Supporting Information

Synthesis, characterization and disorder-order phase transition of inorganic-organic hybrid materials (H_2dabco-CH_2-Cl)[$M^{II}Cl_4$] (M = Co, Zn)

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Table S1 Hydrogen bonds for $(H_2dabco\text{-}CH_2\text{-}Cl)[CoCl_4]$ and $(H_2dabco\text{-}CH_2\text{-}Cl)[ZnCl_4]$ at two temperatures

Hydrogen bonds of $(H_2dabco\text{-}CH_2\text{-}Cl)[CoCl_4]$ at 358 K

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (°)
N2-H2···Cl2	0.83(5)	2.74(3)	3.349(4)	132(2)
N2-H2···Cl2[a]	0.83(5)	2.74(3)	3.349(4)	132(2)
C1-H1···Cl3[b]	0.98(5)	2.72(5)	3.635(6)	155(4)
C1-H1···Cl3[c]	0.98(5)	2.72(5)	3.635(6)	155(4)
C5-H5A···Cl3[b]	0.97	2.76	3.630(4)	149

Symmetry transformations used to generate equivalent atoms: a = x, 1/2-y, z; b = 1+x, y, z; c = 1+x, 1/2-y, z.

Hydrogen bonds of $(H_2dabco\text{-}CH_2\text{-}Cl)[CoCl_4]$ at 100 K

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (°)
N2-H2···Cl1[a]	0.88(2)	2.57(2)	3.246(2)	134(1)
N2-H2··· Cl4[a]	0.88(2)	2.78(2)	3.384(2)	127(1)
N2-H2···Cl2[b]	0.88(2)	2.79(2)	3.325(2)	120(1)
C1-H1A···Cl2	0.99	2.79	3.651(2)	145
C2-H2A···Cl2	0.99	2.70	3.584(2)	149
C3-H3B···Cl1[b]	0.99	2.76	3.680(2)	156
C4-H4B···Cl2	0.99	2.68	3.571(2)	150
C5-H5A···Cl2[b]	0.99	2.79	3.444(2)	124
C5-H5B···Cl3[c]	0.99	2.82	3.471(2)	124
C6-H6A···Cl1[d]	0.99	2.74	3.492(2)	133
C6-H6B···Cl4[c]	0.99	2.77	3.517(2)	133
C7-H7A···Cl4[c]	0.99	2.76	3.506(2)	133
C7-H7B···Cl1[d]	0.99	2.74	3.494(2)	133

Symmetry transformations used to generate equivalent atoms: a = x, y, 1+z;b = x, 1/2-y, 1/2+z;c = 1-x, -y, 1-z;d = 2-x, -y, 1-z.

Hydrogen bonds of (H_2dabco-CH_2-Cl)[$ZnCl_4$] at 363 K

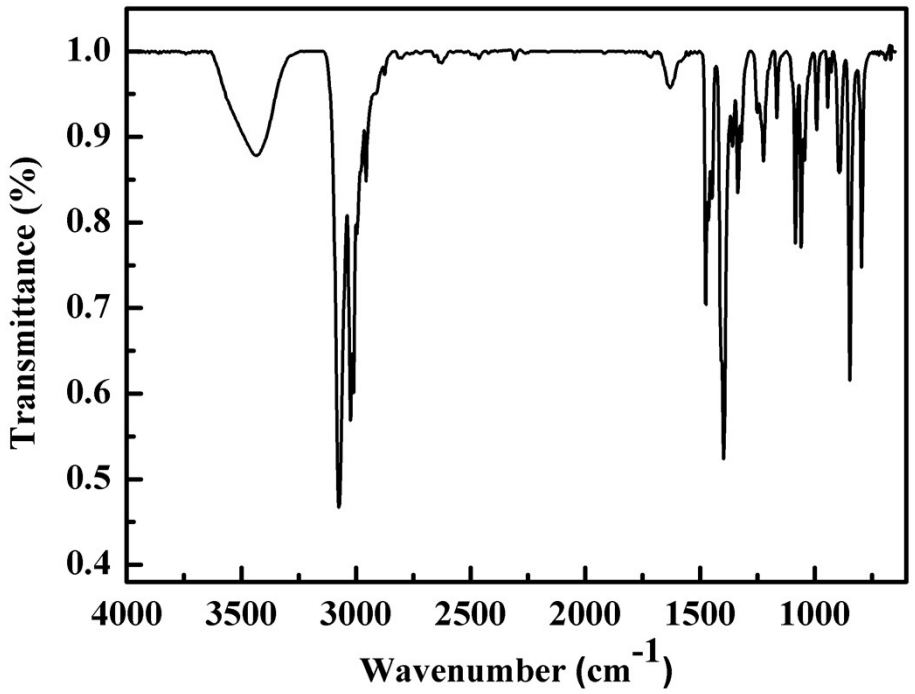
D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (°)
N2-H2···Cl1[a]	0.90(3)	2.68(17)	3.359(4)	132(14)
N2-H2···Cl1[b]	0.90(3)	2.68(17)	3.359(4)	132(14)
C1-H1A···Cl3	0.97(16)	2.80(17)	3.652(5)	149(15)
C1-H1AC···Cl3	0.97(16)	2.74(17)	3.652(5)	156(15)
C5-H5A···Cl3	0.96	2.78	3.639(3)	149

