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Supporting information for article:

On the Hirshfeld Surface for copper(II) atoms in different coordination environments

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Supporting information

S1. Structure Description

The asymmetric unit for compound **4** is composed of a copper(II) metallic centre, coordinated to four nitrogen atoms from two 1,10-phenanthroline molecules, and one chlorine ion. There is also a 4-nitrophthalic acid molecule not coordinated to the copper(II) centre, one deprotonated 4-nitrophthalato ion (presenting a short intramolecular H-bond) and two crystallization water molecules.

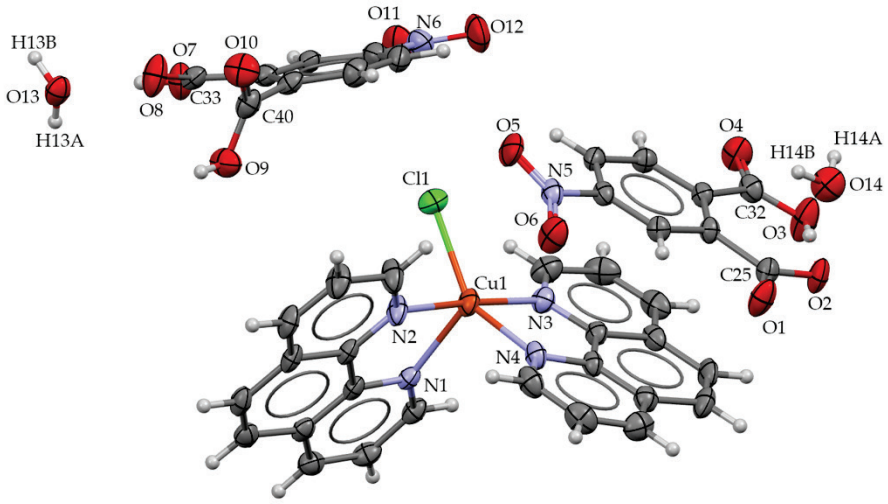


Figure S1 Asymmetric unit for compound **4**, $[CuCl(phen)_2]^+ \cdot 4\text{-Npha}^- \cdot 4\text{-Npha} \cdot 2H_2O$.

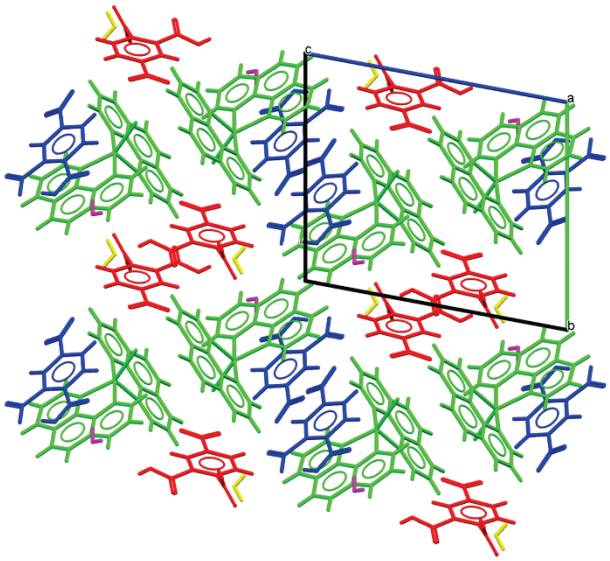


Figure S2 Packing diagram for compound **4** seen along the crystallographic *a* axis. Colors according to symmetry equivalence.

Table S1 Geometric parameters for compound **4** (Å, º).

