Supplementary Information

Cupric coordination compounds with various anions: A promising strategy for regulation of energetic materials

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Contents

1. The FT-IR spectra of compounds 2-4

Fig. S1 FT-IR spectra of **2**

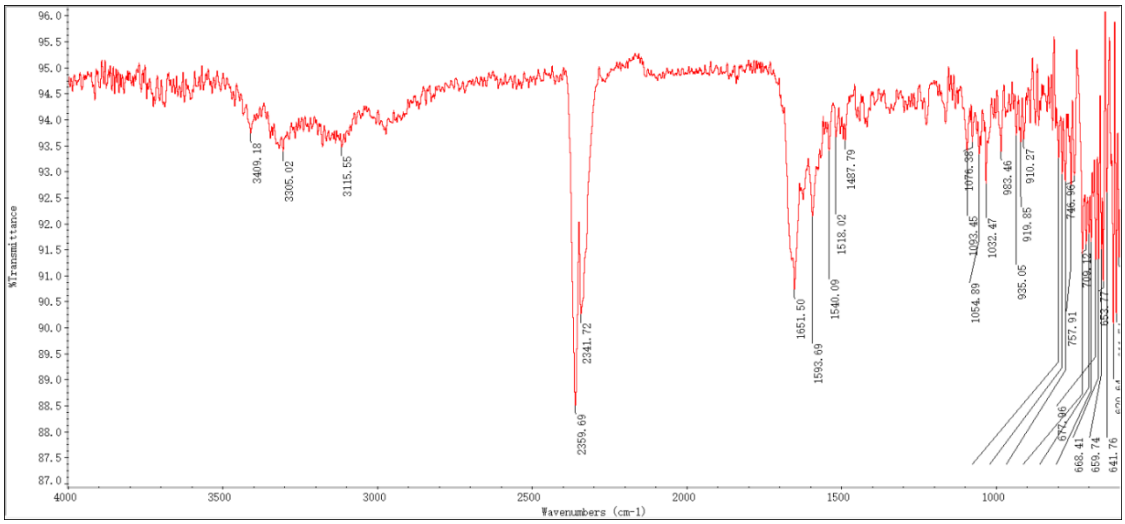


Fig. S2 FT-IR spectra of **3**

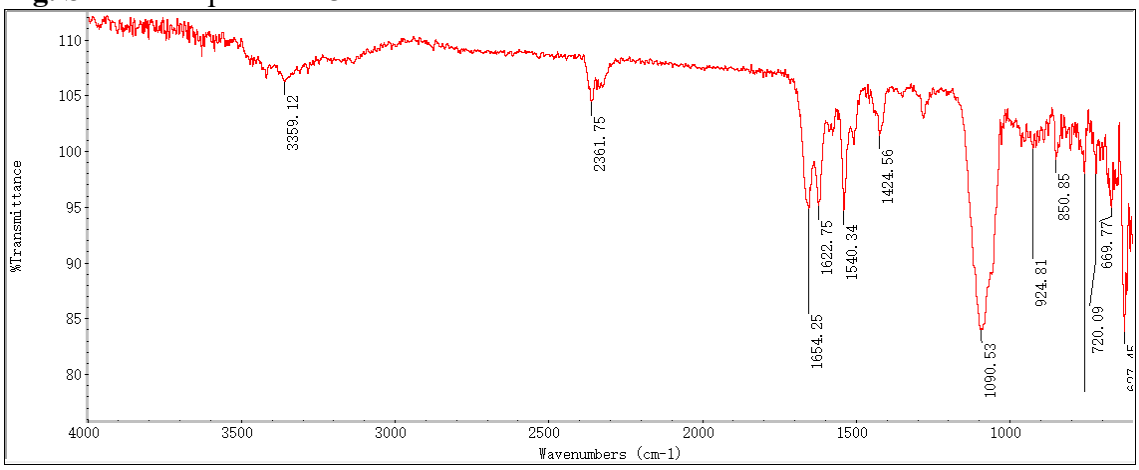
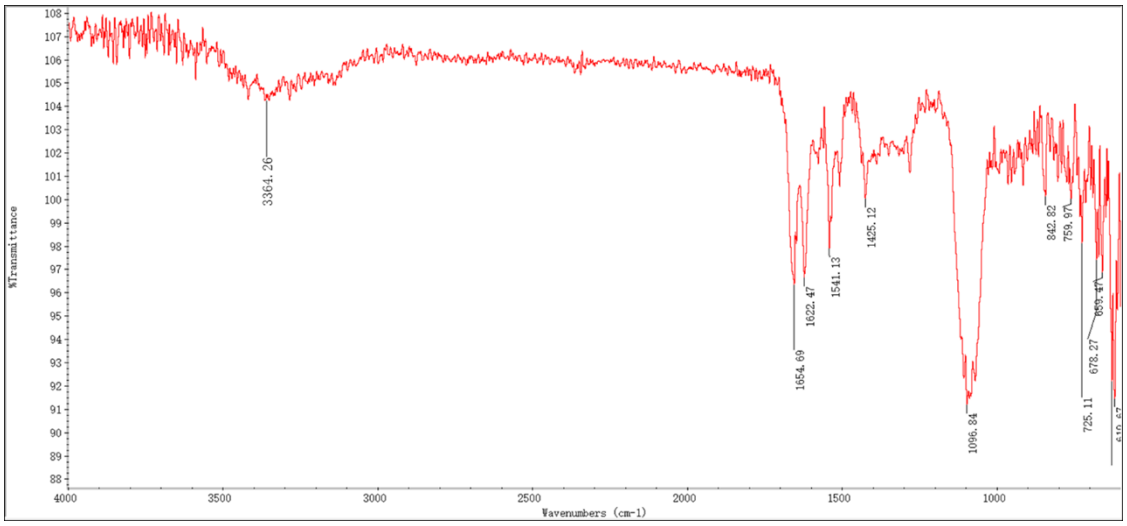
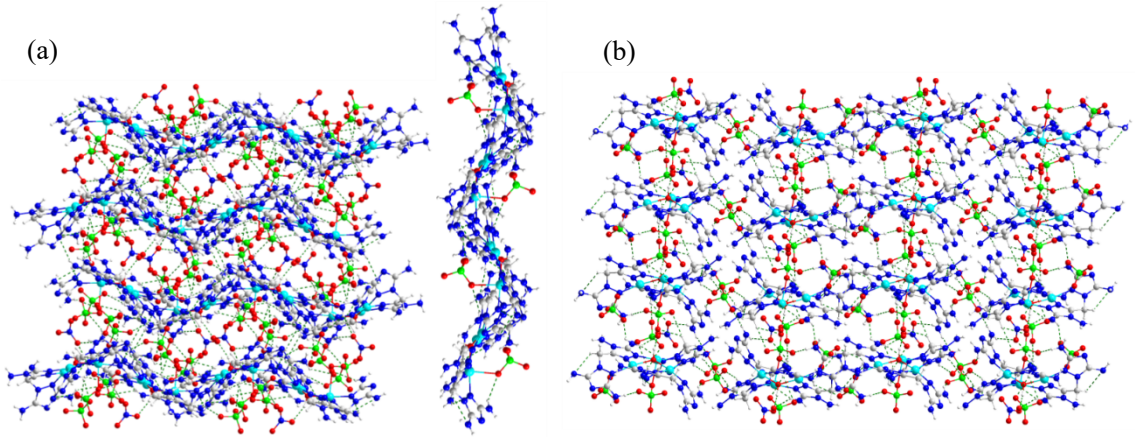


