Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Reversible Thermochromism to Tune Bandgap of Organic-Inorganic Hybrid Halide Materials

Min Wan, [a] Hao-Ran Chen, [a] Yan-Ning Wang, [a] Ke Shi, [a] Jing-Yuan Liu, [a] Zi-Mu Li, [a] Si-Yu Ye, [a] Jun-Yi Li *[a] and Li-Zhuang Chen *[a]

[a] School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, People's Republic of China

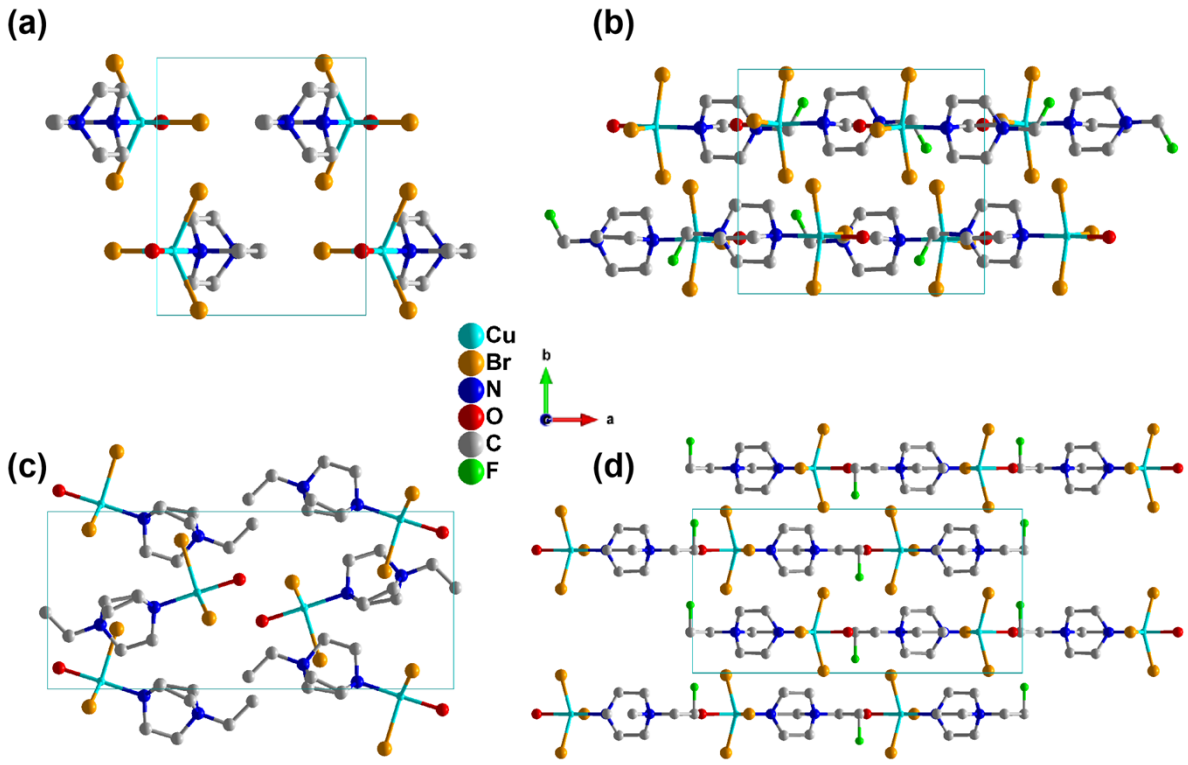

Fig. S1 Structural illustration of (a) (Medabco)$CuBr_3(H_2O)$, (b) (FMedabco)$CuBr_3(H_2O)$, (c) (Etdabco)$CuBr_3(H_2O)$ and (d) (FEtdabco)$CuBr_3(H_2O)$ viewed along the c-axis.

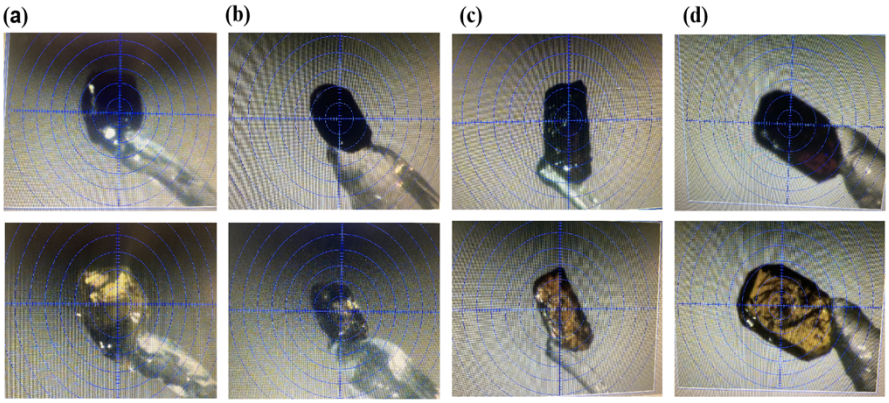

Fig. S2 Temperature-induced reversible color change in (a) (Medabco)$CuBr_3(H_2O)$, (b) (FMedabco)$CuBr_3(H_2O)$, (c) (Etdabco)$CuBr_3(H_2O)$ and (d) (FEtdabco)$CuBr_3(H_2O)$.