Cu1—N3	1.999 (3)	C7—C9	1.425 (6)
Cu1—N2	2.004 (3)	C8—C9	1.413 (5)
Cu1—N4	2.083 (3)	C9—C10	1.404 (5)
Cu1—N1	2.181 (3)	C10—C11	1.362 (6)
Cu1—Cl1	2.2716 (12)	C11—C12	1.399 (5)
N1—C1	1.333 (4)	C13—C14	1.391 (6)
N1—C5	1.365 (4)	C14—C15	1.357 (6)
N2—C12	1.333 (5)	C15—C16	1.407 (6)
N2—C8	1.356 (5)	C16—C17	1.403 (5)
N3—C13	1.326 (5)	C16—C18	1.425 (6)
N3—C17	1.358 (5)	C17—C20	1.430 (5)
N4—C24	1.327 (5)	C18—C19	1.348 (6)
N4—C20	1.364 (4)	C19—C21	1.435 (5)
N5—O6	1.214 (4)	C20—C21	1.404 (5)
N5—O5	1.221 (4)	C21—C22	1.407 (6)
N5—C28	1.475 (4)	C22—C23	1.364 (6)
N6—O12	1.222 (4)	C23—C24	1.391 (6)
N6—O11	1.228 (5)	C25—C26	1.530 (5)
N6—C36	1.469 (5)	C26—C27	1.392 (5)
O1—C25	1.230 (5)	C26—C31	1.413 (5)
O2—C25	1.272 (4)	C27—C28	1.370 (5)
O3—C32	1.272 (5)	C28—C29	1.377 (5)
O4—C32	1.217 (5)	C29—C30	1.382 (5)
O7—C33	1.305 (4)	C30—C31	1.400 (5)
O8—C33	1.188 (4)	C31—C32	1.536 (5)

O9—C40	1.307 (5)	C33—C34	1.508 (5)
O10—C40	1.214 (5)	C34—C35	1.382 (5)
C1—C2	1.400 (6)	C34—C39	1.401 (5)
C2—C3	1.368 (5)	C35—C36	1.391 (5)
C3—C4	1.413 (5)	C36—C37	1.364 (6)
C4—C5	1.394 (5)	C37—C38	1.386 (6)
C4—C6	1.435 (5)	C38—C39	1.391 (5)
C5—C8	1.440 (5)	C39—C40	1.501 (5)
C6—C7	1.353 (5)		
N3—Cu1—N2	175.33 (14)	C17—C16—C18	119.0 (3)
N3—Cu1—N4	81.03 (12)	C15—C16—C18	124.3 (3)
N2—Cu1—N4	94.45 (12)	N3—C17—C16	123.2 (3)
N3—Cu1—N1	100.14 (12)	N3—C17—C20	117.2 (3)
N2—Cu1—N1	79.70 (12)	C16—C17—C20	119.6 (3)
N4—Cu1—N1	103.22 (11)	C19—C18—C16	121.6 (3)
N3—Cu1—Cl1	93.50 (10)	C18—C19—C21	120.9 (4)
N2—Cu1—Cl1	90.89 (10)	N4—C20—C21	123.5 (3)
N4—Cu1—Cl1	145.50 (9)	N4—C20—C17	116.2 (3)
N1—Cu1—Cl1	111.26 (8)	C21—C20—C17	120.3 (3)
C1—N1—C5	116.9 (3)	C20—C21—C22	116.6 (3)
C1—N1—Cu1	132.8 (2)	C20—C21—C19	118.6 (3)
C5—N1—Cu1	110.1 (2)	C22—C21—C19	124.8 (4)
C12—N2—C8	118.6 (3)	C23—C22—C21	119.5 (4)
C12—N2—Cu1	125.7 (3)	C22—C23—C24	120.2 (4)
C8—N2—Cu1	115.5 (2)	N4—C24—C23	122.4 (4)
C13—N3—C17	118.2 (3)	O1—C25—O2	122.8 (3)

C13—N3—Cu1	127.9 (3)	O1—C25—C26	117.0 (3)
C17—N3—Cu1	114.0 (2)	O2—C25—C26	120.1 (3)
C24—N4—C20	117.8 (3)	C27—C26—C31	118.3 (3)
C24—N4—Cu1	130.6 (3)	C27—C26—C25	112.7 (3)
C20—N4—Cu1	111.5 (2)	C31—C26—C25	129.0 (3)
O6—N5—O5	124.1 (3)	C28—C27—C26	120.8 (3)
O6—N5—C28	118.1 (3)	C27—C28—C29	122.5 (3)
O5—N5—C28	117.7 (3)	C27—C28—N5	118.1 (3)
O12—N6—O11	124.0 (4)	C29—C28—N5	119.4 (3)
O12—N6—C36	118.1 (4)	C28—C29—C30	117.1 (3)
O11—N6—C36	117.9 (3)	C29—C30—C31	122.6 (3)
N1—C1—C2	123.4 (3)	C30—C31—C26	118.7 (3)
C3—C2—C1	119.2 (3)	C30—C31—C32	113.3 (3)
C2—C3—C4	119.4 (4)	C26—C31—C32	128.0 (3)
C5—C4—C3	117.2 (3)	O4—C32—O3	122.0 (3)
C5—C4—C6	119.6 (3)	O4—C32—C31	118.5 (3)
C3—C4—C6	123.2 (4)	O3—C32—C31	119.5 (3)
N1—C5—C4	123.8 (3)	O8—C33—O7	125.4 (4)
N1—C5—C8	116.6 (3)	O8—C33—C34	122.2 (3)
C4—C5—C8	119.6 (3)	O7—C33—C34	112.4 (3)
C7—C6—C4	120.9 (4)	C35—C34—C39	119.6 (3)
C6—C7—C9	121.3 (3)	C35—C34—C33	119.9 (3)
N2—C8—C9	122.4 (3)	C39—C34—C33	120.4 (3)
N2—C8—C5	117.9 (3)	C34—C35—C36	118.6 (3)
C9—C8—C5	119.7 (3)	C37—C36—C35	123.1 (4)
C10—C9—C8	117.2 (3)	C37—C36—N6	118.4 (4)

