(5)
S(1)-Ni(1)-S(2)	92.45(5)	S(3)-Ni(1)-S(4)	92.20(5)
S(1)-Ni(1)-S(4)	175.26(5)	S(2)-Ni(1)-S(4)	88.49(5)
C(11)-N(5)-C(15)	111.2(5)	C(11)-N(5)-C(13)	112.4(5)
C(15)-N(5)-C(13)	107.6(4)	C(11)-N(5)-C(9)	110.0(5)
C(15)-N(5)-C(9)	109.0(5)	C(13)-N(5)-C(9)	106.5(5)

Table S2: Bond lengths and bond angles in both anions and cations in **2** at 293 K.

		2	
Ni(1)-S(1)	2.1555(11)	Ni(1)-S(2)	2.1551(17)
Ni(1)-S(3)	2.1602(17)	Ni(1)-S(4)	2.1544(11)
S(1)-C(2)	1.724(3)	S(2)-C(3)	1.720(3)
S(3)-C(6)	1.720(3)	S(4)-C(7)	1.727(3)
C(1)-C(2)	1.438(4)	C(2)-C(3)	1.367(4)
C(3)-C(4)	1.444(4)	C(5)-C(6)	1.443(4)
C(6)-C(7)	1.365(4)	C(7)-C(8)	1.438(4)
N(1)-C(1)	1.141(4)	N(2)-C(4)	1.140(4)
N(3)-C(5)	1.144(4)	N(4)-C(8)	1.144(4)
C(9)-C(10)	1.516(4)	N(5)-C(10)	1.521(4)
C(11)-C(12)	1.514(4)	N(5)-C(12)	1.530(4)
C(13)-C(14)	1.504(5)	N(5)-C(14)	1.527(3)
C(15)-C(16)	1.519(5)	C(16)-C(17)	1.515(4)
N(5)-C(17)	1.516(3)	Cl(1)-C(15)	1.769(4)
S(3)-Ni(1)-S(1)	87.57(4)	S(3)-Ni(1)-S(2)	179.47(4)
S(1)-Ni(1)-S(2)	92.22(4)	S(3)-Ni(1)-S(4)	92.53(4)
S(1)-Ni(1)-S(4)	178.94(3)	S(2)-Ni(1)-S(4)	87.68(4)
C(17)-N(5)-C(10)	106.8(2)	C(17)-N(5)-C(14)	111.4(2)
C(10)-N(5)-C(14)	110.8(2)	C(17)-N(5)-C(12)	110.6(2)
C(10)-N(5)-C(12)	110.6(2)	C(14)-N(5)-C(12)	106.6(2)

Table S3: Bond lengths and bond angles in both anions and cations in **3** at 293 K.

		3	
Ni(1)-S(1)	2.154(3)	Ni(1)-S(2)	2.152(3)
Ni(1)-S(3)	2.158(3)	Ni(1)-S(4)	2.154(3)
S(1)-C(2)	1.718(12)	S(2)-C(3)	1.720(12)
S(3)-C(6)	1.722(11)	S(4)-C(7)	1.716(11)
C(1)-C(2)	1.449(17)	C(2)-C(3)	1.365(15)

C(3)-C(4)	1.444(16)	C(5)-C(6)	1.436(16)
C(6)-C(7)	1.374(15)	C(7)-C(8)	1.440(16)
N(1)-C(1)	1.139(16)	N(2)-C(4)	1.135(15)
N(3)-C(5)	1.141(15)	N(4)-C(8)	1.136(16)
C(9)-C(10)	1.517(18)	N(5)-C(10)	1.523(14)
C(11)-C(12)	1.518(17)	N(5)-C(12)	1.523(14)
C(13)-C(14)	1.505(19)	N(5)-C(14)	1.526(14)
C(15)-C(16)	1.520(16)	C(16)-C(17)	1.540(18)
N(5)-C(15)	1.507(13)	Br(1)-C(17)	1.930(14)
S(3)-Ni(1)-S(1)	87.54(12)	S(3)-Ni(1)-S(2)	178.50(15)
S(1)-Ni(1)-S(2)	92.81(13)	S(3)-Ni(1)-S(4)	92.35(12)
S(1)-Ni(1)-S(4)	179.75(16)	S(2)-Ni(1)-S(4)	87.29(12)
C(15)-N(5)-C(12)	106.9(8)	C(15)-N(5)-C(10)	110.7(9)
C(12)-N(5)-C(10)	110.9(10)	C(15)-N(5)-C(14)	111.2(9)
C(12)-N(5)-C(14)	110.8(9)	C(10)-N(5)-C(14)	106.4(9)

Table S4: Bond lengths and bond angles in both anions and cations in **4** at 293 K.

