

## Supplementary Information for Manuscript

### **On the importance of $\pi$ -stacking interactions in the complexes of copper and zinc bearing pyridine-2,6-dicarboxylic acid *N*-oxide and *N*-donor auxiliary ligands**

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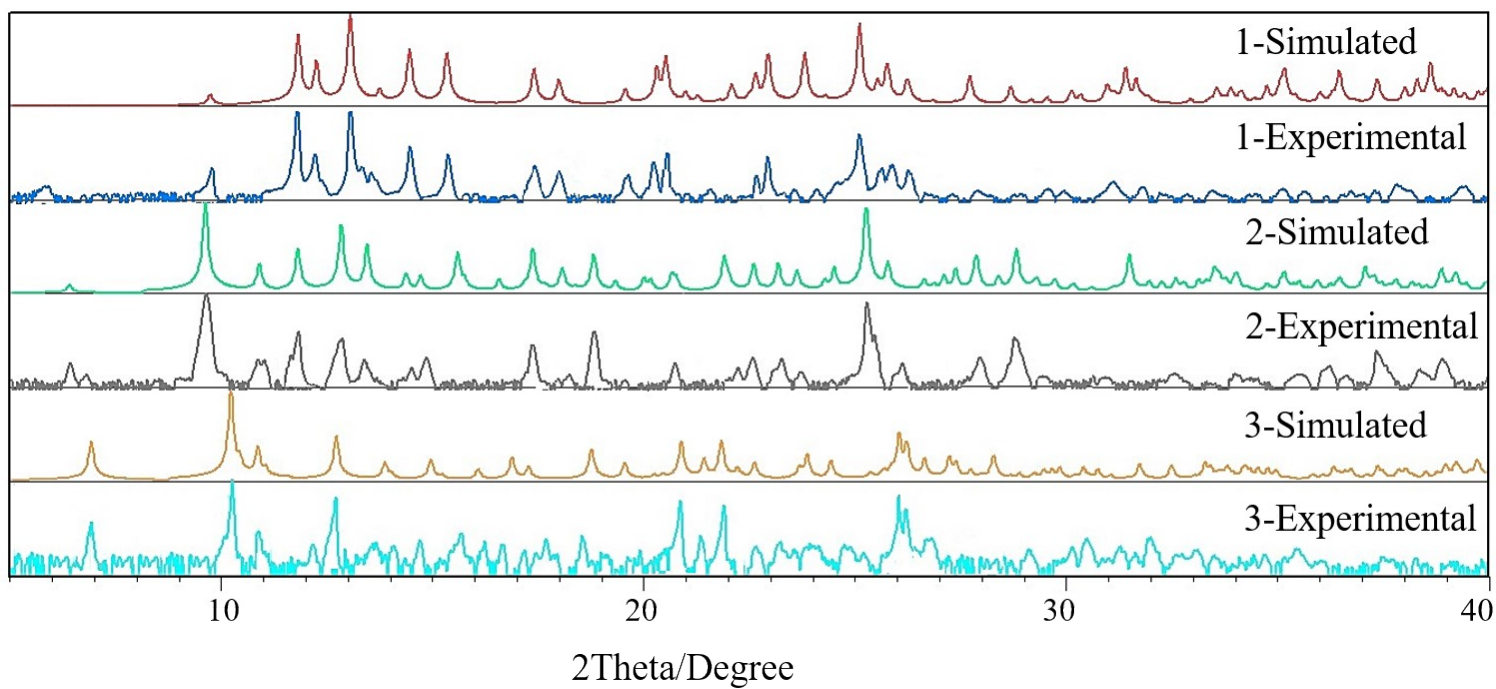
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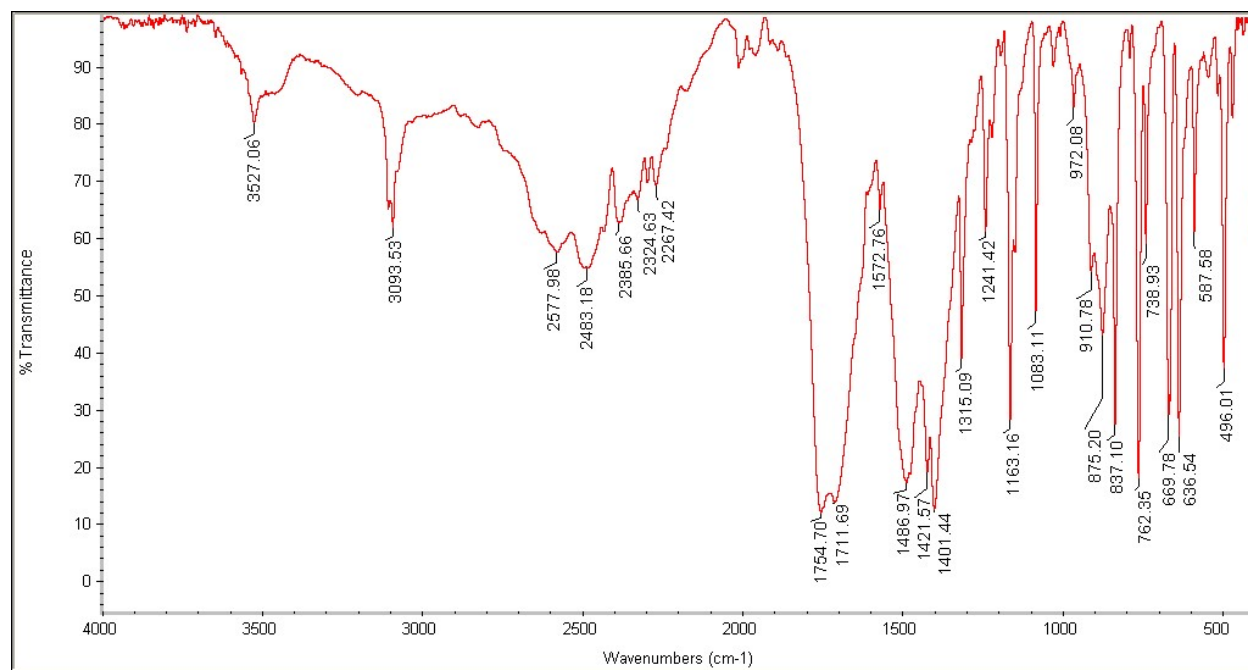
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**Fig. S1.** PXRD results (simulated and experimental) for 1-3.