Symmetry transformations used to generate equivalent atoms: a = -1+x, y, z; b = -1+x, 3/2-y, z.

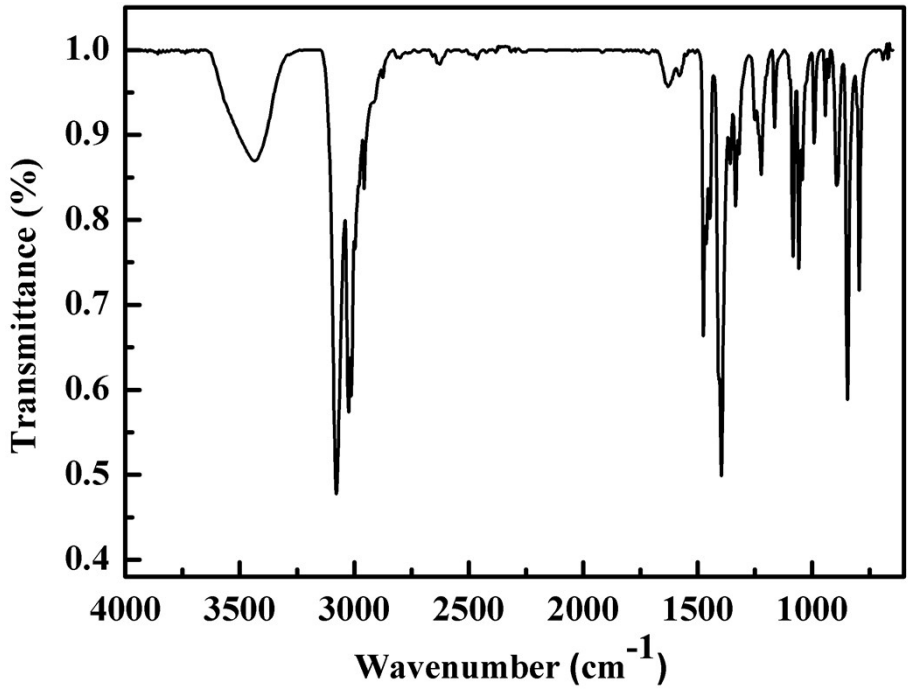
Hydrogen bonds of (H_2dabco-CH_2-Cl)[$ZnCl_4$] at 100 K

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (°)
N2-H2···Cl2[a]	0.90(5)	2.51(5)	3.239(5)	139(5)
N2-H2···Cl4[a]	0.90(5)	2.77(6)	3.383(5)	127(5)
C1-H1B···Cl1[b]	0.99	2.81	3.663(6)	144
C2-H2B···Cl1[b]	0.99	2.69	3.576(6)	149
C3-H3A···Cl2[c]	0.99	2.76	3.681(6)	156
C4-H4A···Cl2[d]	0.99	2.76	3.499(6)	132
C4-H4B···Cl4[e]	0.99	2.73	3.491(6)	134
C5-H5A···Cl4[e]	0.99	2.77	3.512(6)	132
C5-H5B···Cl2[d]	0.99	2.71	3.476(6)	134
C6-H6A···Cl1[b]	0.99	2.68	3.568(6)	150
C7-H7A···Cl1[c]	0.99	2.80	3.444(6)	124
C7-H7C···Cl3[e]	0.99	2.82	3.466(6)	124

Symmetry transformations used to generate equivalent atoms: a = x, -1+y, 1+z; b = x, -1+y, z; c = x, 1/2-y, 1/2+z; d = 2-x, 1-y, 1-z; e = 1-x, 1-y, 1-z.