Fig. S3 FT-IR spectra of **4**



2. The packing diagram of 4

Fig. S4. (a) The packing diagram of **4** viewed along the a-axis; (b) The packing diagram of **4** viewed along the b-axis



3. The TG-DTG curves of compounds 2-4

Fig. S5. TG-DTG curve of **2**

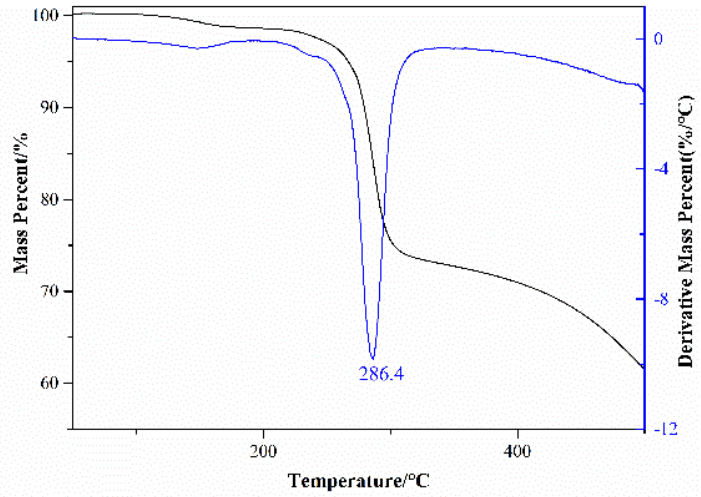


Fig. S6 TG-DTG curve of **3**

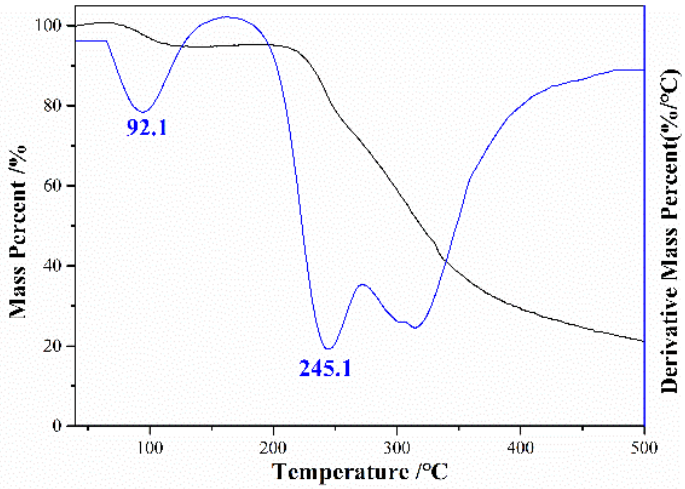
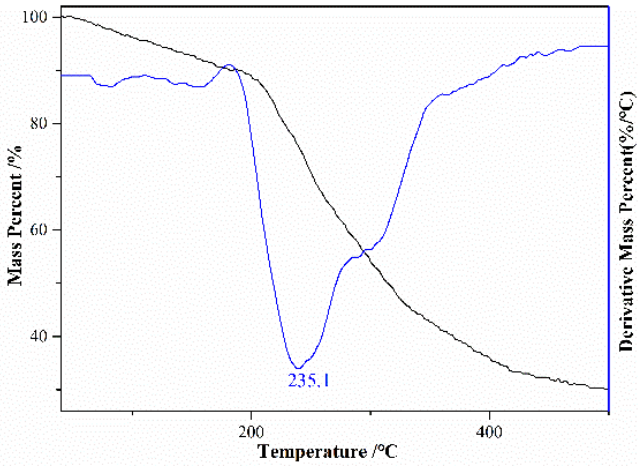


Fig. S7 TG-DTG curve of **4**.