C10—C9—C7	123.7 (3)	C35—C36—N6	118.5 (4)
C8—C9—C7	119.1 (3)	C36—C37—C38	117.8 (4)
C11—C10—C9	119.8 (3)	C37—C38—C39	121.2 (4)
C10—C11—C12	119.8 (4)	C38—C39—C34	119.5 (3)
N2—C12—C11	122.2 (4)	C38—C39—C40	117.4 (3)
N3—C13—C14	122.2 (4)	C34—C39—C40	123.0 (3)
C15—C14—C13	120.2 (4)	O10—C40—O9	126.4 (4)
C14—C15—C16	119.6 (4)	O10—C40—C39	121.6 (4)
C17—C16—C15	116.6 (4)	O9—C40—C39	111.8 (3)

S1.1. Intermolecular Interactions

Table S2 H-bond geometric parameters for compound **4**. Calculated through PLATON (Spek, 2015).

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O(3)–H(3A)···O(2)*	0.82	1.57	2.3838(1)	172
O(7)–H(7A)···O(13)	0.82	1.75	2.5717(1)	174
O(9)–H(9)···O(13)	0.82	1.83	2.6293(1)	166
O(13)–H(13A)···O(14)	0.85	1.80	2.6358(1	168
O(13)–H(13B)···O(1)	0.85	1.81	2.6489(1)	169
O(14)–H(14A)···O(10)	0.85	2.16	2.8509(1)	138
O(14)–H(14B)···O(4)	0.85	1.97	2.7955(1)	164
C(2)–H(2)···O(8)	0.93	2.49	3.1685(1)	130
C(6)–H(6)···Cl(1)	0.93	2.81	3.6984(1)	160
C(10)–H(10)···O(12)	0.93	2.43	3.3044(1)	156
C(18)–H(18)···O(2)	0.93	2.55	3.4627(1)	168
C(19)–H(19)···O(14)	0.93	2.59	3.5070(1)	169
C(24)–H(24)···O(6)	0.93	2.58	3.3400(1)	139
C(27)–H(27)···O(1)*	0.93	2.26	2.6327(1)	103
C(30)–H(30)···O(4)*	0.93	2.31	2.6813(1)	104
C(37)–H(37)···O(2)	0.93	2.54	3.3395(1)	144

*Intramolecular

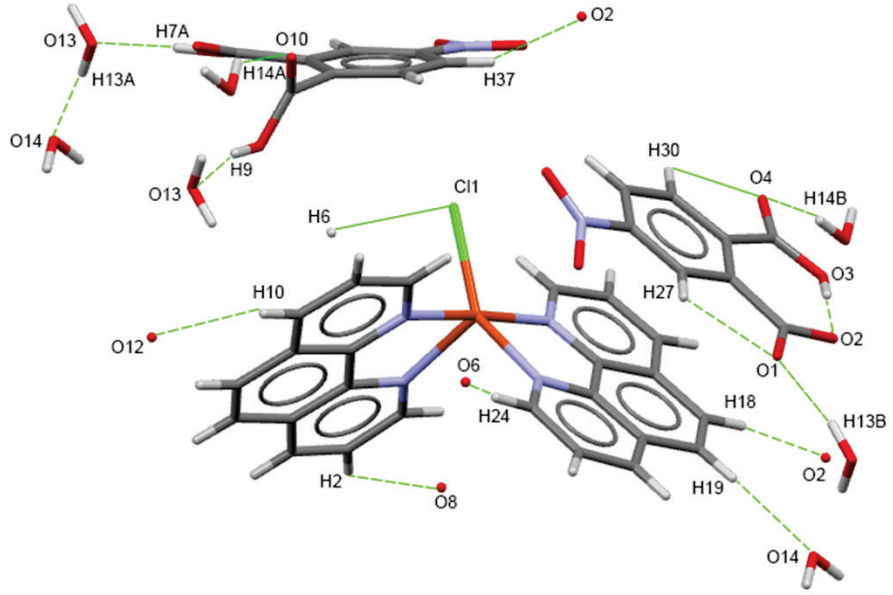


Figure S3 Representative scheme of H-bonds in compound **4**.