**Fig. S2.** FTIR spectrum of H<sub>2</sub>pydco.

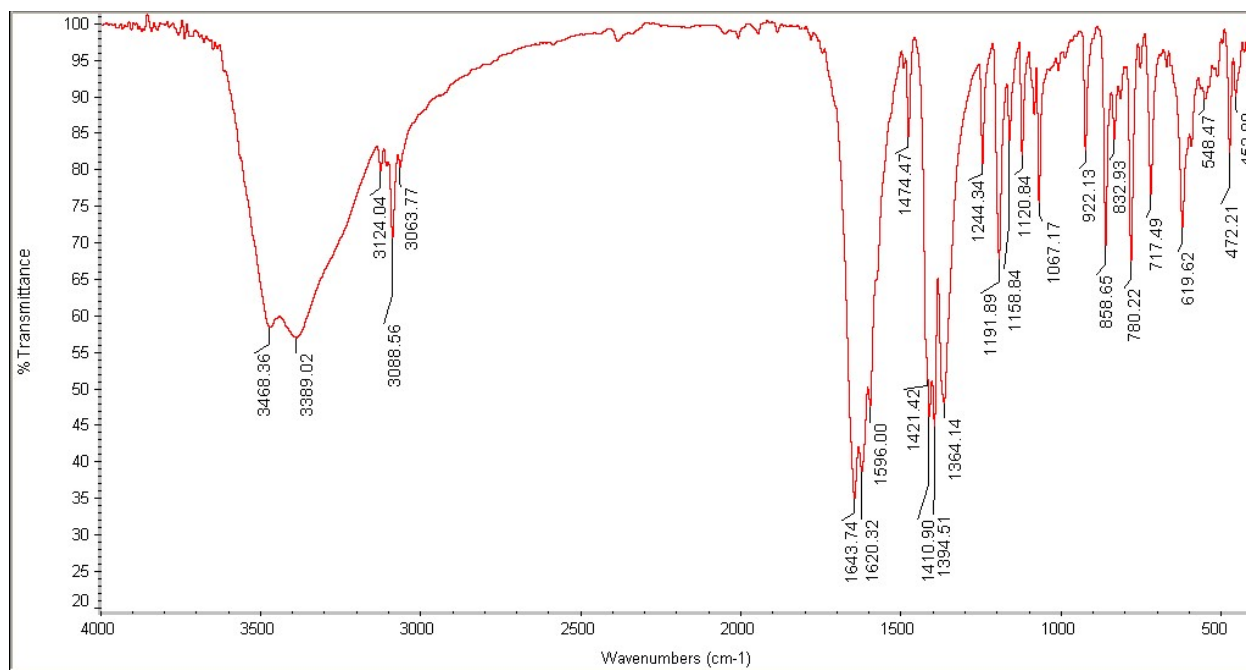


Fig. S3. FTIR spectrum of 1.

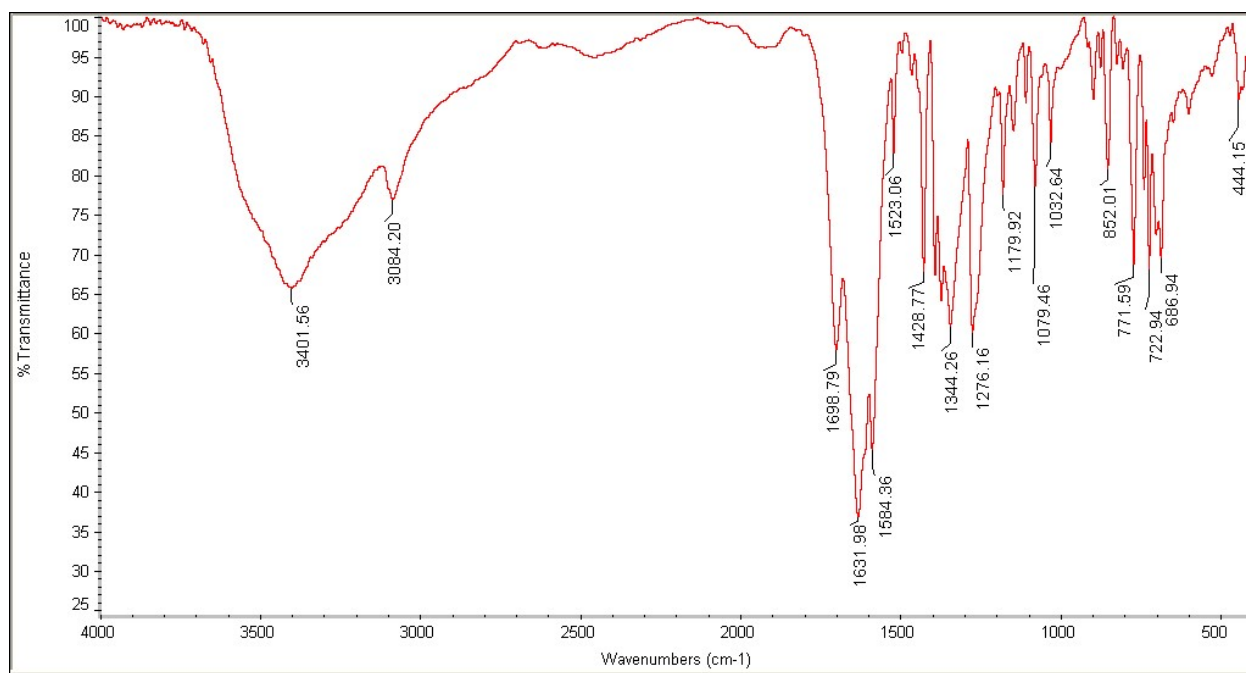


Fig. S4. FTIR spectrum of 2.