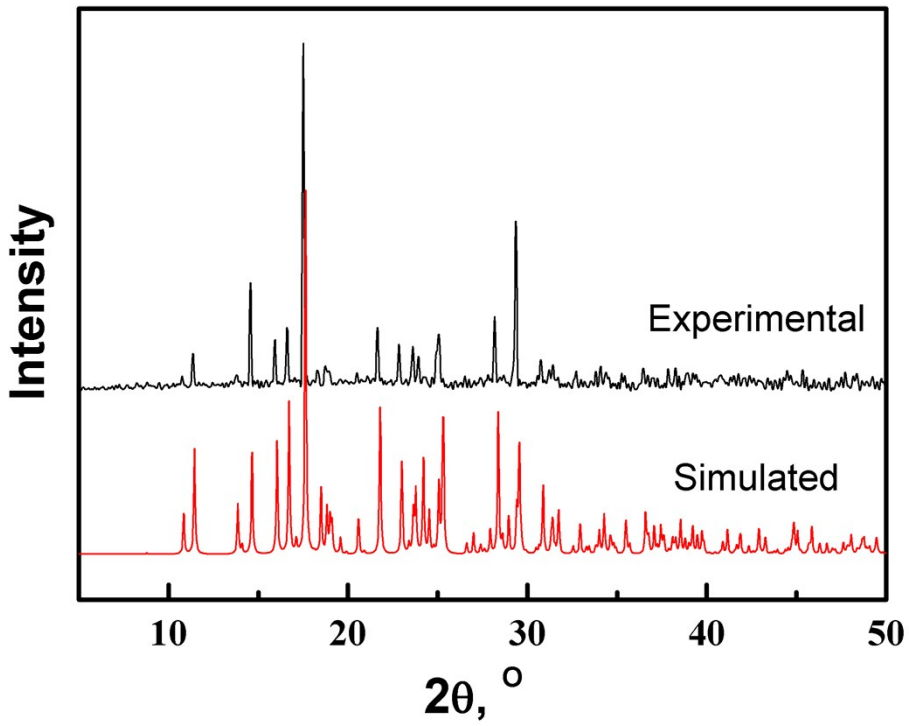


(a)

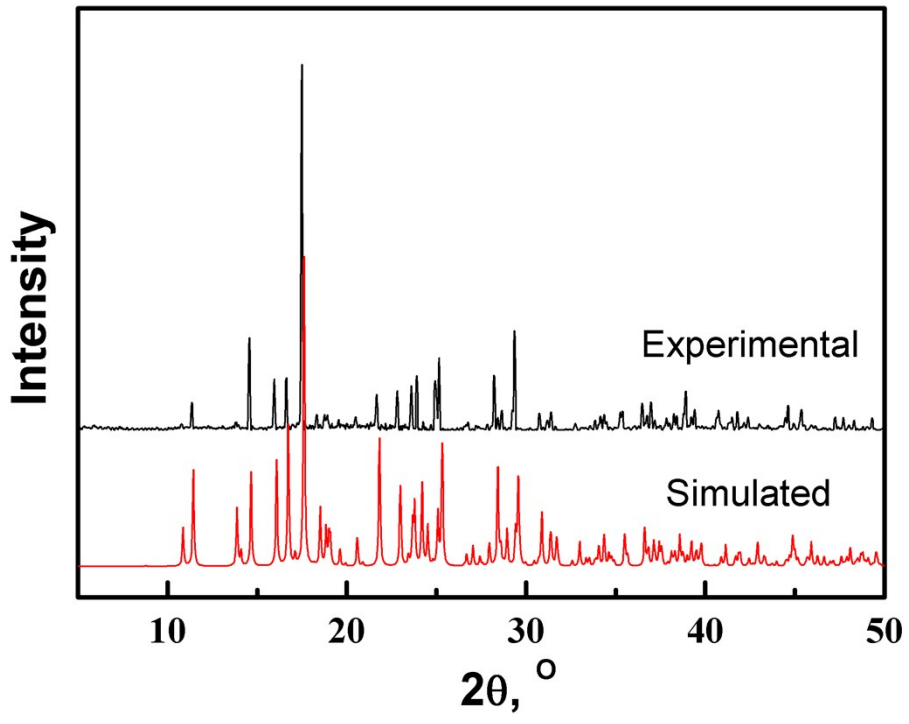


(b)

Fig. S1 IR spectra of (H_2dabco-CH_2-Cl)[$CoCl_4$] (a) and (H_2dabco-CH_2-Cl)[$ZnCl_4$] (b).