In addition to H-bonds, π-π interactions also contribute to the packing arrangement in compound **4**. Two aromatic rings from one phen ligand interact with the aromatic rings from another phen generated through symmetry operations. The centroid-centroid distance for the rings is 3.592 Å. The other phen ligand also interacts to the 4-nitrophthalate ion through π-π interactions, with centroid-centroid distance of 3.756 Å (Figure S4).

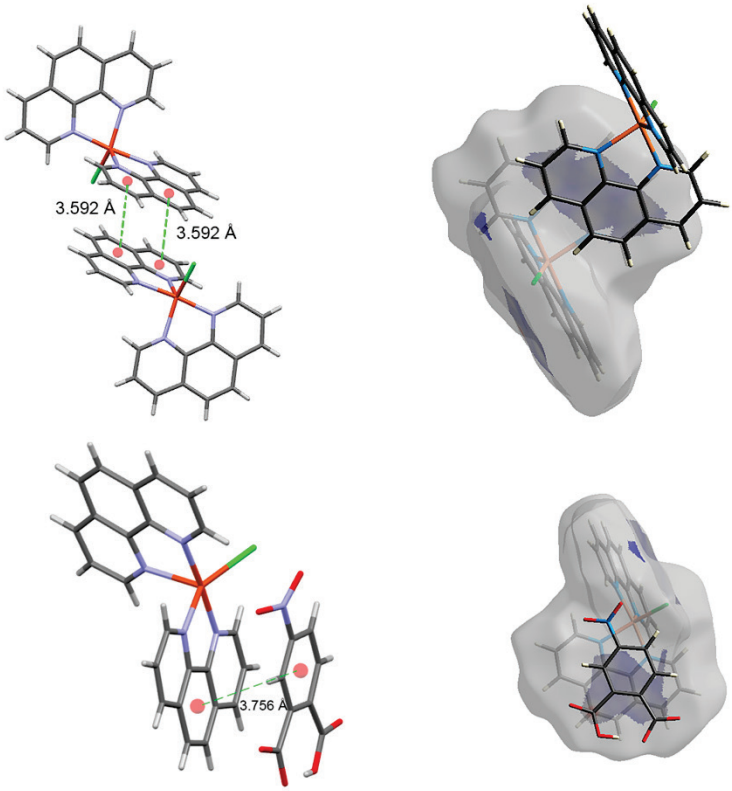


Figure S4 π-π interactions on compound **4** and Hirshfeld surface for the complex ion, highlighting the C···C contact.