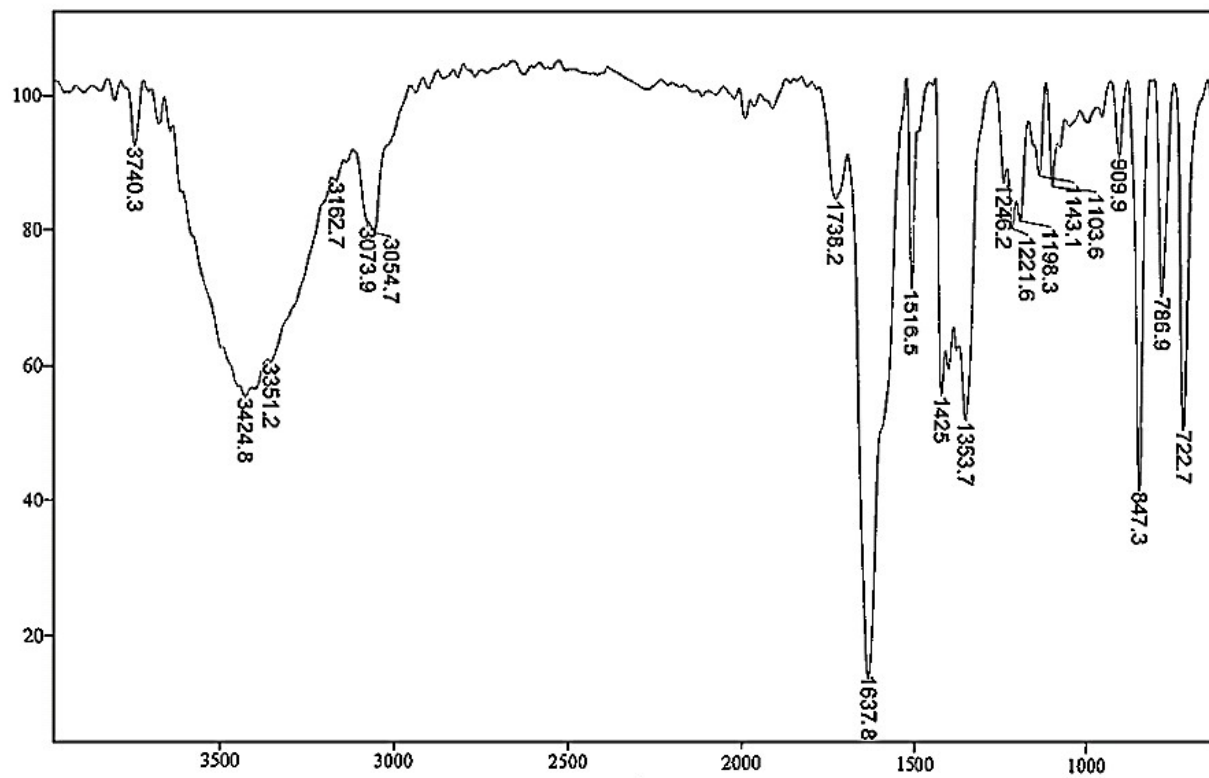


Fig. S5. FTIR spectrum of 3.