4. X-ray crystallography

Table S1. Bond Lengths for compound **2**

Bond	Length/Å	Bond	Length/Å	Bond	Length/Å
N1-C2	1.316(5)	N5-H5A	0.89	N9-H9A	0.86
N1-N2	1.421(5)	N5-H5B	0.89	N9-H9B	0.86
N2-C1	1.319(5)	N6-C5	1.342(5)	N10-C5	1.363(5)
N3-C2	1.375(5)	N6-N7	1.414(4)	N10-H10A	0.86
N3-C1	1.378(5)	N6-C3	1.469(5)	N10-H10B	0.86
N3-N5	1.417(4)	N7-C4	1.327(5)	C2-C3	1.495(5)
N4-C1	1.362(5)	N8-C5	1.349(5)	C3-H3A	0.97
N4-H4A	0.86	N8-C4	1.377(5)	C3-H3B	0.97
N4-H4B	0.86	N9-C4	1.369(5)		

Table S2. Bond Angles for for compound **2**

Bond	Angle/˚	Bond	Angle/˚	Bond	Angle/˚
C2-N1-N2	107.5(3)	C4-N7-N6	101.4(3)	N3-C2-C3	124.2(3)
C1-N2-N1	106.8(3)	C5-N8-C4	102.3(3)	N6-C3-C2	113.8(3)
C2-N3-C1	106.0(3)	C4-N9-H9A	120	N6-C3-H3A	108.8
C2-N3-N5	129.3(3)	C4-N9-H9B	120	C2-C3-H3A	108.8
C1-N3-N5	124.7(3)	H9A-N9-H9B	120	N6-C3-H3B	108.8
C1-N4-H4A	120	C5-N10-H10A	120	C2-C3-H3B	108.8
C1-N4-H4B	120	C5-N10-H10B	120	H3A-C3-H3B	107.7
H4A-N4-H4B	120	H10A-N10-H10B	120	N7-C4-N9	123.3(4)
N3-N5-H5A	109.1	N2-C1-N4	128.0(4)	N7-C4-N8	116.0(4)
N3-N5-H5B	108.9	N2-C1-N3	109.9(4)	N9-C4-N8	120.5(4)
H5A-N5-H5B	109.5	N4-C1-N3	122.1(4)	N6-C5-N8	110.8(3)
C5-N6-N7	109.4(3)	N1-C2-N3	109.8(3)	N6-C5-N10	125.2(4)
C5-N6-C3	129.7(3)	N1-C2-C3	126.0(4)	N8-C5-N10	123.9(4)
N7-N6-C3	120.0(3)				

Table S3. Torsion Angles for compound **2**

Bond	Angle/˚	Bond	Angle/˚	Bond	Angle/˚
C2-N1-N2-C1	-0.4(4)	N2-N1-C2-C3	179.6(3)	N6-N7-C4-N8	-0.1(4)
C5-N6-N7-C4	0.4(4)	C1-N3-C2-N1	-0.1(4)	C5-N8-C4-N7	-0.2(5)
C3-N6-N7-C4	170.5(3)	N5-N3-C2-N1	-179.8(3)	C5-N8-C4-N9	-175.3(4)
N1-N2-C1-N4	-177.4(4)	C1-N3-C2-C3	-179.4(3)	N7-N6-C5-N8	-0.5(4)
N1-N2-C1-N3	0.3(4)	N5-N3-C2-C3	0.8(6)	C3-N6-C5-N8	-169.4(4)
C2-N3-C1-N2	-0.1(4)	C5-N6-C3-C2	-111.6(4)	N7-N6-C5-N10	177.5(4)
N5-N3-C1-N2	179.6(3)	N7-N6-C3-C2	80.4(4)	C3-N6-C5-N10	8.6(7)
C2-N3-C1-N4	177.7(4)	N1-C2-C3-N6	105.8(4)	C4-N8-C5-N6	0.4(4)
N5-N3-C1-N4	-2.5(6)	N3-C2-C3-N6	-74.9(5)	C4-N8-C5-N10	-177.7(4)
N2-N1-C2-N3	0.3(4)	N6-N7-C4-N9	174.8(4)		

Table S4. Hydrogen Bonds for compound **2**

D-H…A	d(D-H)/Å	d(H…A)/Å	d(D…A)/Å	D-H…A/°
N4-H4A…N7	0.86	2.267	154.71	3.067
N4-H4B…N5	0.86	2.55	101	2.8396
N5-H5A…N2	0.89	2.218	167.46	3.093
N5-H5B…N9	0.89	2.57	153.55	3.39
N9-H9A…N1	0.86	2.683	120.07	3.202
N9-H9B…N8	0.86	2.385	148.3	3.149
N10-H10A…N8	0.86	2.429	132.13	3.073
N10-H10B…N1	0.86	2.3	163.69	3.135

-x, y+1/2, -z+1/2; -x-1/2, y-1/2, z; x-1/2, y, -z+1/2;-x+1/2, y-1/2, z; -x+1, -y+1, -z; x-1/2, -y+3/2, -z; x+1/2, -y+3/2, -z.