S2. Decomposed Fingerprint Plots for Compounds 1-6

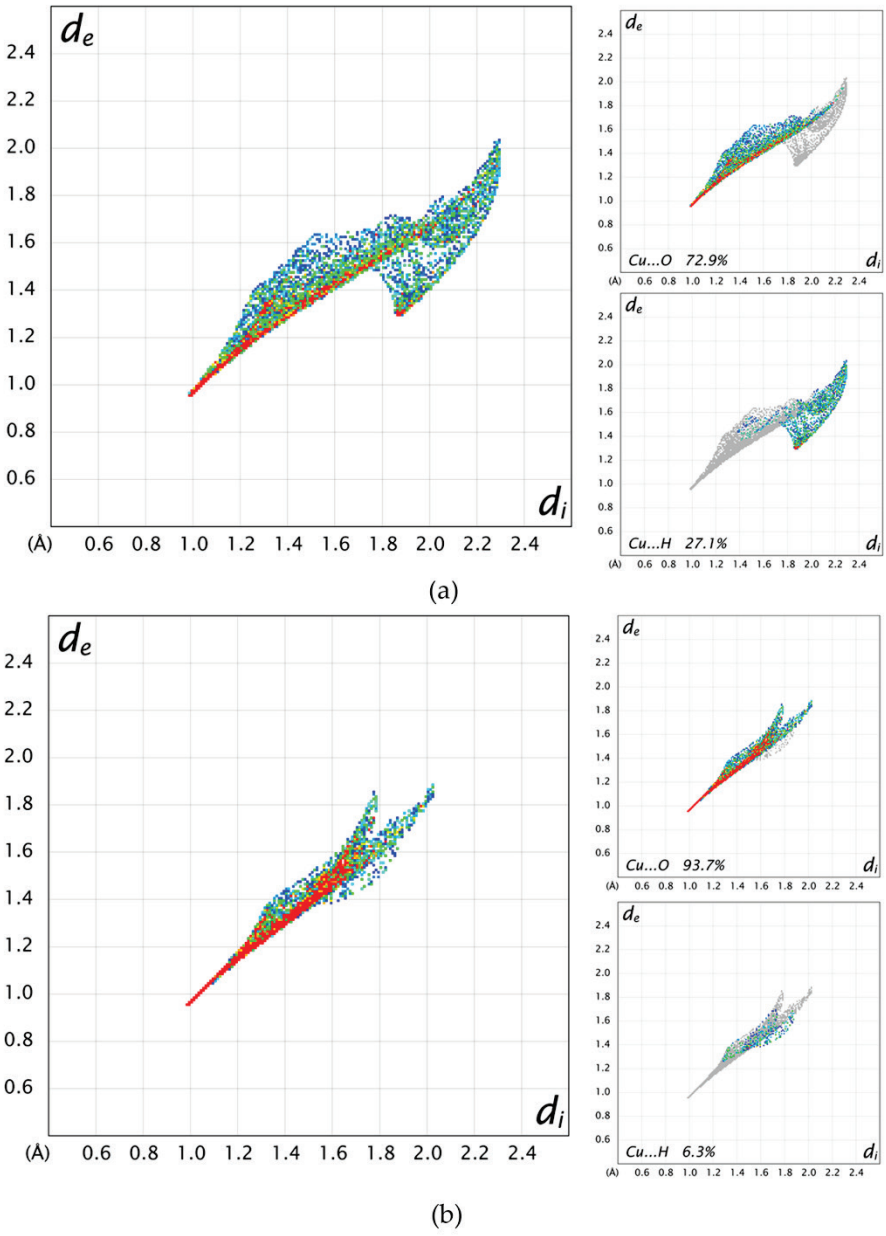
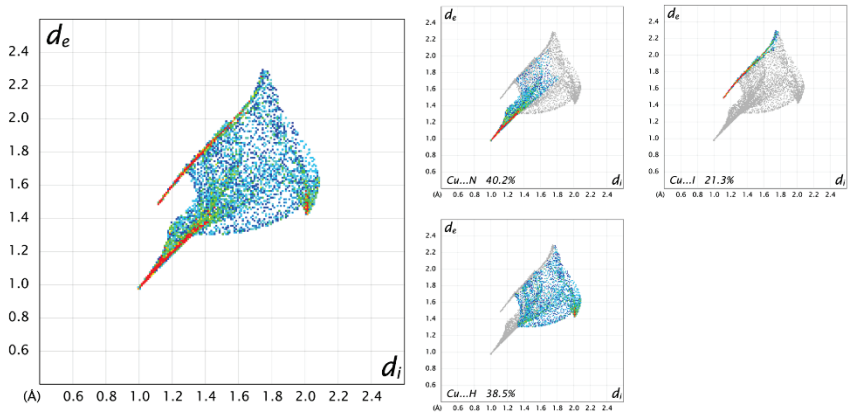
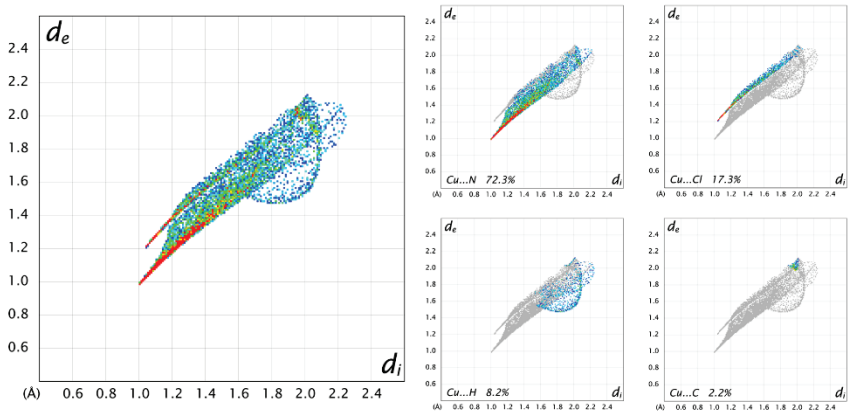


Figure S5 Decomposed fingerprint plots for the copper(II) center in (a) compound **1** and (b) compound **2**.