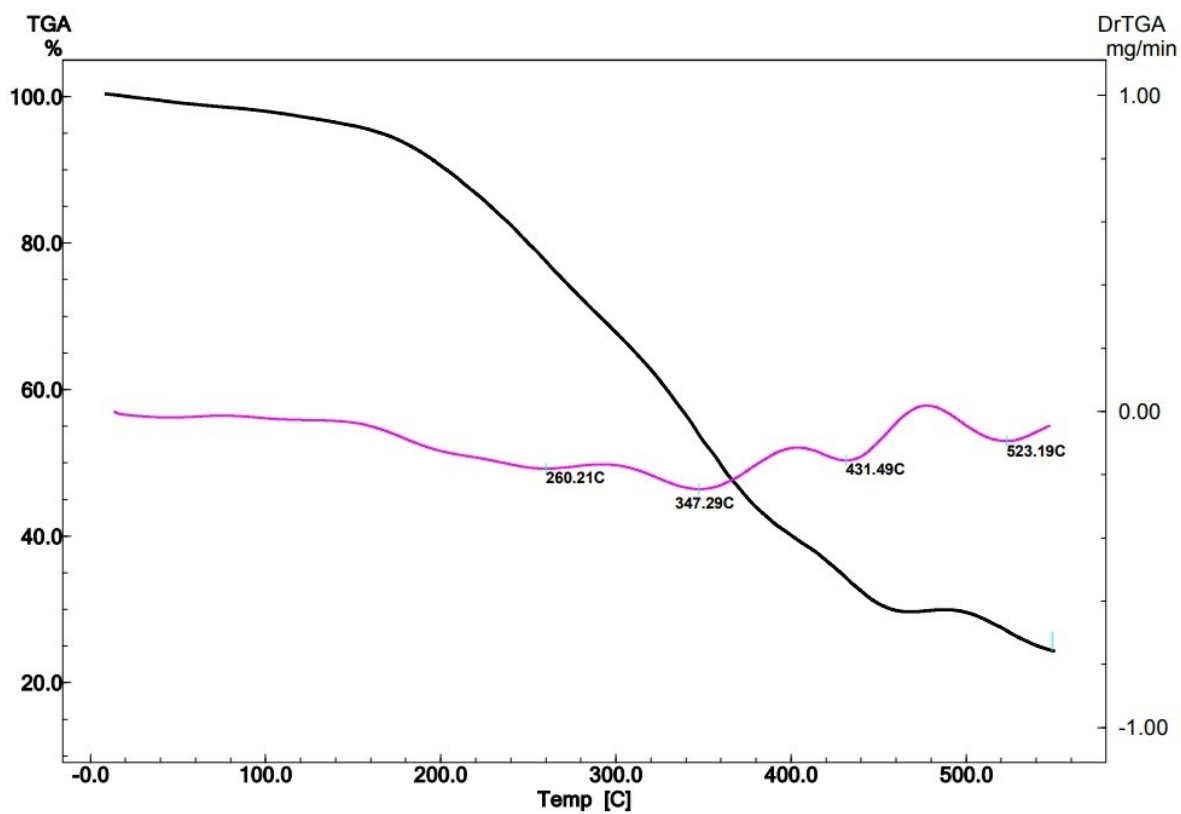
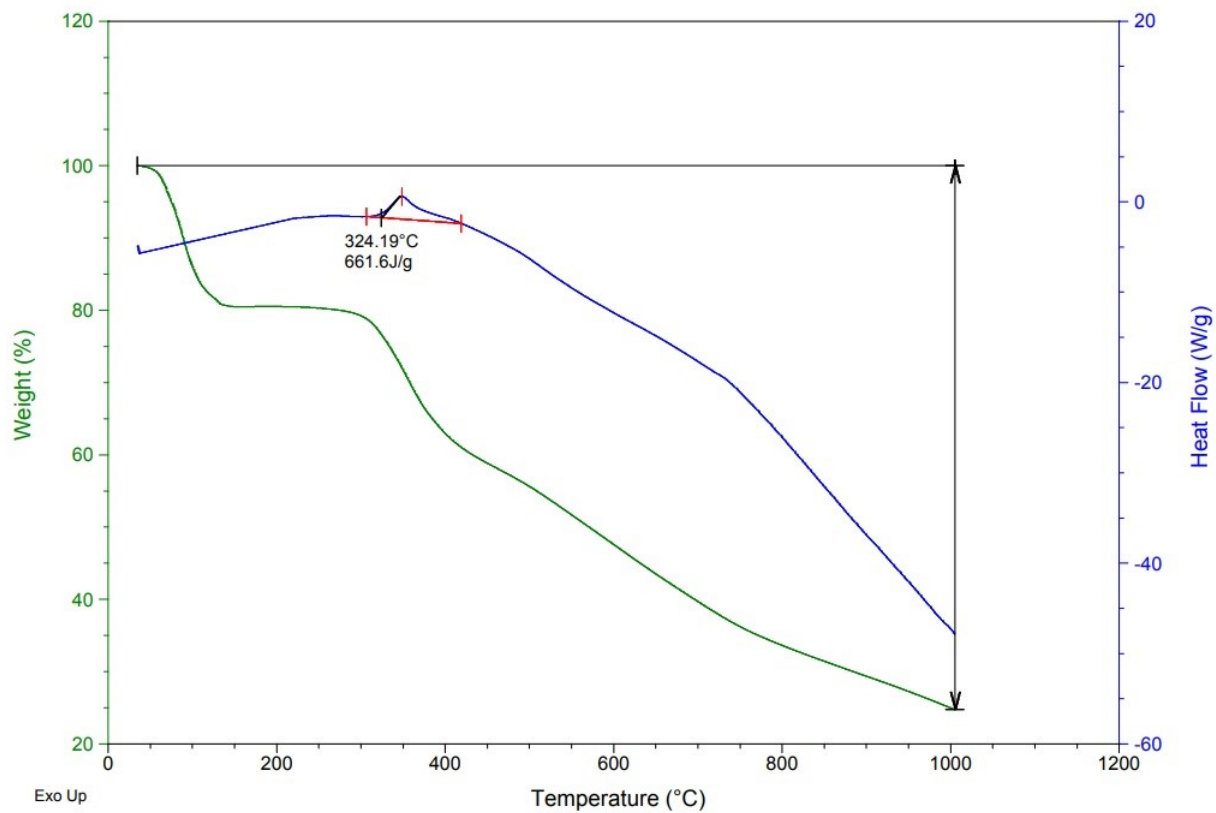


Fig. S6. TGA curve of 1.