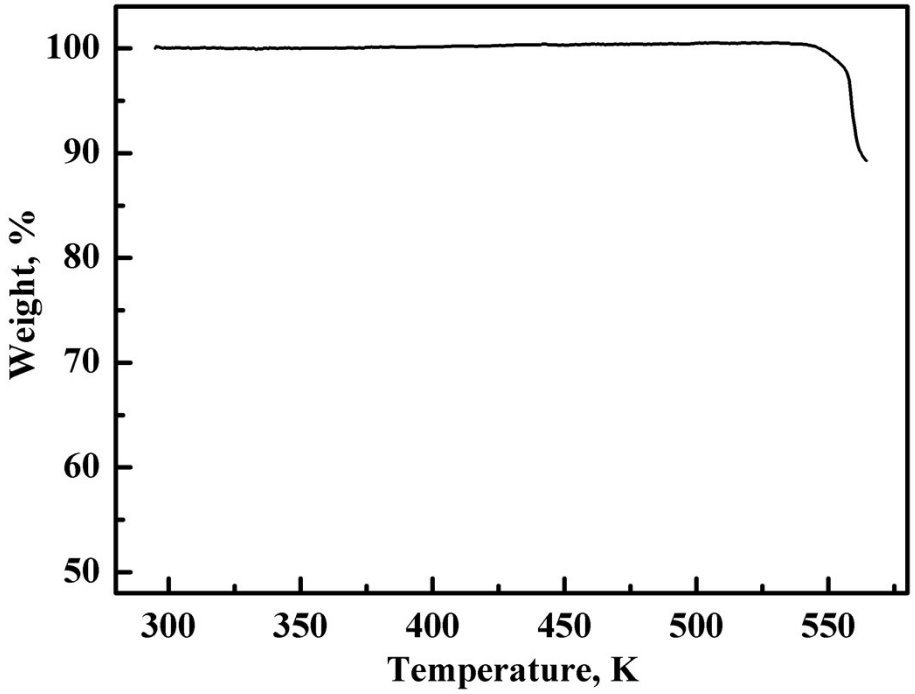
(a)



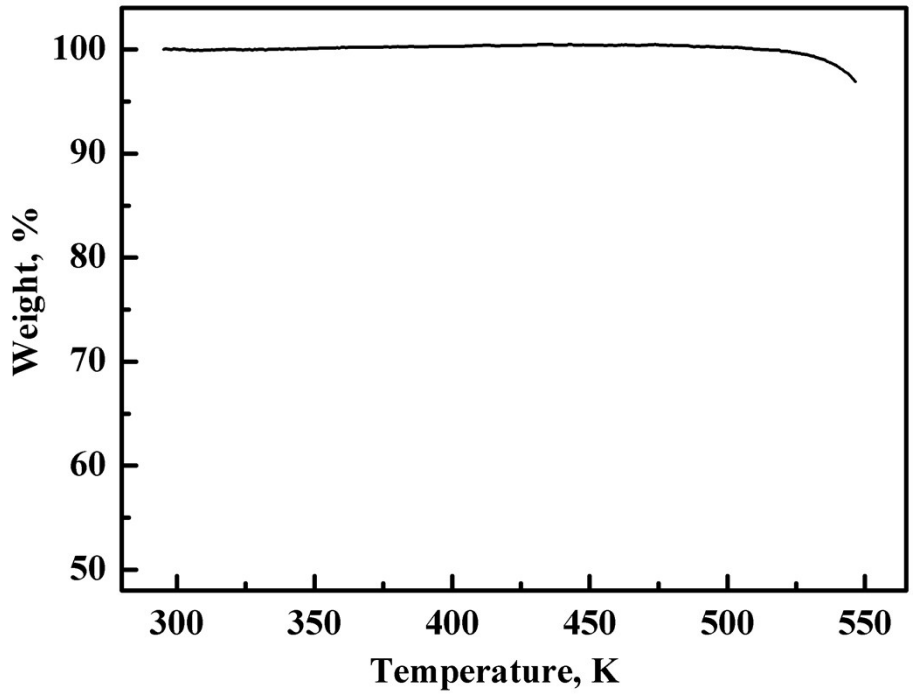
(b)

Fig. S2 PXRD patterns of (H_2dabco-CH_2-Cl)[$CoCl_4$] (a) and (H_2dabco-CH_2-Cl)[$ZnCl_4$] (b).