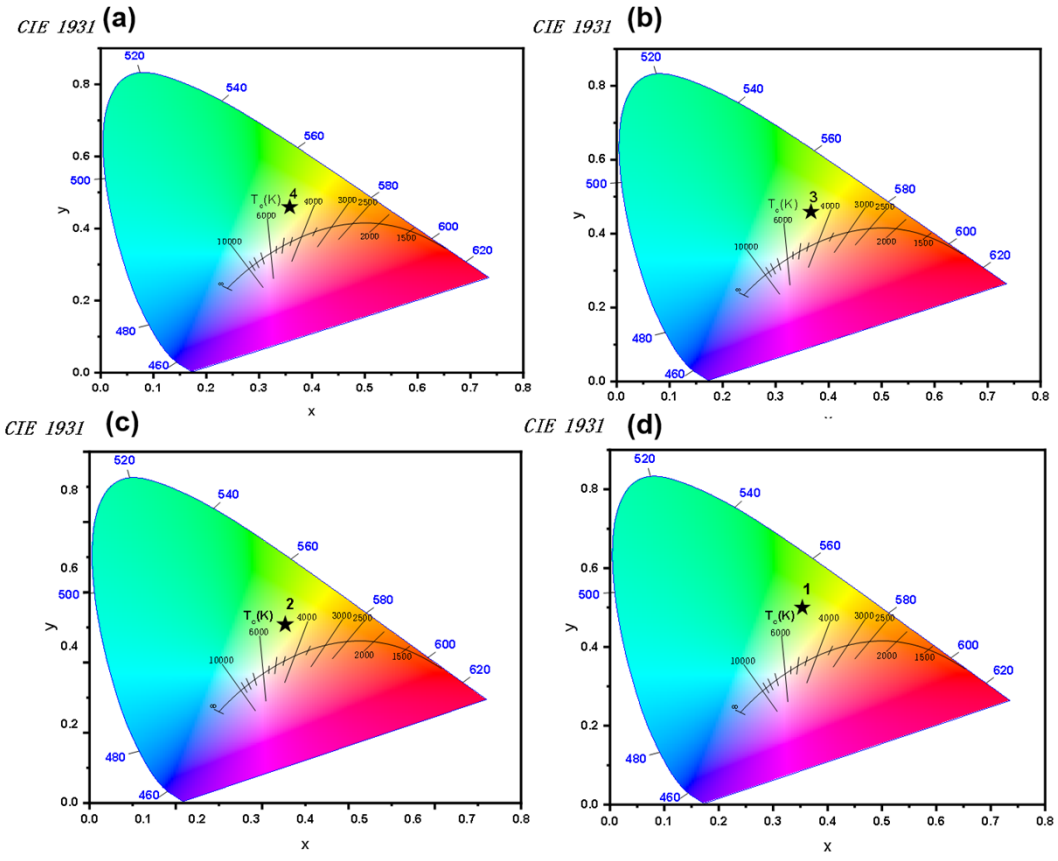

Fig. S3 CIE chromaticity coordinates of (a) (Medabco)$CuBr_3(H_2O)$, (b) (FMedabco)$CuBr_3(H_2O)$, (c) (Etdabco)$CuBr_3(H_2O)$ and (d) (FEtdabco)$CuBr_3(H_2O)$ at 296 K.

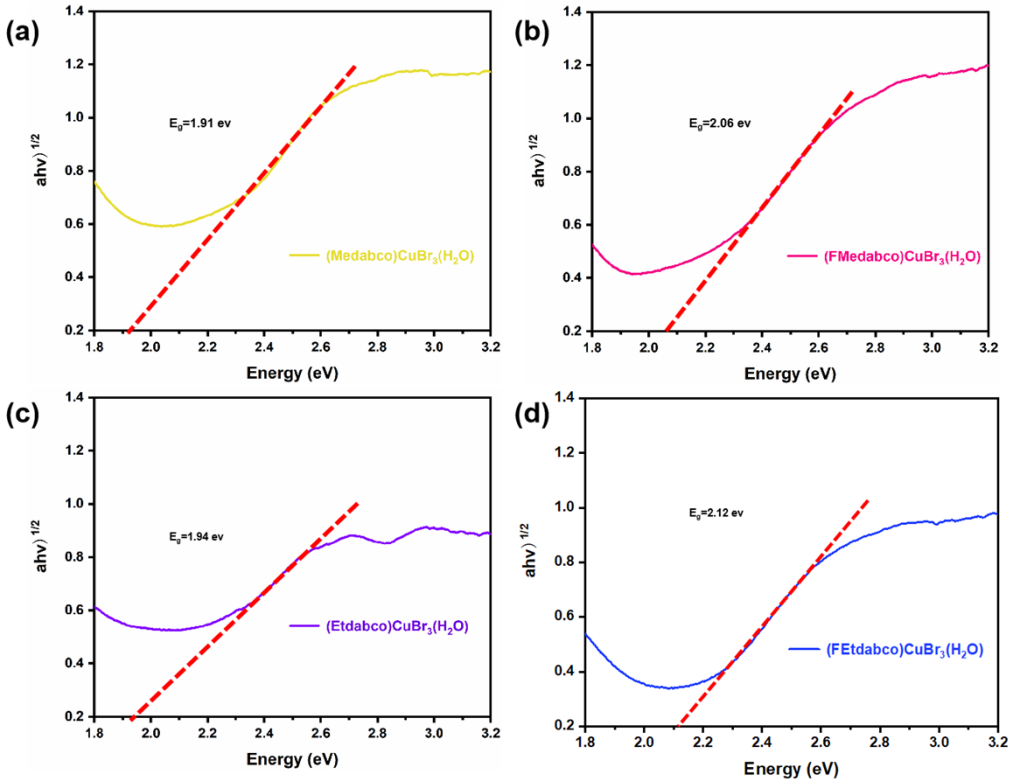

Fig. S4 That shows the Tauc plot for determining the band gap of (a) (Medabco)$CuBr_3(H_2O)$, (b) (FMedabco)$CuBr_3(H_2O)$, (c) (Etdabco)$CuBr_3(H_2O)$ and (d) (FEtdabco)$CuBr_3(H_2O)$, with 1.91 eV, 2.06 eV, 1.94 eV and 2.12 eV.

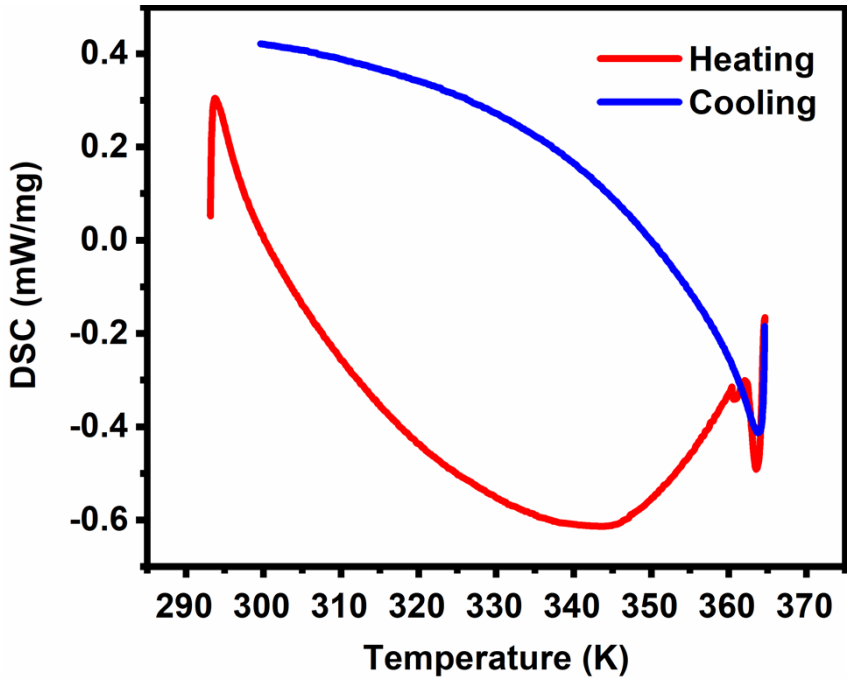

Fig. S5 Differential scanning calorimetry (DSC) of (FEtdabco)$CuBr_3(H_2O)$ with scan rate of 20 K/min under N_2 atmosphere.