Table S5. Bond Lengths for compound **3**

Bond	Length/Å	Bond	Length/Å	Bond	Length/Å
C1-N4	1.343(6)	C15-N25	1.320(6)	N22-N23	1.411(5)
C1-N3	1.344(6)	C15-N22	1.345(6)	N27-N28	1.398(5)
C1-N1	1.355(6)	C15-N21	1.350(6)	N29-N30	1.393(4)
C2-N3	1.327(6)	Cl1-O3	1.424(4)	Cl2-O9B	1.303(9)
C2-N5	1.332(6)	Cl1-O4	1.430(3)	Cl2-O9A	1.350(6)
C2-N2	1.344(6)	Cl1-O1	1.434(3)	Cl2-O7B	1.364(9)
C3-N5	1.445(5)	Cl1-O2	1.445(3)	Cl2-O8	1.382(6)
C3-C4	1.483(6)	Cu1-N6	1.950(3)	Cl2-O7A	1.392(6)
C4-N6	1.298(5)	Cu1-N18	1.969(3)	Cl2-O6A	1.423(6)
C4-N9	1.350(5)	Cu1-N4	1.993(4)	Cl2-O6B	1.480(8)
C5-N8	1.321(6)	Cu1-O5	2.021(3)	Cl3-O12	1.418(4)
C5-N7	1.332(5)	Cu1-O1	2.361(3)	Cl3-O13	1.418(4)
C5-N9	1.365(5)	Cu2-N17	1.940(3)	Cl3-O11	1.440(4)
C6-N18	1.324(5)	Cu2-N30	1.960(3)	Cl3-O10	1.446(4)
C6-N19	1.324(5)	Cu2-N14	1.995(3)	Cl4-O16	1.411(4)
C6-N16	1.365(5)	Cu2-O5	2.013(3)	Cl4-O14	1.414(4)
C7-N17	1.297(5)	Cu2-O25	2.398(4)	Cl4-O15	1.420(4)
C7-N16	1.357(5)	Cu3-N29	1.960(3)	Cl4-O17	1.445(4)
C7-C8	1.487(6)	Cu3-N7	1.962(3)	Cl5-O20	1.397(4)
C8-N15	1.445(5)	Cu3-N22	2.018(3)	Cl5-O21	1.418(4)
C9-N13	1.329(6)	Cu3-O5	2.039(3)	Cl5-O18	1.421(5)
C9-N15	1.344(5)	Cu3-O2	2.395(3)	Cl5-O19	1.431(5)
C9-N12	1.351(5)	N4-N5	1.408(5)	C14-N21	1.333(6)
C10-N14	1.332(5)	N6-N7	1.397(5)	C14-N23	1.334(6)
C10-N13	1.350(5)	N9-N10	1.397(5)	C14-N24	1.351(6)
C10-N11	1.364(5)	N14-N15	1.402(5)	C12-C13	1.477(6)
C11-N26	1.322(5)	N16-N20	1.399(5)	C13-N23	1.443(6)
C11-N30	1.327(5)	N17-N18	1.400(5)	C12-N27	1.351(5)
C11-N27	1.364(5)	C12-N29	1.292(5)		

Table S6. Some bond Angles for for compound **3**

Bond	Angle/°	Bond	Angle/°	Bond	Angle/°
N6-Cu1-N18	164.35(15)	O5-Cu2-O25	95.49(13)	N18-N17-Cu2	124.4(3)
N6-Cu1-N4	88.47(14)	N29-Cu3-N7	161.67(15)	C6-N18-Cu1	134.8(3)
N18-Cu1-N4	98.09(15)	N29-Cu3-N22	90.85(14)	N17-N18-Cu1	117.5(2)
N6-Cu1-O5	85.25(12)	N7-Cu3-N22	97.77(14)	C15-N22-Cu3	130.5(3)
N18-Cu1-O5	88.55(13)	N29-Cu3-O5	86.83(12)	N23-N22-Cu3	117.7(2)
N4-Cu1-O5	173.33(13)	N7-Cu3-O5	85.50(13)	C12-N29-Cu3	125.1(3)
N6-Cu1-O1	103.91(14)	N22-Cu3-O5	175.63(13)	N30-N29-Cu3	124.1(2)
N18-Cu1-O1	90.55(14)	N29-Cu3-O2	100.52(14)	C11-N30-Cu2	135.0(3)
N4-Cu1-O1	88.13(13)	N7-Cu3-O2	95.85(14)	N29-N30-Cu2	117.8(2)
O5-Cu1-O1	91.21(11)	N22-Cu3-O2	88.62(13)	Cl1-O1-Cu1	122.1(2)
N17-Cu2-N30	173.24(14)	O5-Cu3-O2	88.16(11)	Cl1-O2-Cu3	124.39(19)
N17-Cu2-N14	87.95(14)	N5-N4-Cu1	121.5(3)	Cu2-O5-Cu1	115.56(13)
N30-Cu2-N14	96.67(14)	C4-N6-Cu1	123.7(3)	Cu2-O5-Cu3	115.08(13)
N17-Cu2-O5	87.37(13)	N7-N6-Cu1	123.6(2)	Cu1-O5-Cu3	113.82(13)
N30-Cu2-O5	88.82(12)	C5-N7-Cu3	134.5(3)	Cu2-O5-H5	107.5
N14-Cu2-O5	169.89(13)	N6-N7-Cu3	117.4(2)	Cu1-O5-H5	105.5
N17-Cu2-O25	88.56(14)	C10-N14-Cu2	133.3(3)	Cu3-O5-H5	96.9
N30-Cu2-O25	86.25(14)	N15-N14-Cu2	122.9(3)	Cu2-O25-H25C	108.8
N14-Cu2-O25	93.34(15)	C7-N17-Cu2	124.7(3)	Cu2-O25-H25D	109.4