The TG curves of (H_2dabco-CH_2-Cl)[$CoCl_4$] and (H_2dabco-CH_2-Cl)[$ZnCl_4$] are shown in Fig. S3. Because the Cl element is harmful to the sample holder and thermocouple of the TG instrument, the TG measurements were stopped when the compounds begin to decomposition.

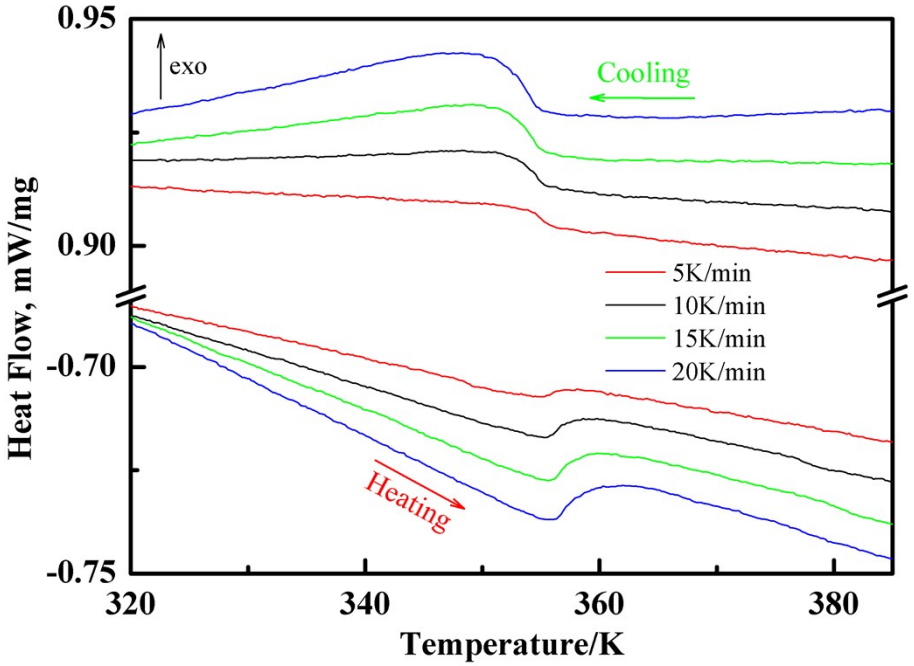


(a)

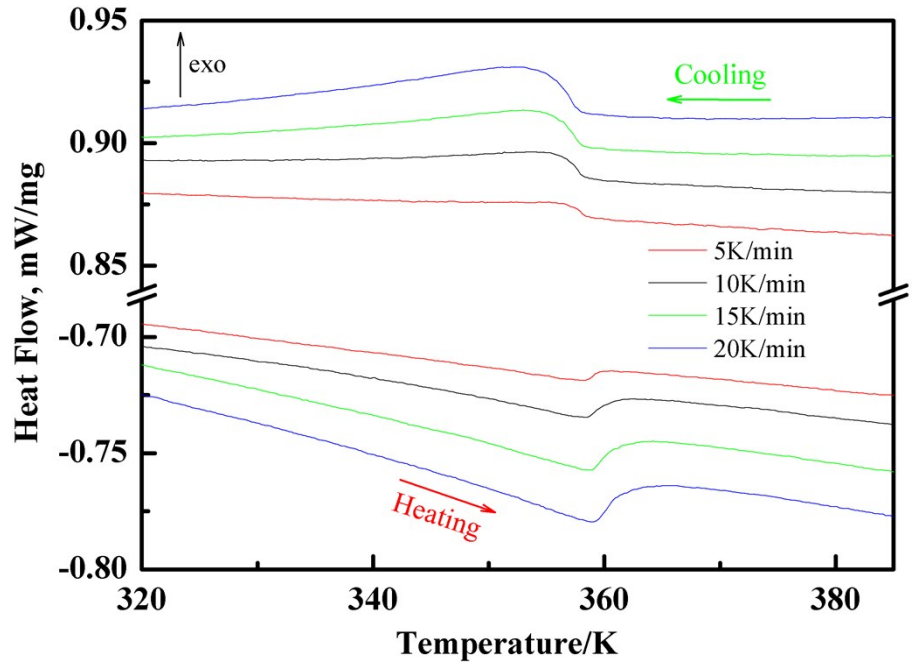


(b)

Fig. S3 TG curves of (H_2dabco-CH_2-Cl)[$CoCl_4$] (a) and (H_2dabco-CH_2-Cl)[$ZnCl_4$] (b).