**Fig. S7.** TGA curve of **2**.

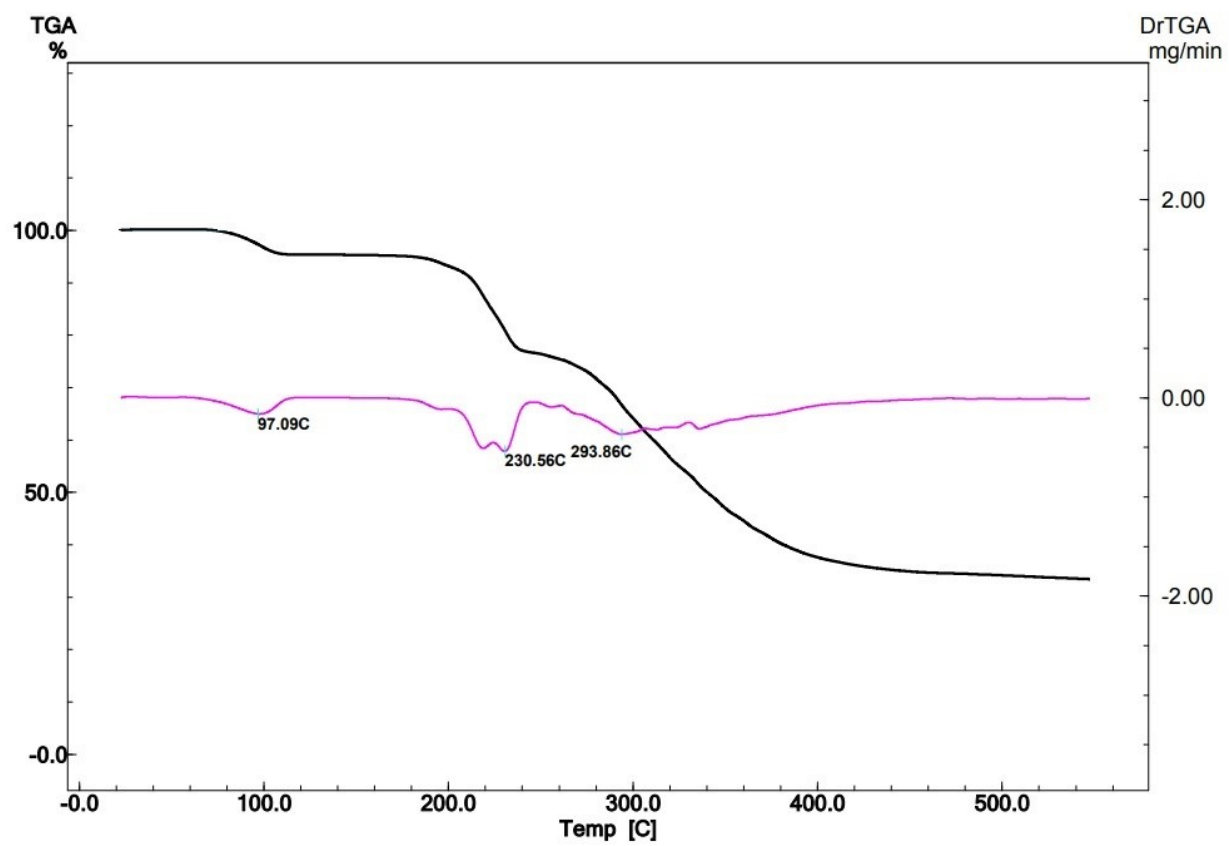