		4	
Ni(1)-S(1)	2.156(3)	Ni(1)-S(2)	2.155(3)
Ni(1)-S(3)	2.159(3)	Ni(1)-S(4)	2.157(3)
S(1)-C(6)	1.712(7)	S(2)-C(7)	1.714(7)
S(3)-C(2)	1.717(8)	S(4)-C(3)	1.731(7)
C(1)-C(2)	1.438(10)	C(2)-C(3)	1.382(10)
C(3)-C(4)	1.437(12)	C(5)-C(6)	1.442(11)
C(6)-C(7)	1.397(10)	C(7)-C(8)	1.422(10)
N(1)-C(1)	1.137(10)	N(2)-C(4)	1.147(11)
N(3)-C(5)	1.148(11)	N(4)-C(8)	1.153(10)
C(9)-C(10)	1.527(12)	N(5)-C(10)	1.532(9)
C(11)-C(12)	1.491(13)	N(5)-C(12)	1.546(9)
C(13)-C(14)	1.515(13)	N(5)-C(14)	1.522(8)
C(15)-C(16)	1.524(14)	C(16)-C(17)	1.544(12)
N(5)-C(17)	1.495(10)	C(15)- I(1)	2.127(12)
S(3)-Ni(1)-S(1)	87.66(11)	S(3)-Ni(1)-S(2)	179.37(9)
S(1)-Ni(1)-S(2)	92.70(10)	S(3)-Ni(1)-S(4)	92.78(11)
S(1)-Ni(1)-S(4)	179.51(8)	S(2)-Ni(1)-S(4)	86.86(10)
C(17)-N(5)-C(14)	112.1(6)	C(17)-N(5)-C(10)	111.4(6)
C(14)-N(5)-C(10)	105.7(6)	C(17)-N(5)-C(12)	105.7(5)
C(14)-N(5)-C(12)	111.3(6)	C(10)-N(5)-C(12)	110.7(6)