Table S7. Torsion Angles for compound **3**

Bond	Angle/°	Bond	Angle/°	Bond	Angle/°
N5-C3-C4-N6	-26.6(6)	N8-C5-N9-N10	-6.0(7)	N25-C15-N21-C14	-179.7(4)
N5-C3-C4-N9	152.2(4)	N7-C5-N9-N10	175.7(4)	N22-C15-N21-C14	0.3(5)
N17-C7-C8-N15	-33.4(6)	N15-C9-N13-C10	2.0(5)	N25-C15-N22-N23	179.7(4)
N16-C7-C8-N15	151.5(4)	N12-C9-N13-C10	179.1(4)	N21-C15-N22-N23	-0.3(5)
N29-C12-C13-N23	-33.9(6)	N14-C10-N13-C9	0.3(5)	N25-C15-N22-Cu3	36.9(6)
N27-C12-C13-N23	148.2(4)	N11-C10-N13-C9	-177.7(4)	N21-C15-N22-Cu3	-143.1(3)
N5-C2-N3-C1	0.7(5)	N13-C10-N14-N15	-2.4(5)	N21-C14-N23-N22	0.0(5)
N2-C2-N3-C1	-178.9(5)	N11-C10-N14-N15	175.6(4)	N24-C14-N23-N22	176.9(4)
N4-C1-N3-C2	0.9(5)	N13-C10-N14-Cu2	-169.2(3)	N21-C14-N23-C13	-167.7(4)
N1-C1-N3-C2	178.9(4)	N11-C10-N14-Cu2	8.8(7)	N24-C14-N23-C13	9.3(7)
N3-C1-N4-N5	-2.0(5)	N13-C9-N15-N14	-3.5(5)	C15-N22-N23-C14	0.2(4)
N1-C1-N4-N5	-180.0(4)	N12-C9-N15-N14	179.2(4)	Cu3-N22-N23-C14	148.9(3)
N3-C1-N4-Cu1	-153.6(3)	N13-C9-N15-C8	176.7(4)	C15-N22-N23-C13	169.3(4)
N1-C1-N4-Cu1	28.5(7)	N12-C9-N15-C8	-0.5(7)	Cu3-N22-N23-C13	-42.0(4)
N3-C2-N5-N4	-2.0(5)	C10-N14-N15-C9	3.5(4)	C12-C13-N23-C14	-127.9(5)
N2-C2-N5-N4	177.6(4)	Cu2-N14-N15-C9	172.1(3)	C12-C13-N23-N22	65.6(5)
N3-C2-N5-C3	-178.5(4)	C10-N14-N15-C8	-176.8(4)	N29-C12-N27-C11	-0.6(4)
N2-C2-N5-C3	1.2(8)	Cu2-N14-N15-C8	-8.2(5)	C13-C12-N27-C11	177.6(4)
C1-N4-N5-C2	2.3(4)	C7-C8-N15-C9	-136.9(4)	N29-C12-N27-N28	170.4(4)
Cu1-N4-N5-C2	157.1(3)	C7-C8-N15-N14	43.4(5)	C13-C12-N27-N28	-11.5(7)

C1-N4-N5-C3	179.1(4)	N17-C7-N16-C6	0.9(5)	N26-C11-N27-C12	-179.5(4)
Cu1-N4-N5-C3	-26.1(5)	C8-C7-N16-C6	176.6(4)	N30-C11-N27-C12	1.4(4)
C4-C3-N5-C2	-130.8(5)	N17-C7-N16-N20	179.3(4)	N26-C11-N27-N28	8.9(6)
C4-C3-N5-N4	53.2(5)	C8-C7-N16-N20	-4.9(6)	N30-C11-N27-N28	-170.1(4)
N9-C4-N6-N7	-1.0(5)	N18-C6-N16-C7	-0.2(5)	N27-C12-N29-N30	-0.5(4)
C3-C4-N6-N7	177.9(4)	N19-C6-N16-C7	176.0(4)	C13-C12-N29-N30	-178.7(4)
N9-C4-N6-Cu1	156.1(3)	N18-C6-N16-N20	-178.7(4)	N27-C12-N29-Cu3	162.2(3)
C3-C4-N6-Cu1	-24.9(6)	N19-C6-N16-N20	-2.5(7)	C13-C12-N29-Cu3	-16.0(6)
N8-C5-N7-N6	-179.4(4)	N16-C7-N17-N18	-1.1(5)	N26-C11-N30-N29	179.3(4)
N9-C5-N7-N6	-1.2(5)	C8-C7-N17-N18	-176.9(4)	N27-C11-N30-N29	-1.7(4)
N8-C5-N7-Cu3	15.7(7)	N16-C7-N17-Cu2	162.4(3)	N26-C11-N30-Cu2	10.0(7)
N9-C5-N7-Cu3	-166.1(3)	C8-C7-N17-Cu2	-13.3(6)	N27-C11-N30-Cu2	-171.0(3)
C4-N6-N7-C5	1.4(5)	N19-C6-N18-N17	-176.4(4)	C12-N29-N30-C11	1.3(4)
Cu1-N6-N7-C5	-155.8(3)	N16-C6-N18-N17	-0.5(4)	Cu3-N29-N30-C11	-161.5(3)
C4-N6-N7-Cu3	169.3(3)	N19-C6-N18-Cu1	16.8(7)	C12-N29-N30-Cu2	172.8(3)
Cu1-N6-N7-Cu3	12.2(4)	N16-C6-N18-Cu1	-167.2(3)	Cu3-N29-N30-Cu2	10.0(4)
N6-C4-N9-C5	0.3(5)	C7-N17-N18-C6	1.0(4)	O3-Cl1-O1-Cu1	67.7(3)
C3-C4-N9-C5	-178.7(4)	Cu2-N17-N18-C6	-162.7(3)	O4-Cl1-O1-Cu1	-170.7(2)
N6-C4-N9-N10	-175.1(4)	C7-N17-N18-Cu1	170.5(3)	O2-Cl1-O1-Cu1	-51.2(3)
C3-C4-N9-N10	5.9(7)	Cu2-N17-N18-Cu1	6.8(4)	O3-Cl1-O2-Cu3	-46.7(3)
N8-C5-N9-C4	178.9(4)	N23-C14-N21-C15	-0.2(5)	O4-Cl1-O2-Cu3	-168.5(2)
N7-C5-N9-C4	0.6(5)	N24-C14-N21-C15	-177.1(4)	O1-Cl1-O2-Cu3	72.3(3)