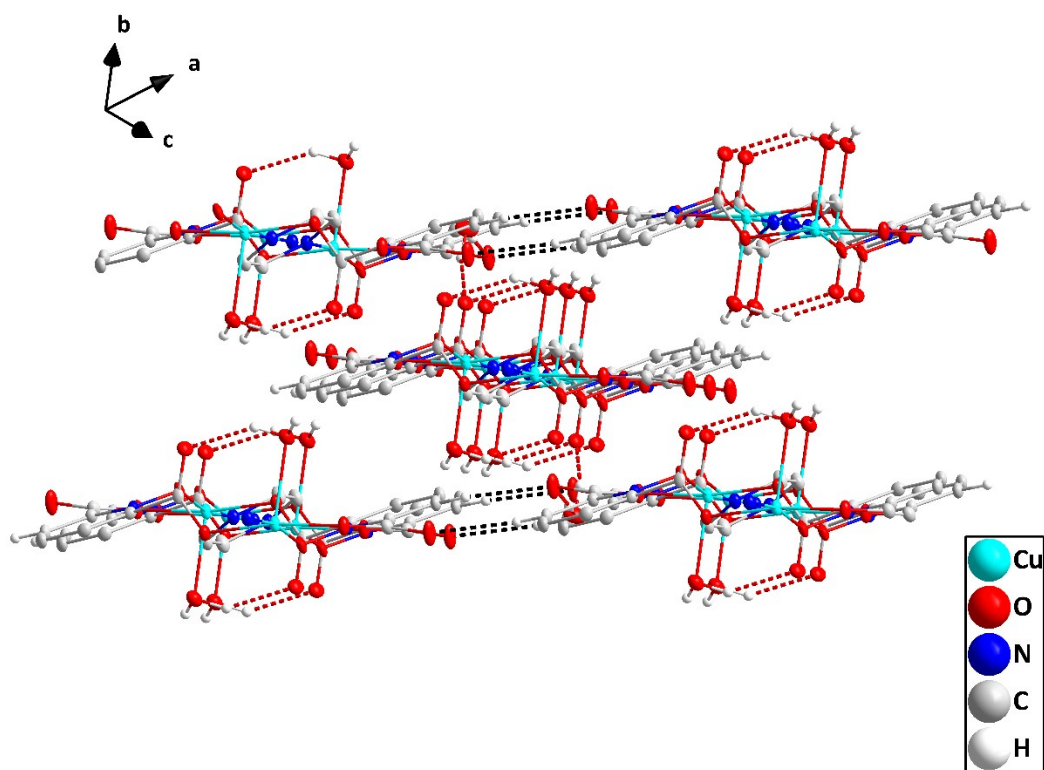
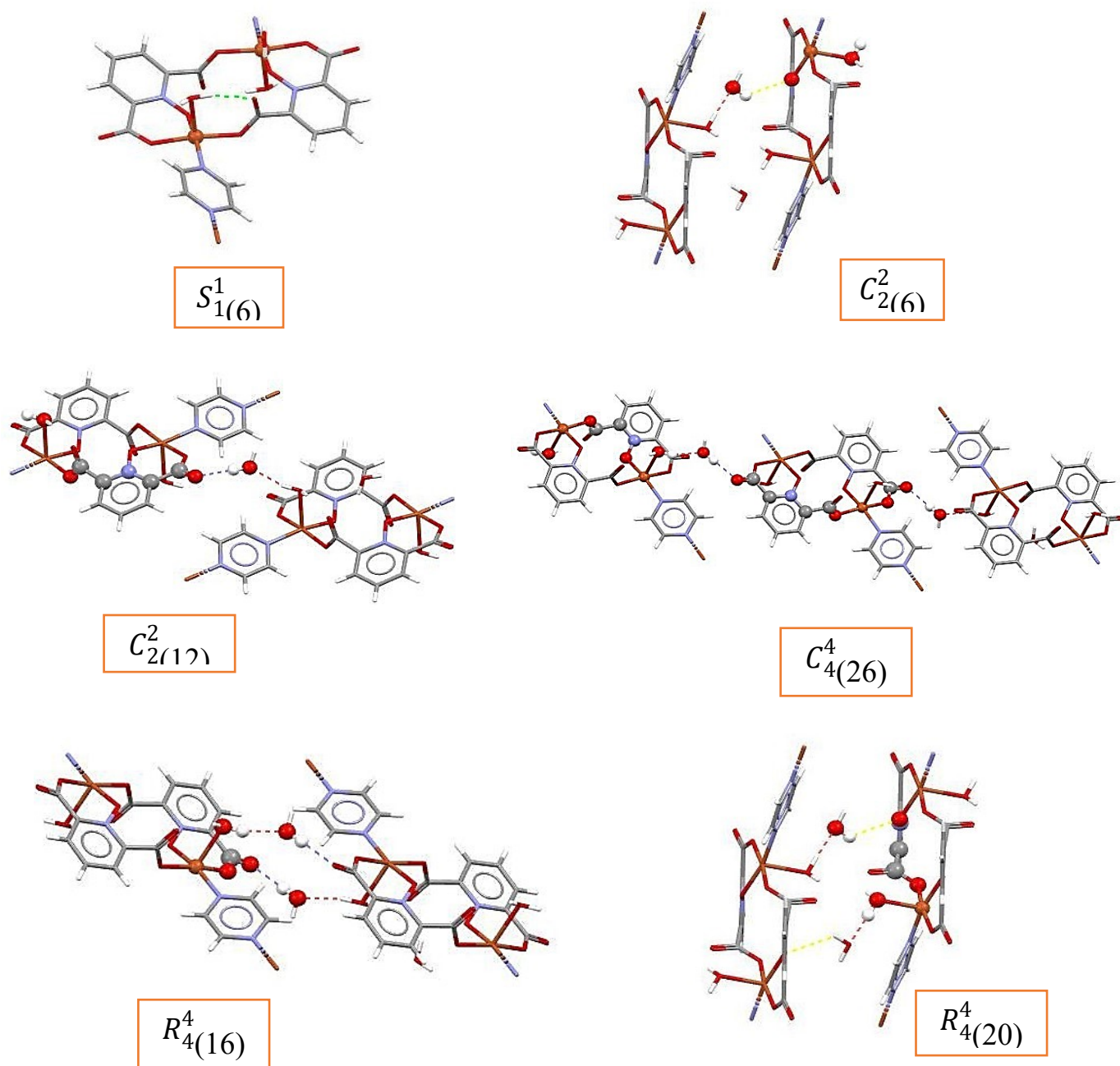