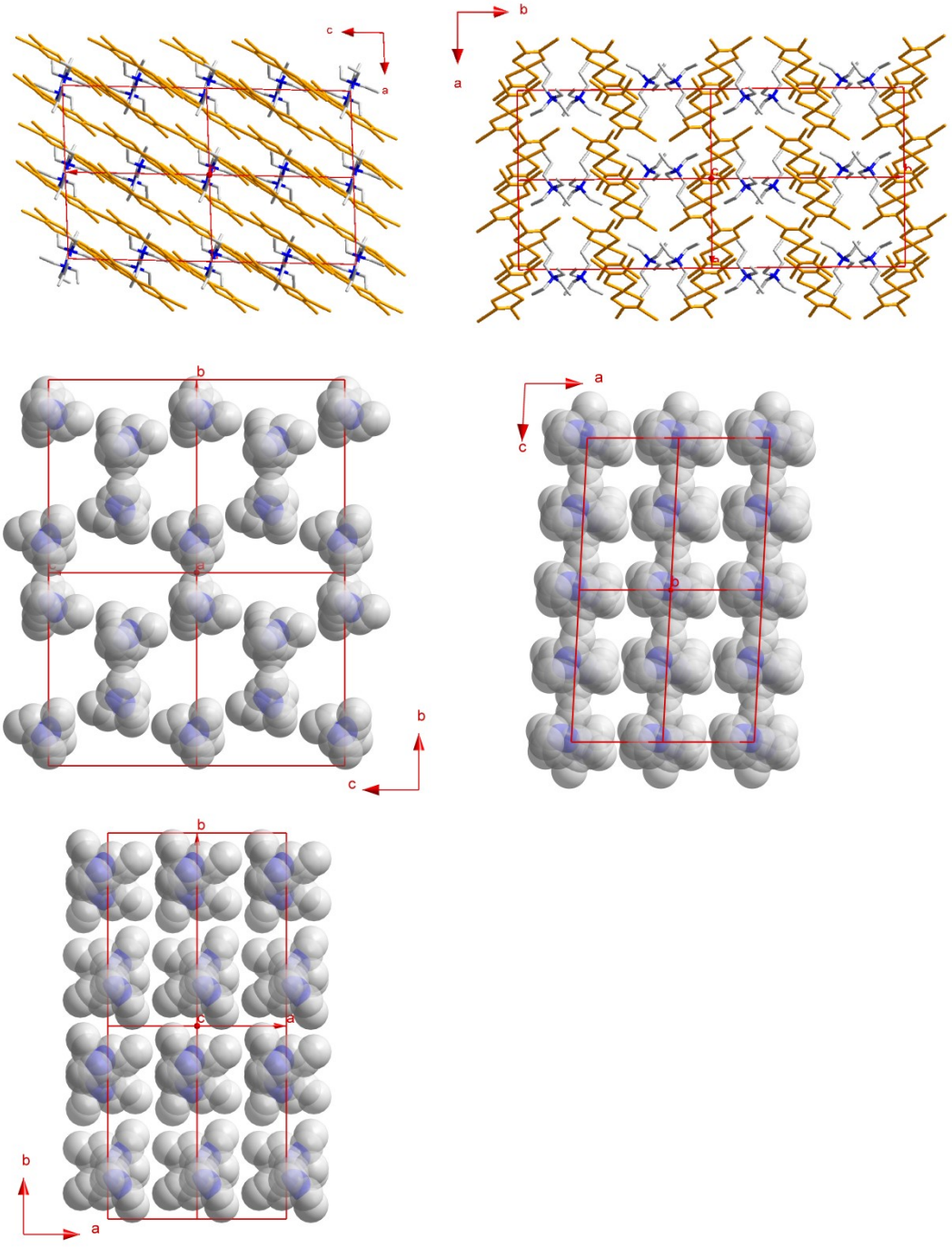

Fig.S9 Packing diagrams of **1** viewd along b-axis and c-axis, and the cation $[Et_3N(CH_2)_2CH_3]^+$of **1** viewed along a-axis, b-axis and c-axis.