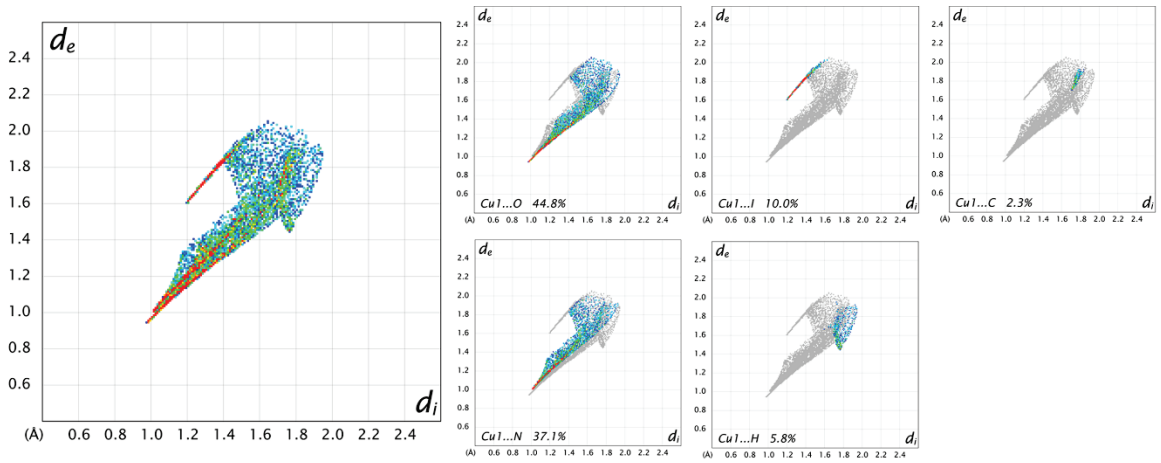


(a)

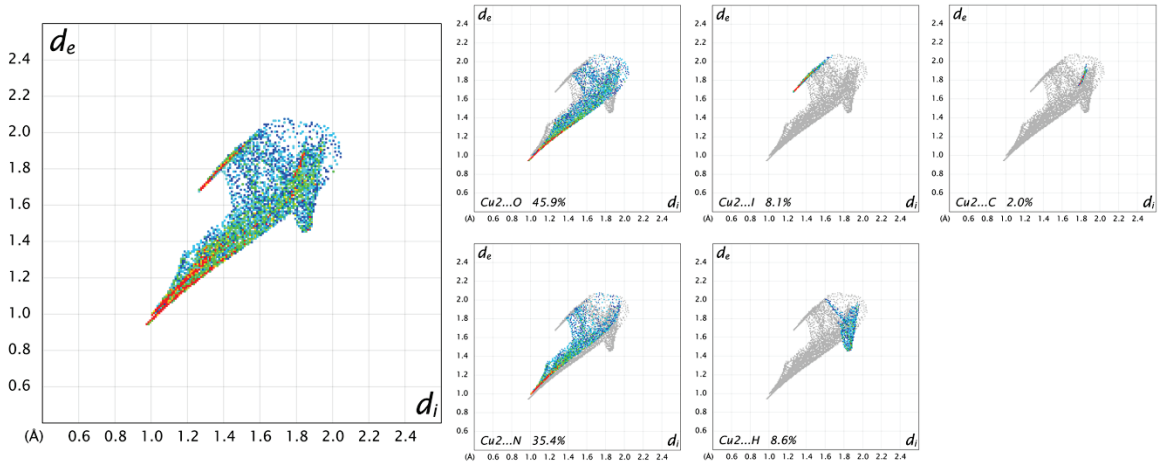


(b)

Figure S6 Decomposed fingerprint plots for the copper(II) center in (a) compound **3** and (b) compound **4**.



(a)



(b)

Figure S7 Decomposed fingerprint plots for the copper(II) center in (a) complex **5** and (b) complex **6**.