Fig. S8. TGA curve of 3.

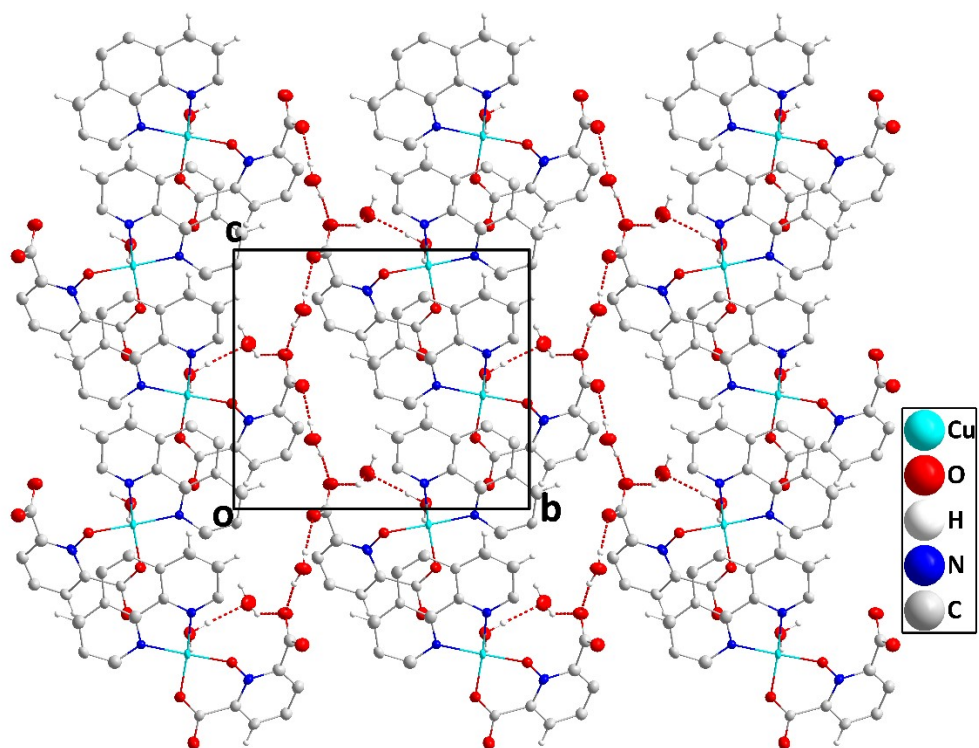




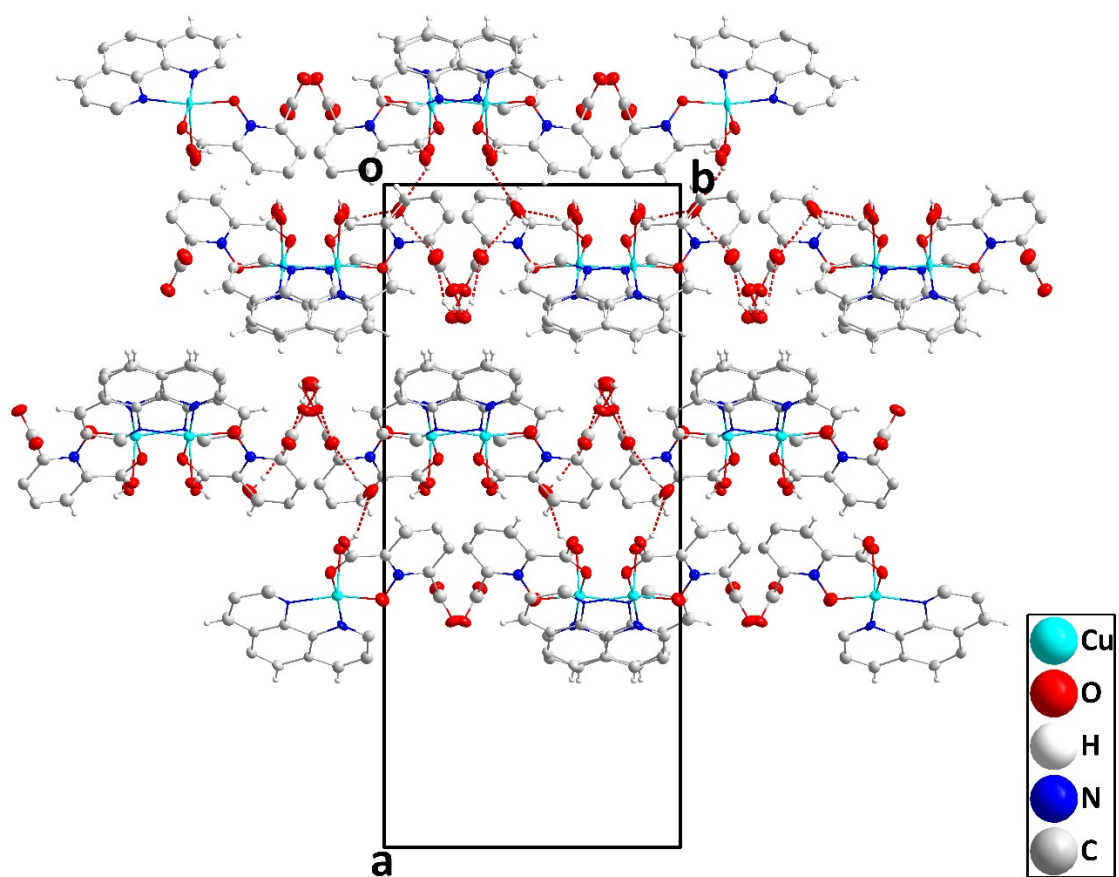
**Fig. S9.** Perspective view of the supramolecular structure of **1** with O–H···O and C–H···O hydrogen bonds depicted, respectively, by red and black dashed lines.



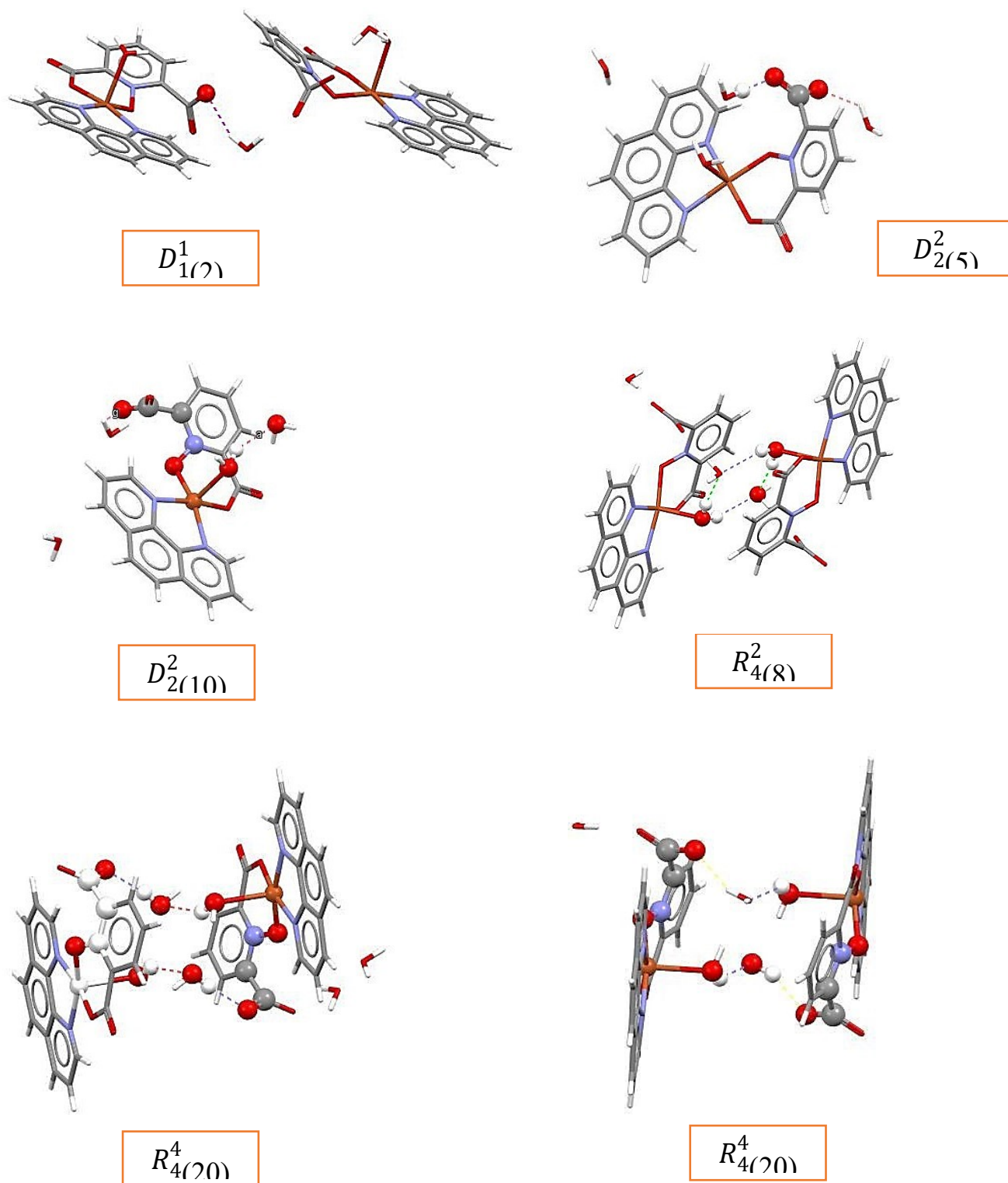
**Fig. S10.** Representation of the H-bond motifs in **1**. Color code: Cu, orange; C, grey; N, blue; O, red; H, white.