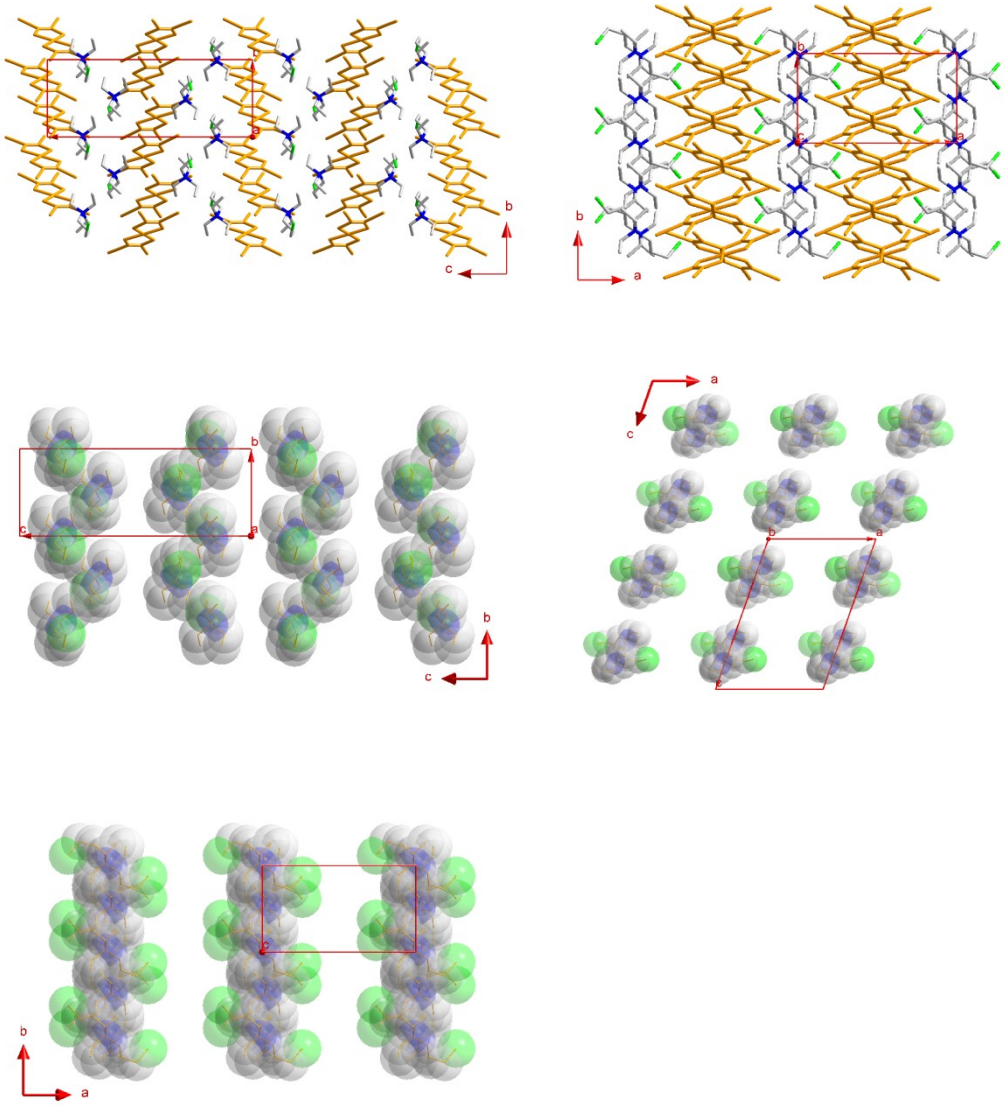

Fig.S10 Packing diagrams of **2** viewd along a-axis and c-axis, and the cation $[Et_3N(CH_2)_3Cl]^+$of **2** viewed along a-axis, b-axis and c-axis.

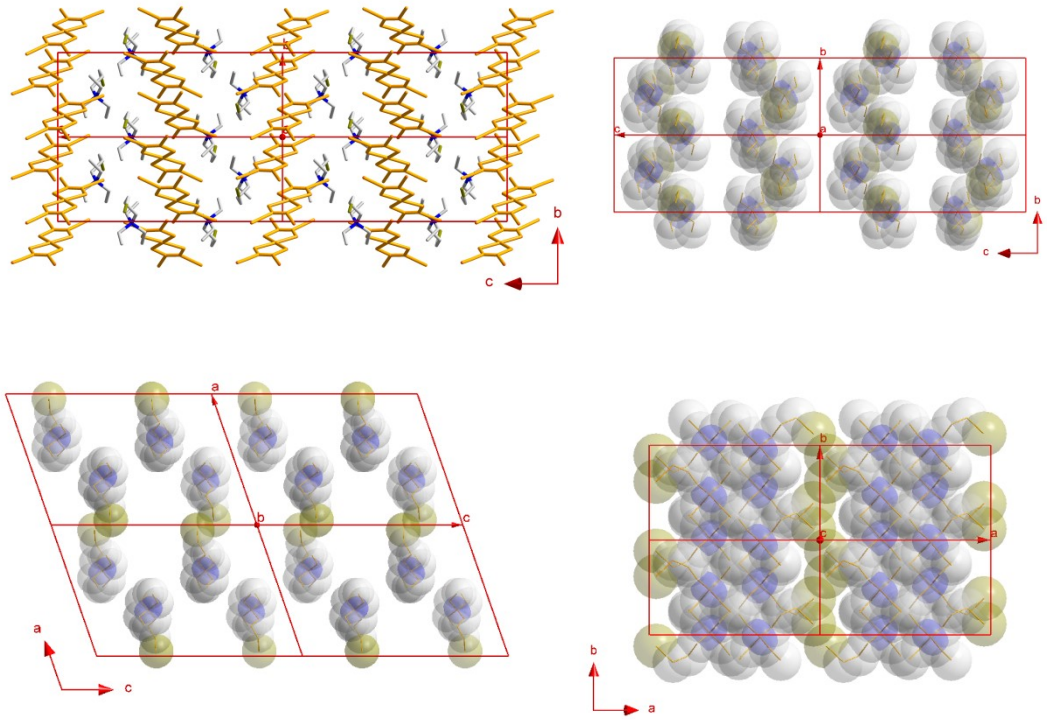

Fig.S11 Packing diagrams of **3** viewd along a-axis, and the cation $[Et_3N(CH_2)_3Br]^+$of **3** viewed along a-axis, b-axis and c-axis.