Table S8. Hydrogen Bonds for compound **3**

D-H…A	d(D-H)/Å	d(H…A)/Å	d(D…A)/Å	D-H…A/°
N26-H1…N28	0.86	2.58	2.8643	101
N26-H1…N12	0.86	2.37	3.2278	173
N28-H2…O19	0.88	2.59	3.0751	116
N28-H2…O21	0.88	2.35	3.1371	148
N28-H3…O12	0.89	2.52	3.342	154
N28-H3…O20	0.89	2.47	3.017	120
O5-H4…O10	0.85	2.06	2.9008	172
O25-H5…O11	0.85	2.06	2.8592	156
O25-H6…O6A	0.85	2.02	2.8675	172
N1-HF…O9A	0.86	2.53	3.2484	142
O22-H7…O10	0.85	2.2	3.011	161
O22-H8…O15	0.85	2.54	2.9408	110
N2-HH…O17	0.86	2.22	3.0267	155
O23-H9…O22	0.85	2.09	2.8678	152
O23-H10…O12	0.85	2.58	3.3121	145
N8-HJ…O14	0.86	2.46	3.1415	136
N8-HJ…O16	0.86	2.48	3.0831	128
O24-H11…O25	0.84	2.49	3.2761	155
N8-HK…O23	0.86	1.99	2.8395	168

N10-HL…O17	0.88	2.4	3.0676	133
N10-HL…N24	0.88	2.6	3.177	124
N10-HM…O22	0.89	2.44	3.1037	132
N11-HN…N30	0.86	2.61	3.248	132
N12HP…O19	0.86	2.53	3.3354	156
N12-HQ…O24	0.86	2.37	3.1843	158
N19-HR…O18	0.86	2.39	3.0413	133
N19-HR…N4	0.86	2.51	3.2016	138
N19-HS…N11	0.86	2.31	3.0574	146
N20-HT…O7A	0.89	2.55	3.3775	154
N20-HU…N13	0.89	2.18	2.9924	153
N24-HV…O16	0.86	2.21	2.9793	149
N24-HW…O12	0.86	2.44	3.2639	162
N25-HX…O15	0.86	2.24	2.9395	139
N25-HY…N21	0.86	2.58	3.3721	153
C3-H…O2	0.97	2.35	3.322	177
C3-H…O4	0.97	2.55	3.1913	124
C8-HC…O24	0.97	2.42	3.1537	132

Table S9. Bond Lengths for compound **4**

Bond	Length/Å	Bond	Length/Å	Bond	Length/Å
C1-N4	1.326(10)	C13-C14	1.501(11)	N14-N15	1.412(9)
C1-N3	1.326(11)	C14-N27	1.287(10)	N16-N20	1.398(10)
C1-N1	1.359(11)	C14-N26	1.353(10)	N17-N18	1.394(9)
C2-N5	1.330(11)	C15-N28	1.316(10)	N24-N25	1.398(9)
C2-N2	1.330(12)	C15-N29	1.322(10)	N26-N30	1.382(9)
C2-N3	1.338(12)	C15-N26	1.374(10)	N27-N28	1.402(9)
C3-N5	1.430(10)	Cl1-O2	1.395(6)	N31-O19	1.228(10)
C3-C4	1.472(11)	Cl1-O3	1.406(7)	N31-O20	1.234(10)
C4-N6	1.304(10)	Cl1-O1	1.418(7)	N31-O18	1.280(11)
C4-N8	1.364(10)	Cl1-O4	1.433(7)	Cl3-O11	1.403(7)
C5-N10	1.317(11)	Cu1-N6	1.941(6)	Cl3-O12	1.410(8)
C5-N7	1.328(10)	Cu1-N28	1.973(7)	Cl3-O10	1.434(8)
C5-N8	1.359(11)	Cu1-O17	2.022(6)	Cl3-O9	1.436(8)
C6-N14	1.337(11)	Cu1-N4	2.026(7)	Cl4-O14	1.300(11)
C6-N11	1.344(11)	Cu1-O1	2.341(7)	Cl4-O15	1.341(11)
C6-N13	1.363(11)	Cu2-N27	1.932(6)	Cl4-O13	1.371(13)
C7-N15	1.330(11)	Cu2-N18	1.959(7)	Cl4-O16	1.408(9)
C7-N13	1.335(11)	Cu2-N24	2.003(6)	Cl2-O8	1.373(8)
C7-N12	1.358(11)	Cu2-O17	2.006(5)	Cl2-O7	1.409(9)
C8-N15	1.432(11)	Cu3-N17	1.953(7)	Cl2-O6	1.424(10)
C8-C9	1.476(11)	Cu3-N7	1.961(6)	Cl2-O5	1.446(11)
C9-N17	1.311(10)	Cu3-N14	2.024(7)	C11-N21	1.362(10)
C9-N16	1.339(10)	Cu3-O17	2.025(5)	C12-N23	1.336(10)

C10-N18	1.323(10)	N4-N5	1.405(9)	C12-N25	1.342(10)
C10-N19	1.334(11)	N6-N7	1.396(9)	C12-N22	1.355(10)
C10-N16	1.361(10)	N8-N9	1.388(9)	C13-N25	1.452(10)
C11-N24	1.314(10)	C11-N23	1.346(10)		