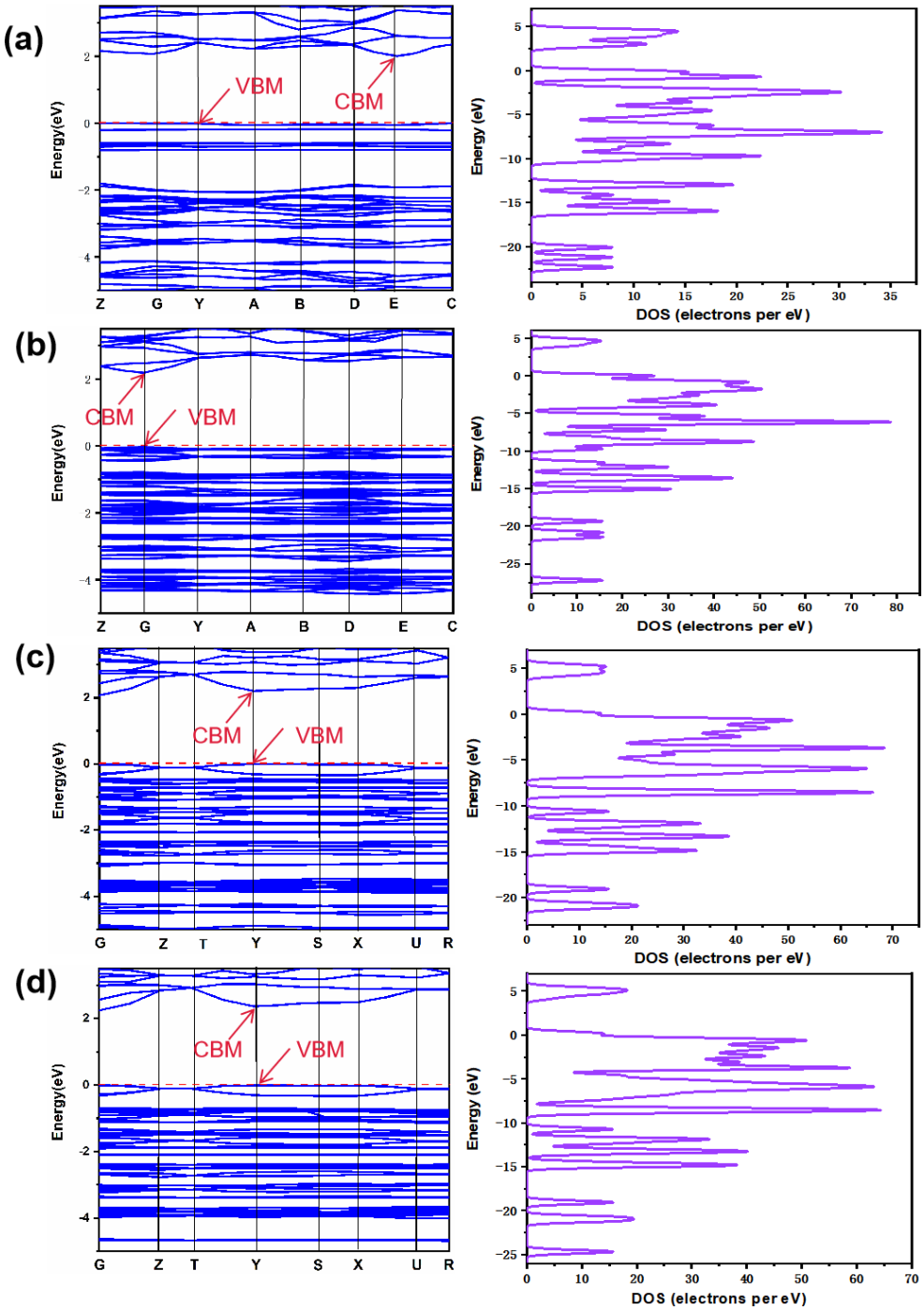

Fig. S6 Calculated band structure and Partial density of states (DOS) of compound (a) (Medabco)$CuBr_3(H_2O)$, (b) (FMedabco)$CuBr_3(H_2O)$, (c) (Etdabco)$CuBr_3(H_2O)$ and (d) (FEtdabco)$CuBr_3(H_2O)$.

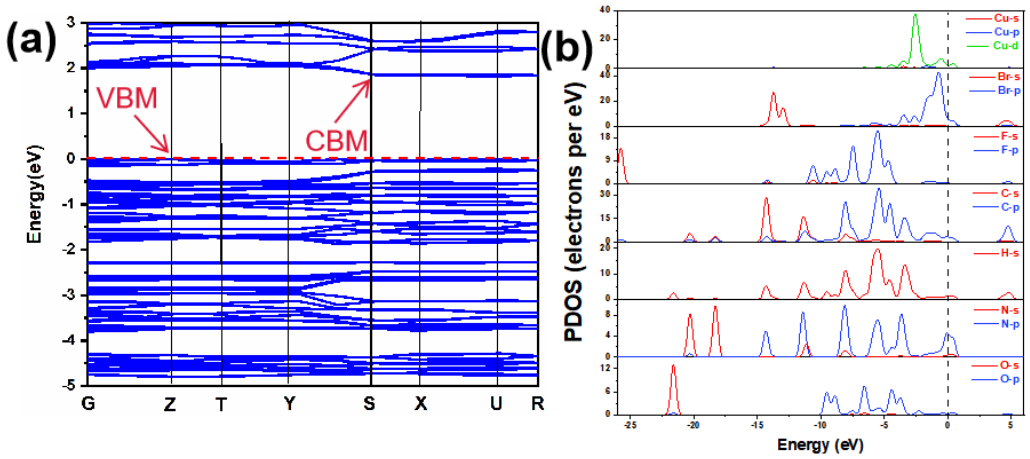

Fig. S7 Band structure (a) and partial density of state (b) of crystal **1** at 365 K.