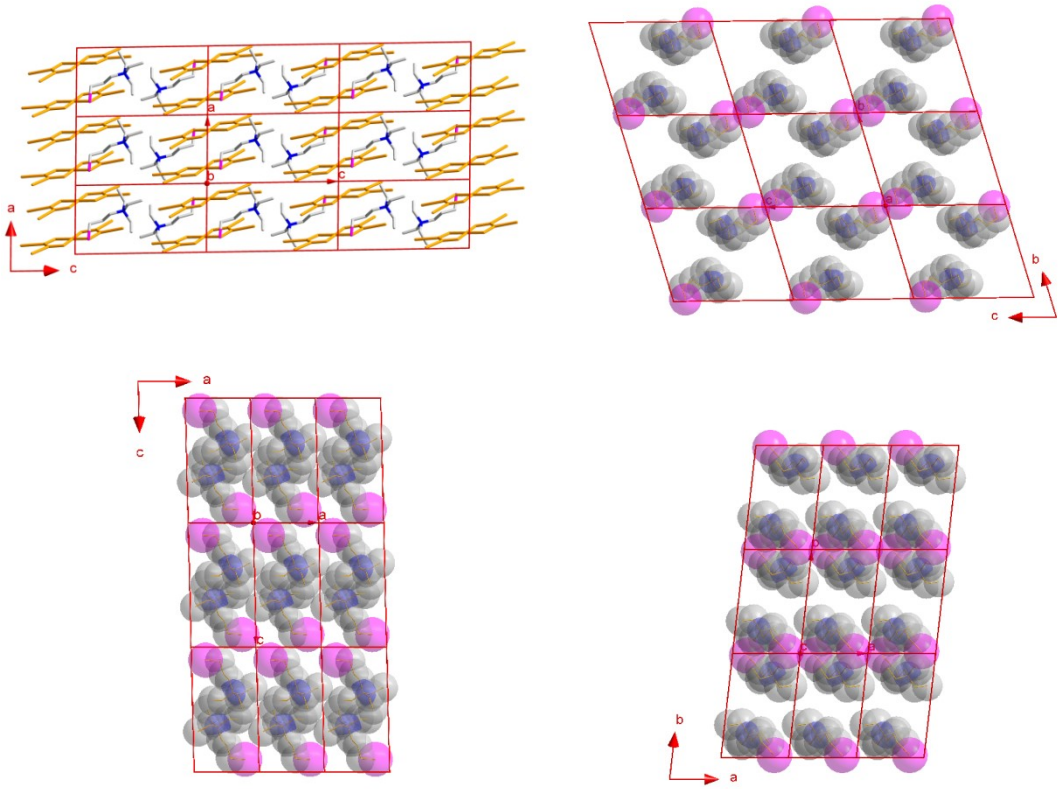

Fig.S12 Packing diagrams of **4** viewd along b-axis, and the cation $[Et_3N(CH_2)_3I]^+$of **4** viewed along a-axis, b-axis and c-axis.

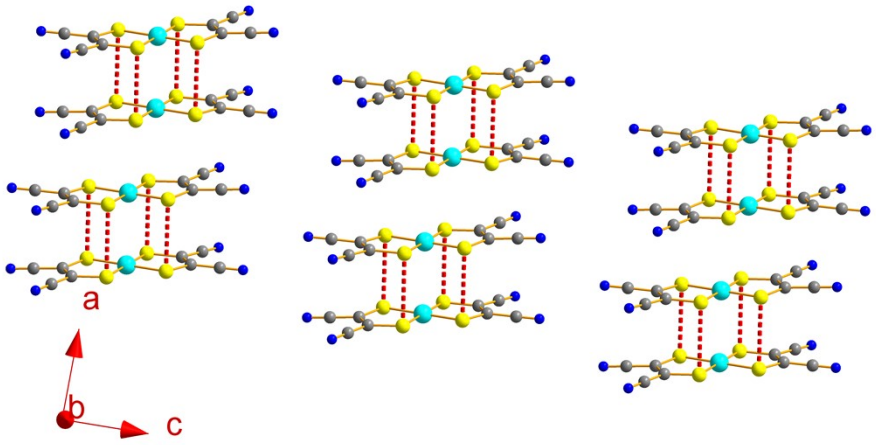

Fig.S13 The charge-assisted H-bonds between the cations and anions in **4**.