Table S10. Bond Angles for for compound **4**

Bond	Angle/˚	Bond	Angle/˚	Bond	Angle/˚
N6-Cu1-N28	165.2(3)	N17-Cu3-N7	165.8(3)	C10-N18-Cu2	136.7(6)
N6-Cu1-O17	85.4(2)	N17-Cu3-N14	90.7(3)	N17-N18-Cu2	116.9(5)
N28-Cu1-O17	89.0(2)	N7-Cu3-N14	97.5(3)	C11-N24-Cu2	133.7(5)
N6-Cu1-N4	88.0(3)	N17-Cu3-O17	87.0(2)	N25-N24-Cu2	122.3(5)
N28-Cu1-N4	98.2(3)	N7-Cu3-O17	86.6(2)	C14-N27-Cu2	126.2(6)
O17-Cu1-N4	172.5(2)	N14-Cu3-O17	171.1(3)	N28-N27-Cu2	124.4(5)
N6-Cu1-O1	104.0(3)	C1-N4-Cu1	131.3(6)	C15-N28-Cu1	135.3(5)
N28-Cu1-O1	89.8(3)	N5-N4-Cu1	120.4(5)	N27-N28-Cu1	116.9(5)
O17-Cu1-O1	90.8(2)	C4-N6-Cu1	123.5(5)	Cl1-O1-Cu1	125.9(5)
N4-Cu1-O1	87.3(3)	N7-N6-Cu1	124.2(5)	Cu2-O17-Cu1	114.7(3)
N27-Cu2-N18	172.3(3)	C5-N7-Cu3	134.3(6)	Cu2-O17-Cu3	115.3(3)
N27-Cu2-N24	87.7(3)	N6-N7-Cu3	116.9(4)	Cu1-O17-Cu3	113.8(2)
N18-Cu2-N24	96.8(3)	C6-N14-Cu3	130.4(6)	Cu2-O17-H17	103.7
N27-Cu2-O17	87.8(2)	N15-N14-Cu3	117.6(5)	Cu1-O17-H17	103.7
N18-Cu2-O17	88.8(2)	C9-N17-Cu3	126.0(5)	Cu3-O17-H17	103.7
N24-Cu2-O17	169.3(3)	N18-N17-Cu3	124.2(5)		

Table S11. Torsion Angles for compound **4**

Bond	Angle/˚	Bond	Angle/˚	Bond	Angle/˚
N5-C3-C4-N6	-27.1(12)	C3-C4-N8-C5	-178.1(8)	N25-C12-N23-C11	1.0(9)
N5-C3-C4-N8	149.4(8)	N6-C4-N8-N9	-175.0(7)	N22-C12-N23-C11	-179.6(8)
N15-C8-C9-N17	-36.5(11)	C3-C4-N8-N9	7.9(13)	N24-C11-N23-C12	0.8(9)
N15-C8-C9-N16	146.1(8)	N15-C7-N13-C6	-0.1(9)	N21-C11-N23-C12	-176.7(7)
N25-C13-C14-N27	-34.9(11)	N12-C7-N13-C6	-176.8(8)	N23-C11-N24-N25	-2.1(9)
N25-C13-C14-N26	148.7(7)	N14-C6-N13-C7	-0.4(10)	N21-C11-N24-N25	175.3(7)
N4-C1-N3-C2	1.8(10)	N11-C6-N13-C7	-179.7(8)	N23-C11-N24-Cu2	-169.4(6)
N1-C1-N3-C2	179.5(8)	N11-C6-N14-N15	179.9(8)	N21-C11-N24-Cu2	7.9(13)
N5-C2-N3-C1	-0.3(10)	N13-C6-N14-N15	0.7(9)	N23-C12-N25-N24	-2.3(9)
N2-C2-N3-C1	-178.1(9)	N11-C6-N14-Cu3	37.6(13)	N22-C12-N25-N24	178.3(7)
N3-C1-N4-N5	-2.4(10)	N13-C6-N14-Cu3	-141.6(6)	N23-C12-N25-C13	175.9(7)
N1-C1-N4-N5	179.9(8)	N13-C7-N15-N14	0.6(9)	N22-C12-N25-C13	-3.5(13)
N3-C1-N4-Cu1	-154.6(6)	N12-C7-N15-N14	177.3(7)	C11-N24-N25-C12	2.5(8)
N1-C1-N4-Cu1	27.7(13)	N13-C7-N15-C8	-169.6(8)	Cu2-N24-N25-C12	171.7(5)
N2-C2-N5-N4	176.6(8)	N12-C7-N15-C8	7.1(14)	C11-N24-N25-C13	-175.7(7)
N3-C2-N5-N4	-1.1(10)	C6-N14-N15-C7	-0.7(8)	Cu2-N24-N25-C13	-6.5(10)
N2-C2-N5-C3	-4.8(15)	Cu3-N14-N15-C7	147.6(6)	C14-C13-N25-C12	-135.0(8)
N3-C2-N5-C3	177.4(8)	C6-N14-N15-C8	170.5(7)	C14-C13-N25-N24	42.9(10)