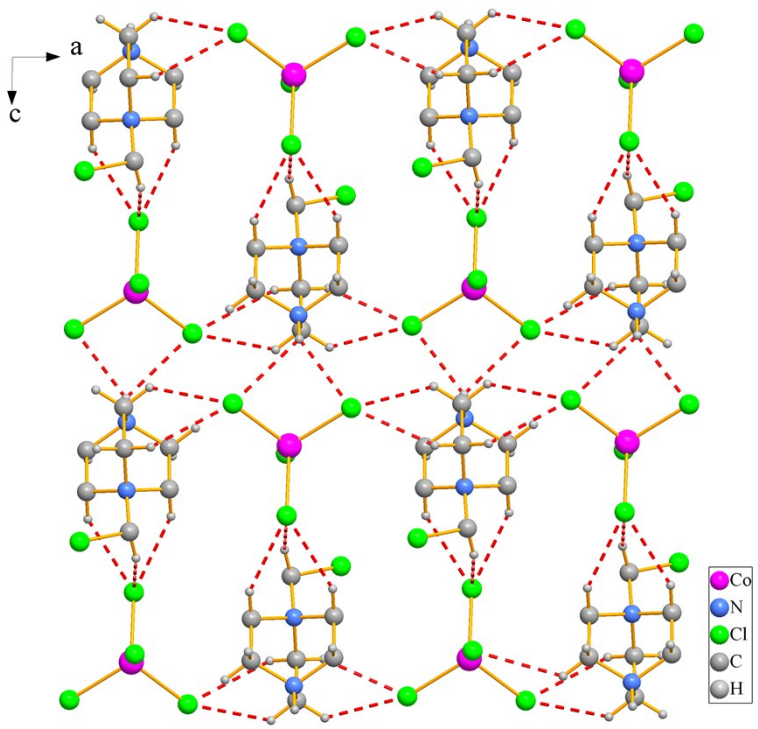


(a)

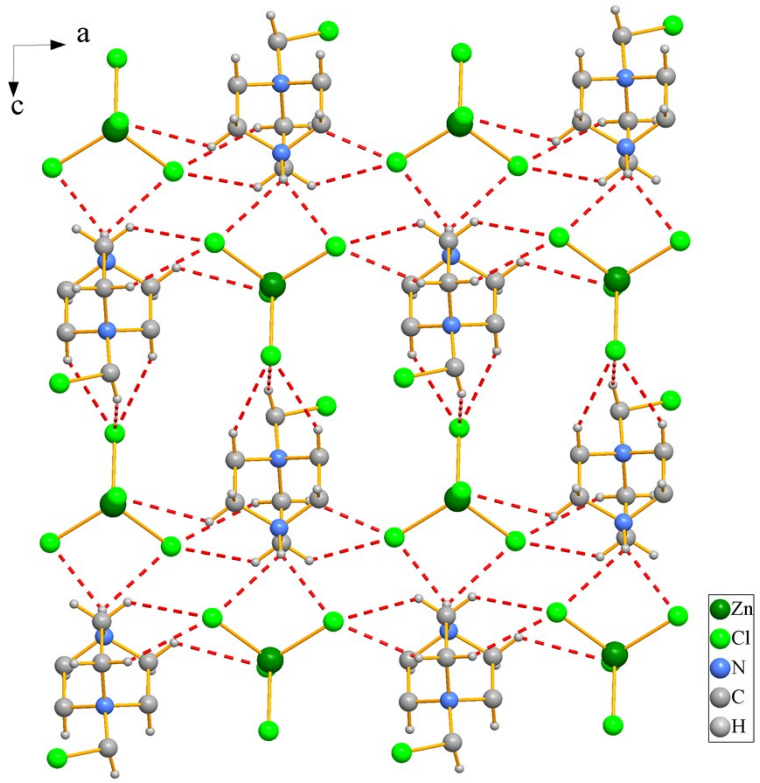


(b)

Fig. S4 DSC curves of (H_2dabco-CH_2-Cl)[$CoCl_4$] (a) and (H_2dabco-CH_2-Cl)[$ZnCl_4$] (b) obtained in a heating-cooling mode at 5 K/min, 10 K/min, 15 K/min and 20 K/min, respectively.



(a)



(b)

Fig. S5 The antiparallel chains are connected by the hydrogen bonds to generate a 2D layers of (H_2dabco-CH_2-Cl)[$CoCl_4$] (a) and (H_2dabco-CH_2-Cl)[$ZnCl_4$] (b).