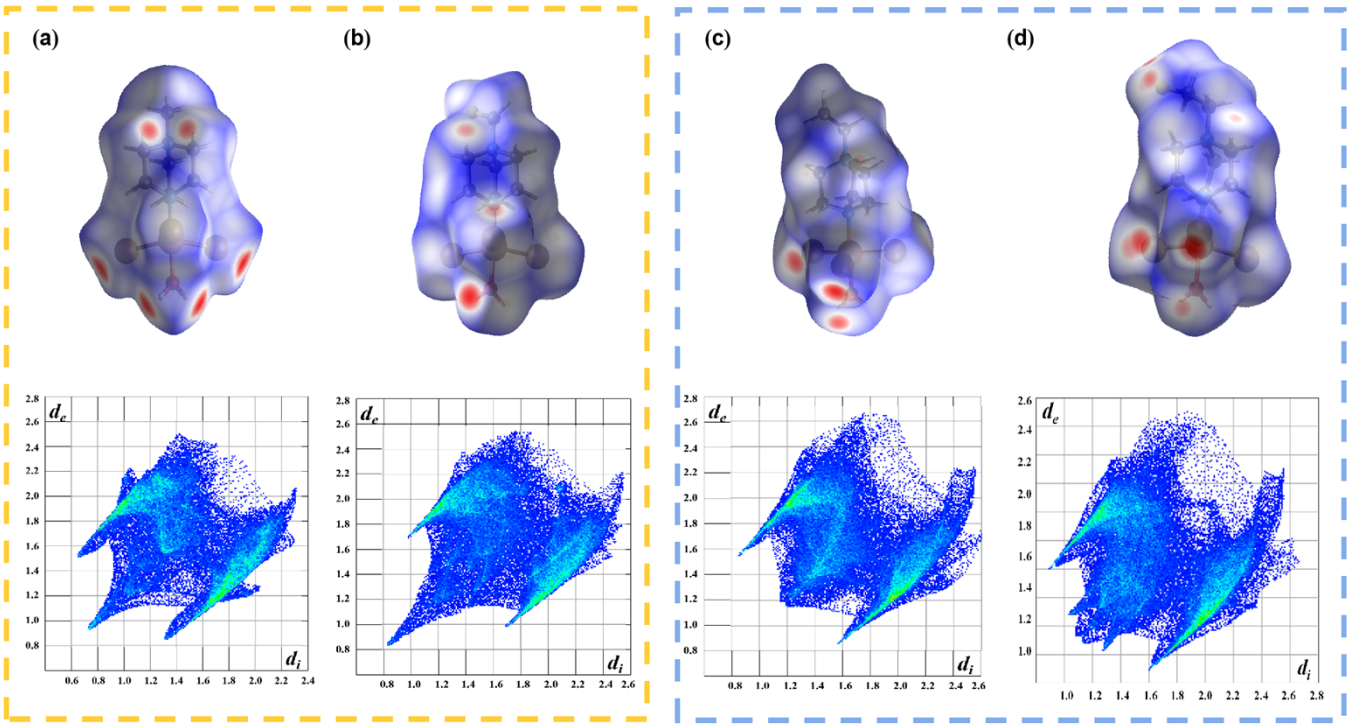

Fig. S7 At 296 K, the close contacts between $All_{inside}\cdots All_{outside}$ of (a) (Medabco)$CuBr_3(H_2O)$, (b) (FMedabco)$CuBr_3(H_2O)$, (c) (Etdabco)$CuBr_3(H_2O)$ and (d) (FEtdabco)$CuBr_3(H_2O)$, respectively. The intensity of molecular interaction is mapped onto the Hirshfeld surface by using a red-blue-white color scheme: where the white regions exactly correspond to the distance of Van der Waals contact, the blue regions correspond to longer contacts, and the red regions represent closer contacts. In 2D fingerprint plots, each point represents an individual pair (d_i, d_e), reflecting the distances to the nearest atom inside (d_i) and outside (d_e) of the Hirshfeld surface, and the frequency of occurrence for these points corresponds to the colors from blue (low), through green, to red (highest).

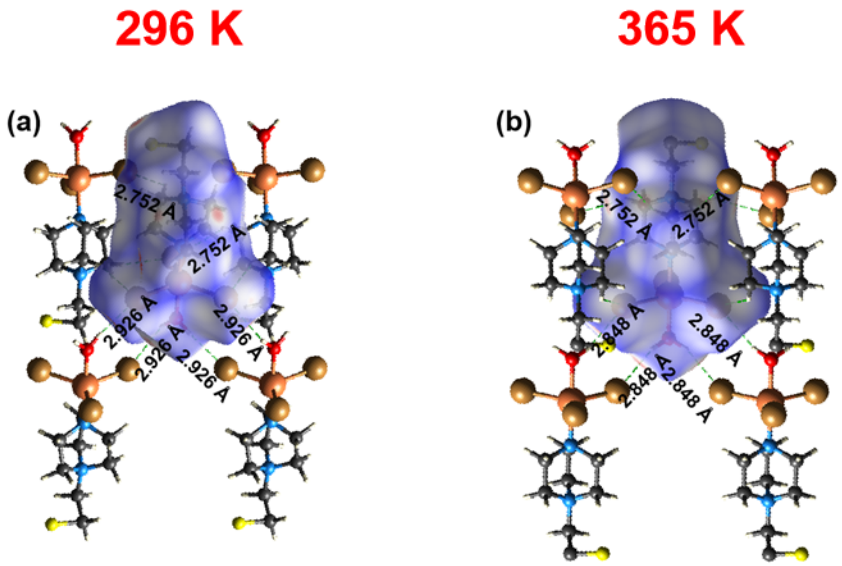

Fig. S8 Hirshfeld surfaces of (FEtdabco)$CuBr_3(H_2O)$ at 296 and 365 K, where the green dashed lines indicate hydrogen bonds.