C1-N4-N5-C2	2.0(9)	Cu3-N14-N15-C8	-41.2(9)	N27-C14-N26-C15	0.7(9)
Cu1-N4-N5-C2	158.1(6)	C9-C8-N15-C7	-124.3(9)	C13-C14-N26-C15	177.5(7)
C1-N4-N5-C3	-176.6(7)	C9-C8-N15-N14	66.6(10)	N27-C14-N26-N30	178.9(7)
Cu1-N4-N5-C3	-20.5(10)	N17-C9-N16-C10	0.5(9)	C13-C14-N26-N30	-4.3(12)
C4-C3-N5-C2	-128.0(9)	C8-C9-N16-C10	178.2(8)	N28-C15-N26-C14	0.3(9)
C4-C3-N5-N4	50.2(10)	N17-C9-N16-N20	171.6(8)	N29-C15-N26-C14	174.7(7)
N8-C4-N6-N7	-0.3(9)	C8-C9-N16-N20	-10.7(14)	N28-C15-N26-N30	-177.9(7)
C3-C4-N6-N7	176.8(8)	N18-C10-N16-C9	-0.1(9)	N29-C15-N26-N30	-3.5(12)
N8-C4-N6-Cu1	158.9(5)	N19-C10-N16-C9	-178.5(8)	N26-C14-N27-N28	-1.4(9)
C3-C4-N6-Cu1	-24.1(12)	N18-C10-N16-N20	-171.7(7)	C13-C14-N27-N28	-178.2(7)
N10-C5-N7-N6	179.4(8)	N19-C10-N16-N20	9.9(13)	N26-C14-N27-Cu2	165.3(5)
N8-C5-N7-N6	-2.2(9)	N16-C9-N17-N18	-0.6(9)	C13-C14-N27-Cu2	-11.5(12)
N10-C5-N7-Cu3	17.0(14)	C8-C9-N17-N18	-178.5(7)	N29-C15-N28-N27	-175.2(8)
N8-C5-N7-Cu3	-164.7(6)	N16-C9-N17-Cu3	164.5(5)	N26-C15-N28-N27	-1.1(8)
C4-N6-N7-C5	1.6(9)	C8-C9-N17-Cu3	-13.3(12)	N29-C15-N28-Cu1	17.9(13)
Cu1-N6-N7-C5	-157.4(6)	N19-C10-N18-N17	178.1(8)	N26-C15-N28-Cu1	-168.0(6)
C4-N6-N7-Cu3	167.6(6)	N16-C10-N18-N17	-0.2(9)	C14-N27-N28-C15	1.5(8)
Cu1-N6-N7-Cu3	8.6(8)	N19-C10-N18-Cu2	-0.6(15)	Cu2-N27-N28-C15	-165.5(5)
N10-C5-N8-C4	-179.5(8)	N16-C10-N18-Cu2	-178.9(6)	C14-N27-N28-Cu1	171.3(5)
N7-C5-N8-C4	2.0(9)	C9-N17-N18-C10	0.5(9)	Cu2-N27-N28-Cu1	4.2(8)
N10-C5-N8-N9	-5.9(14)	Cu3-N17-N18-C10	-165.0(6)	O2-Cl1-O1-Cu1	-170.6(5)
N7-C5-N8-N9	175.7(8)	C9-N17-N18-Cu2	179.5(5)	O3-Cl1-O1-Cu1	65.3(7)
N6-C4-N8-C5	-1.0(9)	Cu3-N17-N18-Cu2	14.0(8)	O4-Cl1-O1-Cu1	-51.5(7)

Table S12. Hydrogen Bonds for compound **4**

D-H…A	d(D-H)/Å	d(H…A)/Å	d(D…A)/Å	D-H…A/°
N1-H1A…O1	0.86	2.54	2.915(11)	108
N2-H2B…O9	0.86	2.19	2.997(11)	155
N10-H10A…O11	0.86	2.52	3.200(10)	136
N10-H10A…O12	0.86	2.36	3.017(11)	134
N11-H11A…O10	0.86	2.21	2.909(11)	138
N12-H12A…O20	0.86	2.35	3.165(11)	157
N12-H12B…O12	0.86	2.2	2.947(12)	146
O17-H17…O18	0.98	1.82	2.748(11)	157
N19-H19A…O16	0.89	2.55	3.276(14)	139
N20-H20A…O6	0.90(10)	2.54(10)	3.110(13)	122(7)
N20-H20A…O7	0.90(10)	2.36(10)	3.091(13)	139(8)
N20-H20B…O8	0.77(10)	2.56(10)	3.029(12)	121(8)
N20-H20B…O20	0.77(10)	2.57(11)	3.220(12)	144(10)
N21-H21A…O3	0.86	2.58	3.034(10)	114
N22-H22A…N19	0.87	2.31	3.136(10)	158
N29-H29A…N4	0.86	2.53	3.226(10)	139
N29-H29A…O5	0.86	2.36	3.054(14)	138
N29-H29B…N21	0.86	2.35	3.070(10)	142

C3-H3A…O2	0.97	2.49	3.142(11)	124
C3-H3A…O4	0.97	2.31	3.283(11)	178
C3-H3B…N2	0.97	2.62	2.978(12)	102

5. The first exothermic decomposition peak temperature with four heating rates

Table S13. The first exothermic decomposition peak temperatures tested at different heating rates of compounds **2~4**

Compound	The first exothermic decomposition peak temperatures (°C)			
	5 °C min^{-1}	10 °C min^{-1}	15 °C min^{-1}	20 °C min^{-1}
2	301.4	308.0	312.6	319.5
3	245.6	248.9	254.1	257.7
4	211.6	218.4	224.9	233.3

6. The percentage contribution of individual atomic contacts to the Hirshfeld surface

Table S14. The percentage contribution of individual atomic contacts to the Hirshfeld surface in compounds **1-7**

Compound	the contribution of atomic contacts to the Hirshfeld surface /%								
	H…H	H…N &N…H	H…O &O…H	H…C &C…H	C…O &O…C	N…O &O…N	Cu…O &O…Cu	O…O	other
1	20.8	12	45.7	2.2	4.7	8.1	0.6	5.7	0.2
7	19.5	9.7	41.5	0.6	5.9	12.5	0.6	4.6	5.1