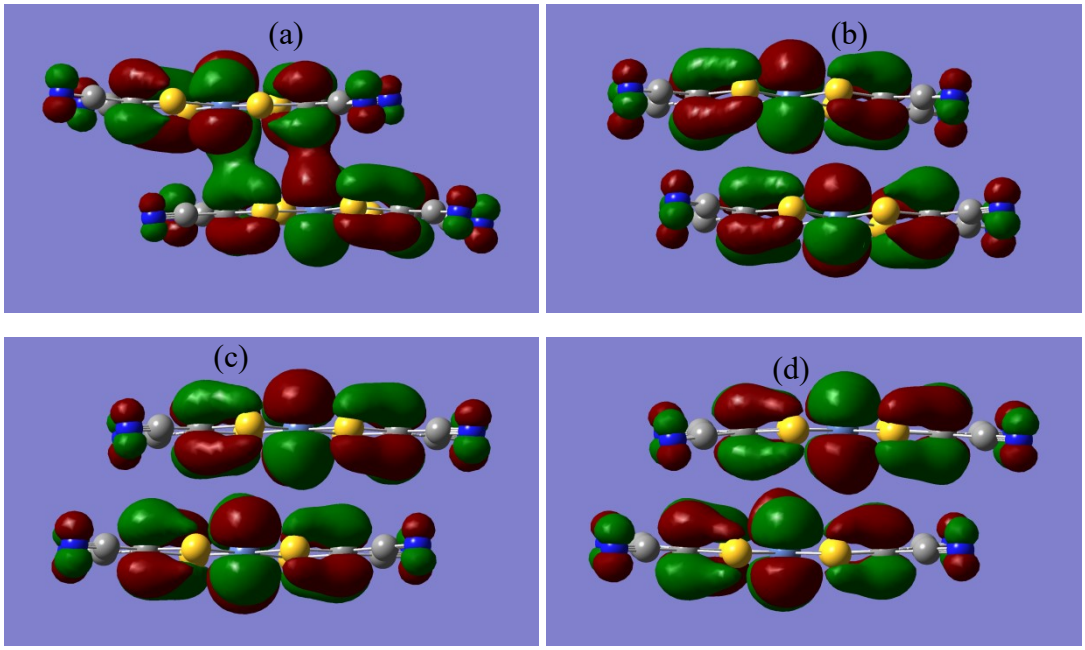

Fig.S14 Kohn–Sham-type orbital of two neighboring $[Ni(mnt)_2]^-$ anions in a stack for the anion pairs with longer Ni···Ni distances in (a) **1**, (b) **2**, (c) **3** and (d) **4**.

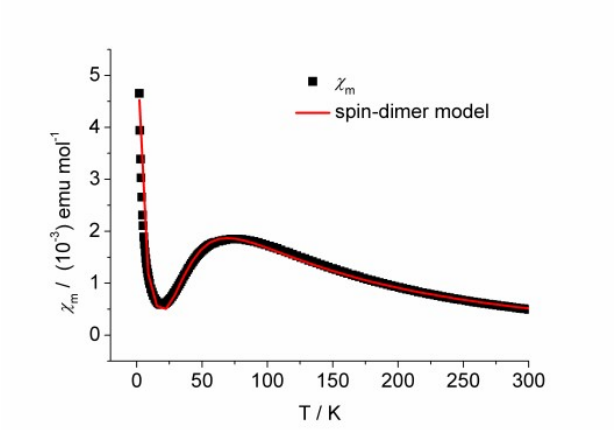

Fig.S15 Temperature-dependent magnetic susceptibility in the temperature range of 2-300 K for **2**.