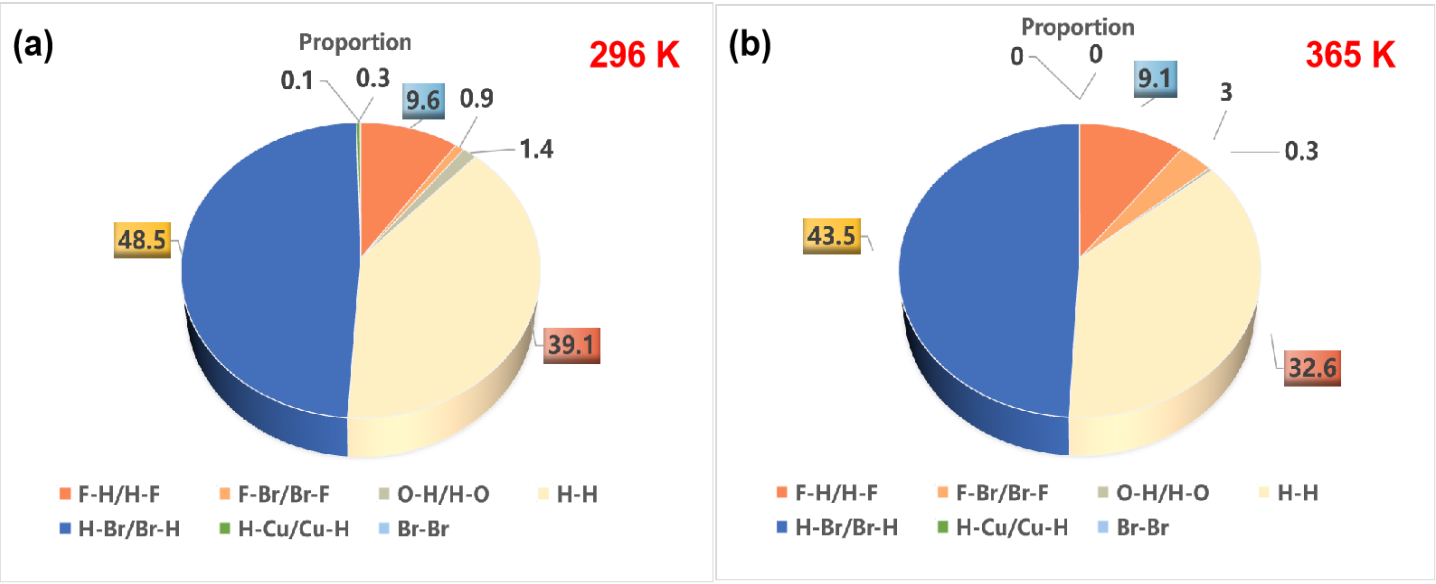

Fig. S9 The scale of (FEtdabco)$CuBr_3(H_2O)$ interaction force distribution at 296 and 365 K.

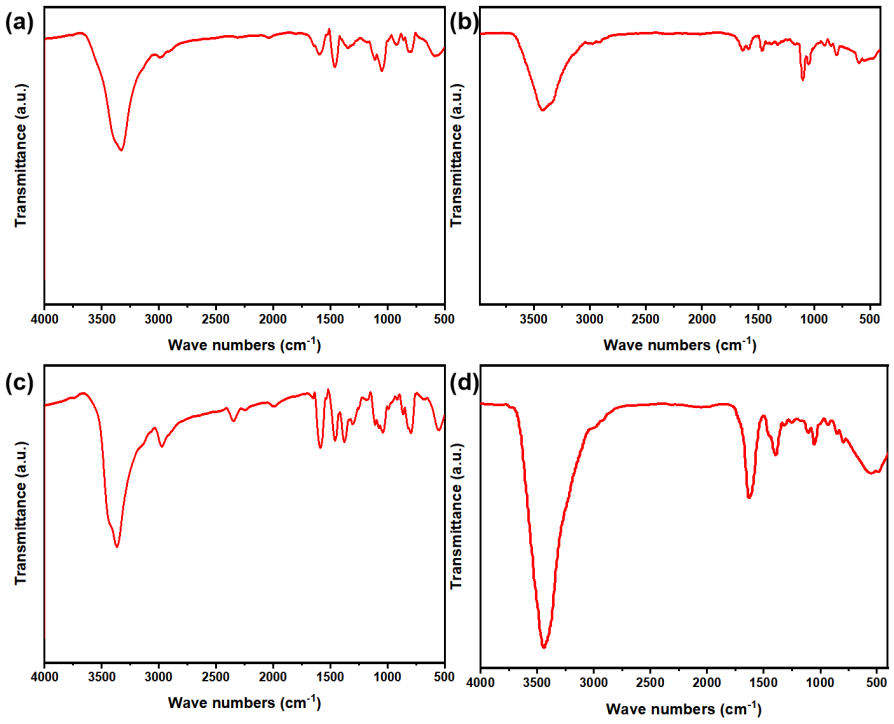

Fig. S10 Infrared (IR) spectra of (a) (Medabco)$CuBr_3(H_2O)$, (b) (FMedabco)$CuBr_3(H_2O)$, (c) (Etdabco)$CuBr_3(H_2O)$ and (d) (FEtdabco)$CuBr_3(H_2O)$ in KBr pellet recorded on a Shimadzu model IR-60 spectrometer at 293 K.

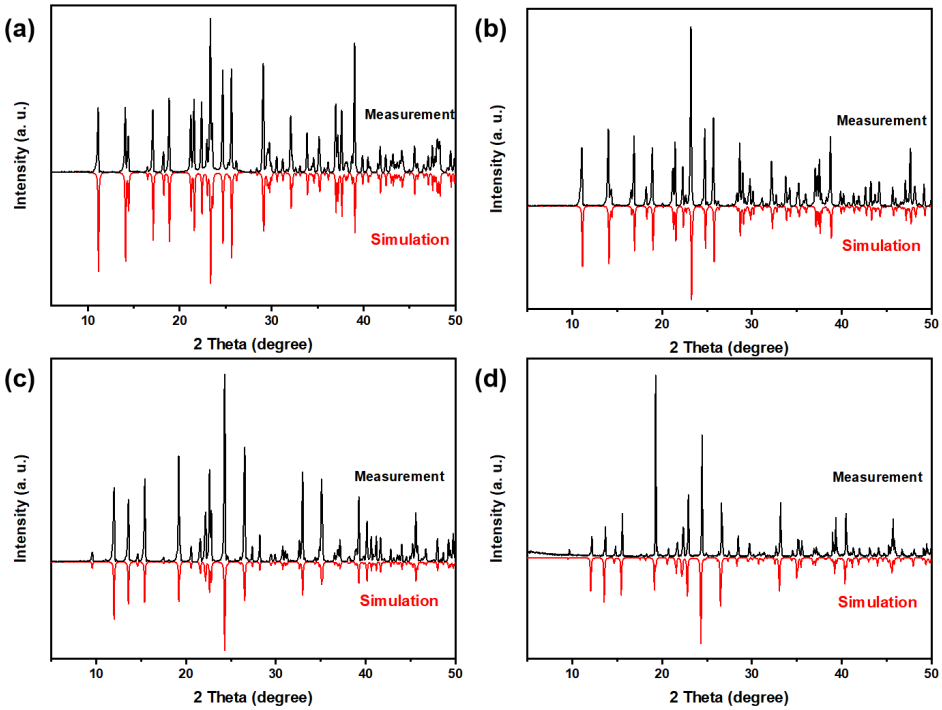

Fig. S11 Experimental powder X-ray diffraction patterns of (a) (Medabco)$CuBr_3(H_2O)$, (b) (FMedabco)$CuBr_3(H_2O)$, (c) (Etdabco)$CuBr_3(H_2O)$ and (d) (FEtdabco)$CuBr_3(H_2O)$ match very well with the simulated ones based on the crystal structures at 296 K.

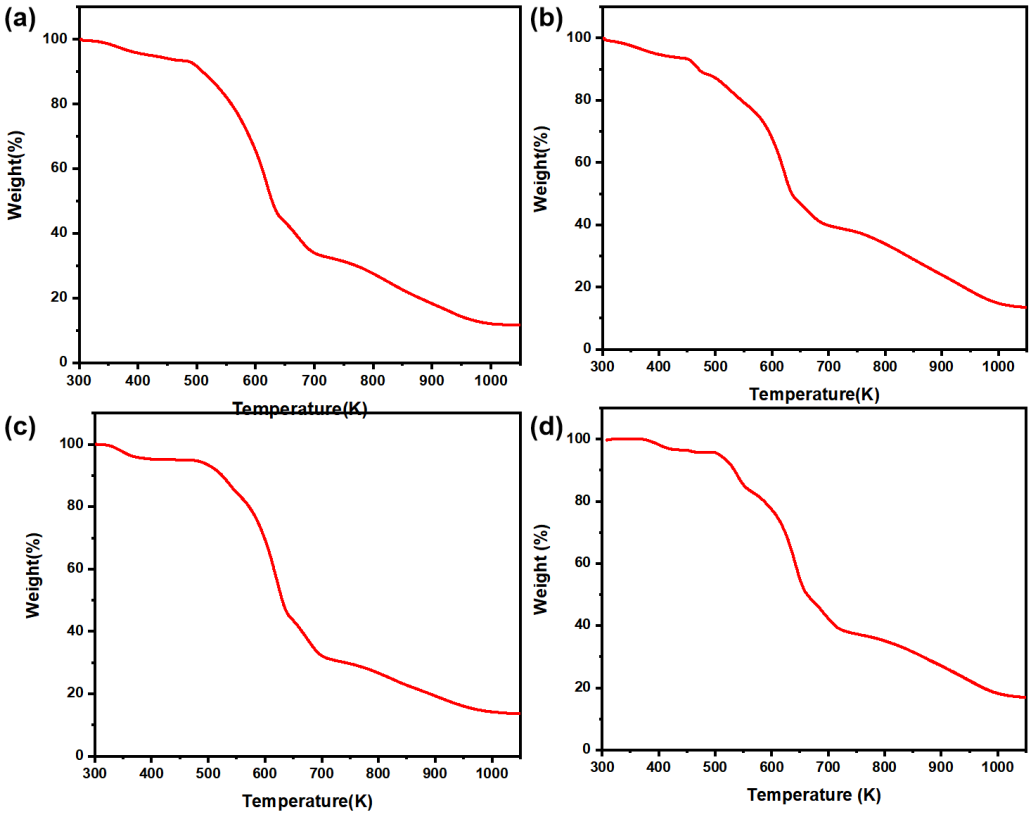

Fig. S12 The TG curves for (a) (Medabco)$CuBr_3(H_2O)$, (b) (FMedabco)$CuBr_3(H_2O)$, (c) (Etdabco)$CuBr_3(H_2O)$ and (d) (FEtdabco)$CuBr_3(H_2O)$, indicating the decent thermal stability of the four compounds.

Table S1 Crystal data and structure refinements for compounds **1-4** at 296 K**.**

Formula	(Medabco)CuBr3(H_2O)	(FMedabco)CuBr3(H_2O)	(Etdabco)CuBr3(H_2O)	(FEtdabco)CuBr3(H_2O)
Formula weight	112.12	463.46	478.89	498.49
Temperature	296.15	296.15	296.15	296.15
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/m$	$P2_1/n$	*Pnma*	*Pnma*
***a*/Å**	7.9966(7)	10.6622(2)	18.4636(6)	18.5303(7)
***b*/Å**	9.7125(9)	9.6800(2)	9.1753(3)	9.1847(3)
***c*/Å**	8.2988(8)	12.4370(3)	8.0380(3)	7.9755(3)
***α*/deg**	90	90	90	90
***β*/deg**	97.549(7)	92.2210(10)	90	90
***γ*/deg**	90	90	90	90
Volume/Å^3	638.96(10)	1282.66(5)	1361.71(8)	1357.39(8)
Z	2	4	4	4
Density g/cm^3	2.331	2.400	2.336	2.429
***R*1[*I*>=2σ (*I*)]**	0.0384	0.0342	0.0434	0.05578
w*R*2[*I*>=2σ (*I*)]	0.0890	0.0849	0.1219	0.1468
GOF	0.998	1.062	1.059	1.089

Table S2 Crystal data and structure refinements for compounds **1-4** at 365 K. (Note: Only cell parameters were measured for crystal **2** at 365 K).

Formula	(Medabco)$CuBr_3(H_2O)$	(FMedabco)$CuBr_3(H_2O)$	(Etdabco)$CuBr_3(H_2O)$	(FEtdabco)CuBr3(H2O)
Formula weight	150.00	465.48		248.75
Temperature	365.0	365.0	365.0	365.0
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/m$	$P2_1/n$	*Pnma*	*Pnma*
***a*/Å**	8.3350(3)	10.7171(15)	16.11	18.6070(4)
***b*/Å**	9.7310(3)	9.7434(14)	18.37	9.2280(2)
***c*/Å**	8.0120(3)	12.5040(2)	18.47	8.0186(16)
***α*/deg**	90	90	90	90
***β*/deg**	97.787(10)	92.2290(5)	90	90
***γ*/deg**	90	90	90	90
Volume/Å^3	643.80(4)	1304.7(3)	1467	1376.8(5)
Z	4	4		8
Density g/cm^3	1.547	2.370		2.400
***R*1[*I*>=2σ (*I*)]**	0.0911	0.0802		0.0599
w*R*2[*I*>=2σ (*I*)]	0.2115	0.2168		0.1492
GOF	1.087	1.069		1.103

Table S3. Hydrogen bonds at 296 K for **1**.

D—H…A	D—H	H…A	D…A	< DHA
O(2)—H(2A)…Br(3)	1.07	2.93	3.438(5)	110
O(2)—H(2A)…F(5)	1.07	2.41	3.399(15)	153
O(2)—H(2B)…Br(3)	1.16	2.32	3.438(5)	161
C(3)—H(3A)…Br(3)	0.97	2.87	3.515(6)	125
C(3)—H(3B)…Br(3)	0.97	2.87	3.515(6)	125
C(5)—H(5A)…Br(2)	0.97	2.79	3.528(6)	125
C(5)—H(5B)…Br(3)	0.97	2.88	3.435(7)	124
C(8)—H(8A)…Br(3)	0.97	2.9	3.435(7)	157
C(8)—H(8B)…Br(3)	0.97	2.9	3.435(7)	157
C(12)—H(12A)…Br(2)	0.97	2.75	3.435(7)	146
C(12)—H(12B)…F(5)	0.97	2.34	3.435(7)	110

Table S4. Hydrogen bonds at 296 K for **2**.

D—H…A	D—H	H…A	D…A	＜DHA
O(1)—H(1)…Br(3)	1.07	2.93	3.438(5)	110
O(1)—H(1)…Br(3)	1.07	2.41	3.399(15)	153
C(3)—H(3A)…Br(3)	1.16	2.32	3.438(5)	161
C(3)—H(3B)…Br(3)	0.97	2.87	3.515(6)	125
C(5)—H(5A)…Br(3)	0.97	2.87	3.515(6)	125
C(5)—H(5B)…Br(2)	0.97	2.79	3.528(6)	125
C(10)—H(10B)…Br(2)	0.97	2.88	3.435(7)	124
C(11)—H(11A)…Br(3)	0.97	2.90	3.435(7)	157
C(11)—H(11B)…Br(3)	0.97	2.90	3.435(7)	157

Table S5. Hydrogen bonds at 296 K for **3**.

D—H…A	D—H	H…A	D…A	< DHA
C(1)—H(1B)…Br(3)	0.97	2.81	3.483(4)	127
C(3)—H(3A)…Br(3)	0.97	2.87	3.506(4)	124
C(3)—H(3B)…Br(2)	0.97	2.79	3.466(4)	127
C(4)—H(4A)…Br(2)	0.97	2.85	3.500(4)	125
C(4)—H(4B)…Br(1)	0.97	2.89	3.528(3)	125
C(5)—H(5A)…Br(2)	0.97	2.89	3.795(5)	156
C(5)—H(5B)…Br(3)	0.97	2.80	3.734(5)	162
C(11)—H(11A)…O(1)	0.97	2.59	3.537(6)	165

Table S6. Hydrogen bonds at 296 K for **4**.

D—H…A	D—H	H…A	D…A	< DHA
O(1)—H(1A)…Br(2)	1.13	2.29	3.325(4)	151
O(1)—H(1B)…Br(2)	1.13	2.63	3.325(4)	119
C(2)—H(2A)…Br(2)	0.97	2.82	3.487(7)	126
C(2)—H(2B)…Br(2)	0.97	2.82	3.487(7)	126
C(4)—H(4A)…Br(2)	0.97	2.84	3.752(7)	156
C(4)—H(4B)…Br(2)	0.97	2.84	3.752(7)	156
C(13)—H(13A)…Br(2)	0.97	2.81	3.485(7)	127

Table S7. Selected Bond Lengths for compound **1** at 293 K

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Br2	2.4761(15)	N3	C12	1.458(10)
Cu1	Br3	2.5367(9)	N3	C12^{1}	1.458(10)
Cu1	Br3^{1}	2.5367(9)	N3	C2	1.496(11)
Cu1	N1	2.062(7)	C3	C8	1.509(2)
Cu1	O2	2.021(7)	C5	C12	1.520(10)
N1	C3	1.501(11)	C2	C4	1.505(15)
N1	C5	1.480(7)	C4	F5^{1}	1.575(12)
N1	C5^{1}	1.480(7)	C4	F5	1.575(12)
N3	C8	1.465(15)	F5	F5^{2}	1.62(2)

Table S8. Selected Bond Lengths for compound **1** at 365 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br01	Cu03	2.535(2)	N006	C00C	1.45(3)
Br02	Cu03	2.475(3)	N006	C00D1	1.46(2)
Cu03	Br011	2.535(2)	N006	C00D	1.46(2)
Cu03	O004	2.017(13)	C007	C00D	1.51(2)
Cu03	N005	2.046(15)	C008	C00C	1.46(3)
N005	C0071	1.448(16)	C009	C00A	1.51(3)
N005	C007	1.448(16)	C00A	F00B1	1.51(3)
N005	C008	1.52(2)	C00A	F00B	1.51(3)
N006	C009	1.49(2)	F00B	F00B2	1.74(5)

Table S9. Selected Bond Lengths for compound **2** at 296 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Cu1	2.5408(5)	N1	C7	1.511(6)
Br2	Cu1	2.4814(9)	N2	C1	1.493(7)
Cu1	Br1^{1}	2.5409(5)	N2	C3^{1}	1.489(4)
Cu1	O1	2.010(4)	N2	C3	1.489(4)
Cu1	N2	2.061(4)	C1	C2	1.503(8)
N1	C2	1.482(8)	C3	C4	1.515(5)
N1	C4	1.464(5)	C7	C8	1.502(8)
N1	C4^{1}	1.464(5)			

Table S10. Selected Bond Lengths for compound **3** at 296 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Cu4	2.4696(7)	N2	C3	1.485(5)
Br2	Cu4	2.5060(6)	C4	C11	1.513(5)
Br3	Cu4	2.5581(6)	N10	C11	1.498(5)
Cu4	N2	2.058(3)	N10	C12	1.493(5)
Cu4	O1	2.021(3)	N10	C2	1.486(5)
C1	N2	1.489(4)	N10	C5	1.501(5)
C1	C12	1.520(5)	F2	C2	1.355(5)
N2	C4	1.494(4)	C3	C5	1.522(6)

Table S11. Selected Bond Lengths for compound **4** at296 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Cu3	2.4656(10)	N8	C2	1.495(8)
Br2	Cu3	2.5477(6)	N10	C15^{1}	1.504(5)
Cu3	Br2^{1}	2.5477(6)	N10	C15	1.504(5)
Cu3	N8	2.057(5)	N10	C4	1.486(9)
Cu3	O1	1.994(5)	N10	C0AA	1.496(8)
N8	C13^{1}	1.491(5)	C13	C15	1.517(7)
N8	C13	1.491(5)	C2	C4	1.512(9)

Table S12. Selected Bond Angles for compound **1** at 296 K.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br2	Cu1	Br3^{1}	120.59(3)	C8	N3	C2	109.1(7)
Br2	Cu1	Br3	120.59(3)	C12	N3	C8	107.5(7)
Br3	Cu1	Br3^{1}	118.17(6)	C12^{1}	N3	C8	107.5(7)
N1	Cu1	Br2	91.3(2)	C12^{1}	N3	C12	106.2(12)
N1	Cu1	Br3^{1}	93.40(10)	C12^{1}	N3	C2	113.1(5)
N1	Cu1	Br3	93.40(10)	C12	N3	C2	113.1(5)
O2	Cu1	Br2	89.1(2)	N1	C3	C8	109.6(8)
O2	Cu1	Br3^{1}	86.41(12)	N1	C5	C12	110.8(6)
O2	Cu1	Br3	86.41(12)	N3	C8	C3	113.6(9)
O2	Cu1	N1	179.6(3)	N3	C12	C5	112.3(7)
C3	N1	Cu1	111.3(5)	N3	C2	C4	116.0(8)
C5	N1	Cu1	111.5(4)	C2	C4	F5^{1}	102.3(6)
C5^{1}	N1	Cu1	111.5(4)	C2	C4	F5	102.3(6)
C5	N1	C3	106.7(4)	F5^{1}	C4	F5	144.2(14)
C5^{1}	N1	C3	106.7(4)	C4	F5	F5^{2}	166.0(14)
C5	N1	C5^{1}	108.9(7)				

Table S13. Selected Bond Angles for compound **1** at 365 K.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br01	Cu03	Br01	118.33(13)	C00C	N006	C009	111.7(16)
Br02	Cu03	Br01	120.45(7)	C00C	N006	C00D[1]	106.4(18)
Br02	Cu03	Br01[1]	120.45(7)	C00C	N006	C00D	106.4(18)
O004	Cu03	Br01	86.2(3)	C00D[1]	N006	C009	112.7(11)
O004	Cu03	Br01[1]	86.2(3)	C00D	N006	C009	112.7(11)
O004	Cu03	Br02	88.8(6)	C00D	N006	C00D[1]	107(3)
O004	Cu03	N005	179.9(7)	N005	C007	C00D	111.6(12)
N005	Cu03	Br01[1]	93.8(2)	C00C	C008	N005	110.0(14)
N005	Cu03	Br01	93.8(2)	N006	C009	C00A	116.9(19)
N005	Cu03	Br02	91.1(4)	F00B	C00A	C009	102.4(19)
C007[1]	N005	Cu03	111.9(8)	F00B[1]	C00A	C009	102.4(19)
C007	N005	Cu03	111.9(8)	F00B	C00A	F00B[1]	147(4)
C007	N005	C007[1]	108.9(16)	C00A	F00B	F00B[2]	166(5)
C007[1]	N005	C008	106.0(10)	N006	C00C	C008	115.0(17)
C007	N005	C008	106.0(10)	N006	C00D	C007	112.2(14)
C008	N005	Cu03	111.8(10)				

Table S14. Selected Bond Angles for compound **2** at 296 K.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br1	Cu1	Br1[1]	119.52(3)	C4	N1	C7	112.0(3)
Br2	Cu1	Br1[1]	119.917(17)	C4[1]	N1	C7	112.0(3)
Br2	Cu1	Br1	119.917(17)	C1	N2	Cu1	111.7(3)
O1	Cu1	Br1[1]	86.49(6)	C3	N2	Cu1	111.2(2)
O1	Cu1	Br1	86.49(6)	C3[1]	N2	Cu1	111.2(2)
O1	Cu1	Br2	89.03(12)	C3	N2	C1	107.3(3)
O1	Cu1	N2	179.31(17)	C3[1]	N2	C1	107.3(3)
N2	Cu1	Br1	93.16(6)	C3[1]	N2	C3	107.9(4)
N2	Cu1	Br1[1]	93.17(6)	N2	C1	C2	110.4(4)
N2	Cu1	Br2	91.66(12)	N1	C2	C1	112.2(5)
C2	N1	C7	109.6(4)	N2	C3	C4	110.8(3)
C4[1]	N1	C2	107.6(4)	N1	C4	C3	111.7(3)
C4	N1	C2	107.6(4)	C8	C7	N1	114.9(5)
C4[1]	N1	C4	107.8(6)				

Table S15. Selected Bond Angles for compound **3** at 296 K.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br1	Cu4	Br2	119.72(2)	C3	N2	C1	107.8(3)
Br1	Cu4	Br3	118.46(2)	C3	N2	C4	108.2(3)
Br2	Cu4	Br3	120.69(3)	N2	C4	C11	111.7(3)
N2	Cu4	Br1	95.53(9)	C11	N10	C5	107.9(3)
N2	Cu4	Br2	93.10(8)	C12	N10	C11	108.9(4)
N2	Cu4	Br3	92.00(8)	C12	N10	C5	108.7(3)
O1	Cu4	Br1	90.62(11)	C2	N10	C11	111.5(3)
O1	Cu4	Br2	84.39(8)	C2	N10	C12	108.6(3)
O1	Cu4	Br3	84.47(8)	C2	N10	C5	111.2(3)
O1	Cu4	N2	173.82(14)	N10	C11	C4	110.0(3)
N2	C1	C12	111.8(3)	N10	C12	C1	109.8(3)
C1	N2	Cu4	112.3(2)	N2	C3	C5	111.9(3)
C1	N2	C4	106.8(3)	F2	C2	N10	108.0(3)
C4	N2	Cu4	110.7(2)	N10	C5	C3	109.6(3)
C3	N2	Cu4	110.8(2)				

Table S16. Selected Bond Angles for compound **4** at 296 K.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br1	Cu3	Br2	117.86(2)	C13^{1}	N8	C2	107.8(3)
Br1	Cu3	Br2^{1}	117.86(2)	C13	N8	C2	107.8(3)
Br2^{1}	Cu3	Br2	123.06(4)	C2	N8	Cu3	109.2(4)
N8	Cu3	Br1	95.90(14)	C15	N10	C15^{1}	109.0(5)
N8	Cu3	Br2	92.60(7)	C4	N10	C15^{1}	107.7(4)
N8	Cu3	Br2^{1}	92.60(7)	C4	N10	C15	107.7(4)
O1	Cu3	Br1	91.23(14)	C4	N10	C0AA	111.2(5)
O1	Cu3	Br2^{1}	84.04(7)	C0AA	N10	C15	110.6(3)
O1	Cu3	Br2	84.04(7)	C0AA	N10	C15^{1}	110.6(3)
O1	Cu3	N8	172.87(19)	N8	C13	C15	111.8(4)
C13	N8	Cu3	112.4(3)	N10	C15	C13	110.1(4)
C13^{1}	N8	Cu3	112.4(3)	N8	C2	C4	111.3(5)
C13^{1}	N8	C13	107.1(5)	N10	C4	C2	111.0(5)