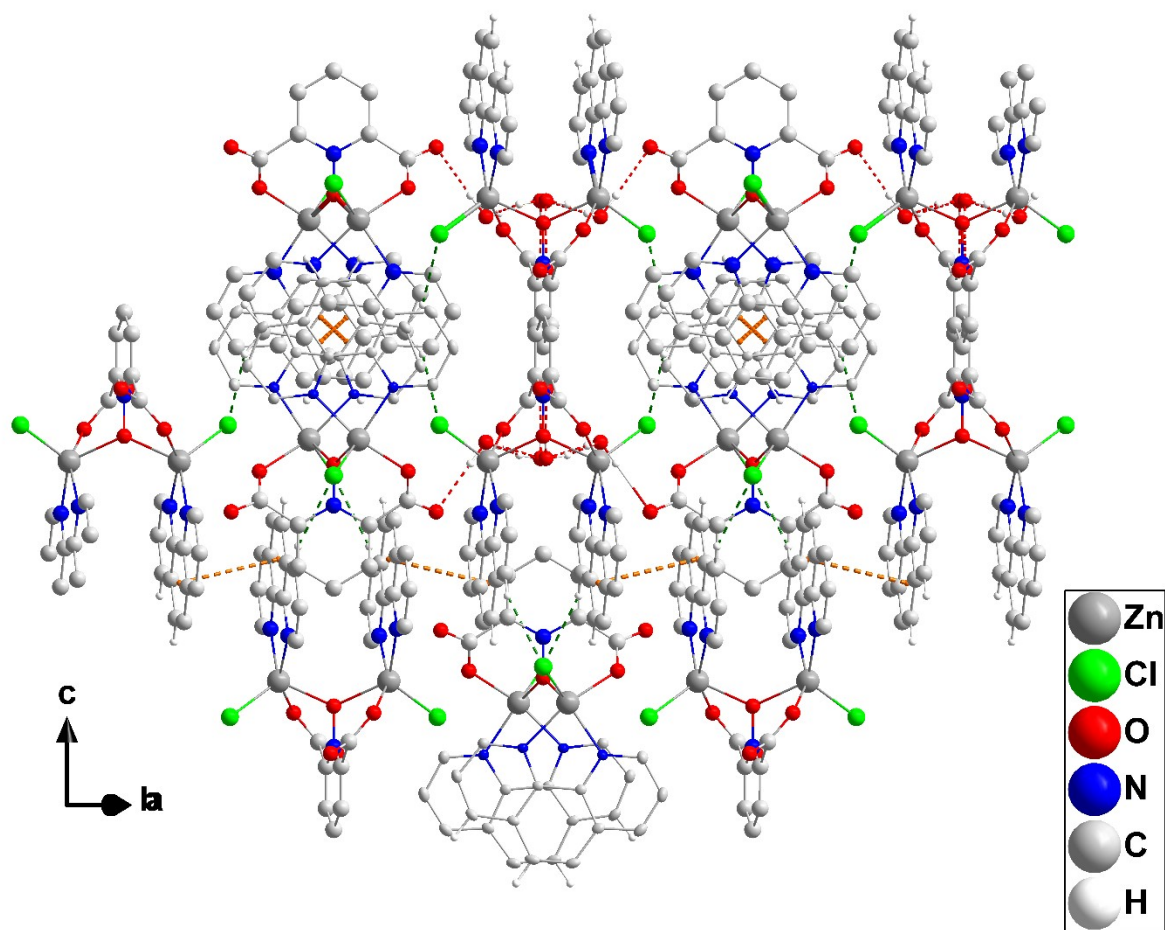
**Fig. S11.** The supramolecular structure of **2** is viewed along the *a*-axis direction with O–H...O hydrogen bonds depicted by red dashed lines.



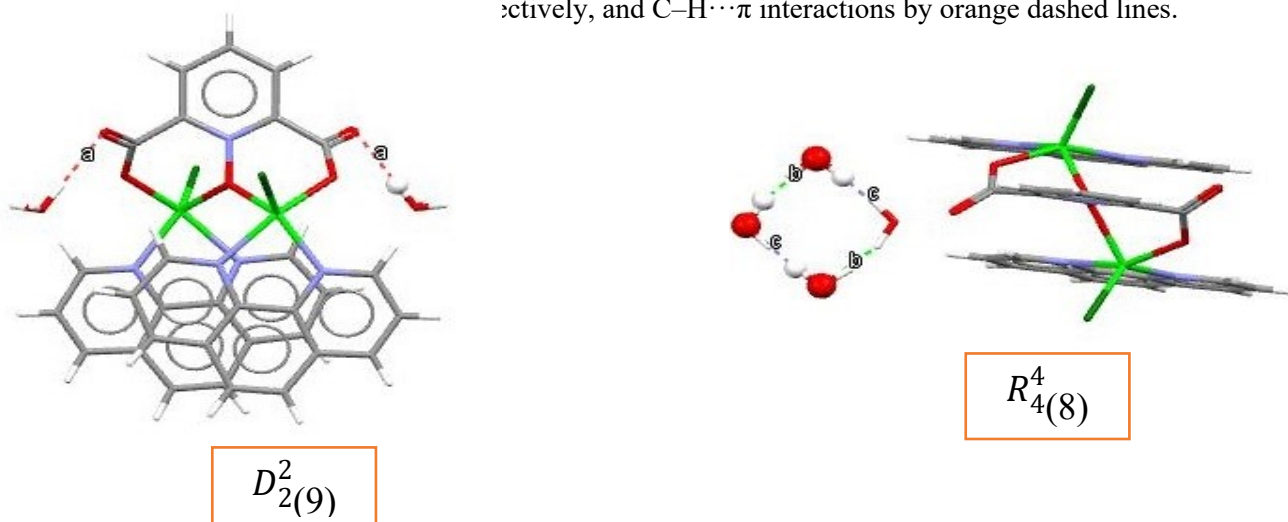
**Fig. S12.** The supramolecular structure of **2** is viewed along the *c*-axis direction with O–H···O hydrogen bonds depicted by red dashed lines. Molecules containing Cu1 and Cu2 are in the lower and upper layers, respectively.



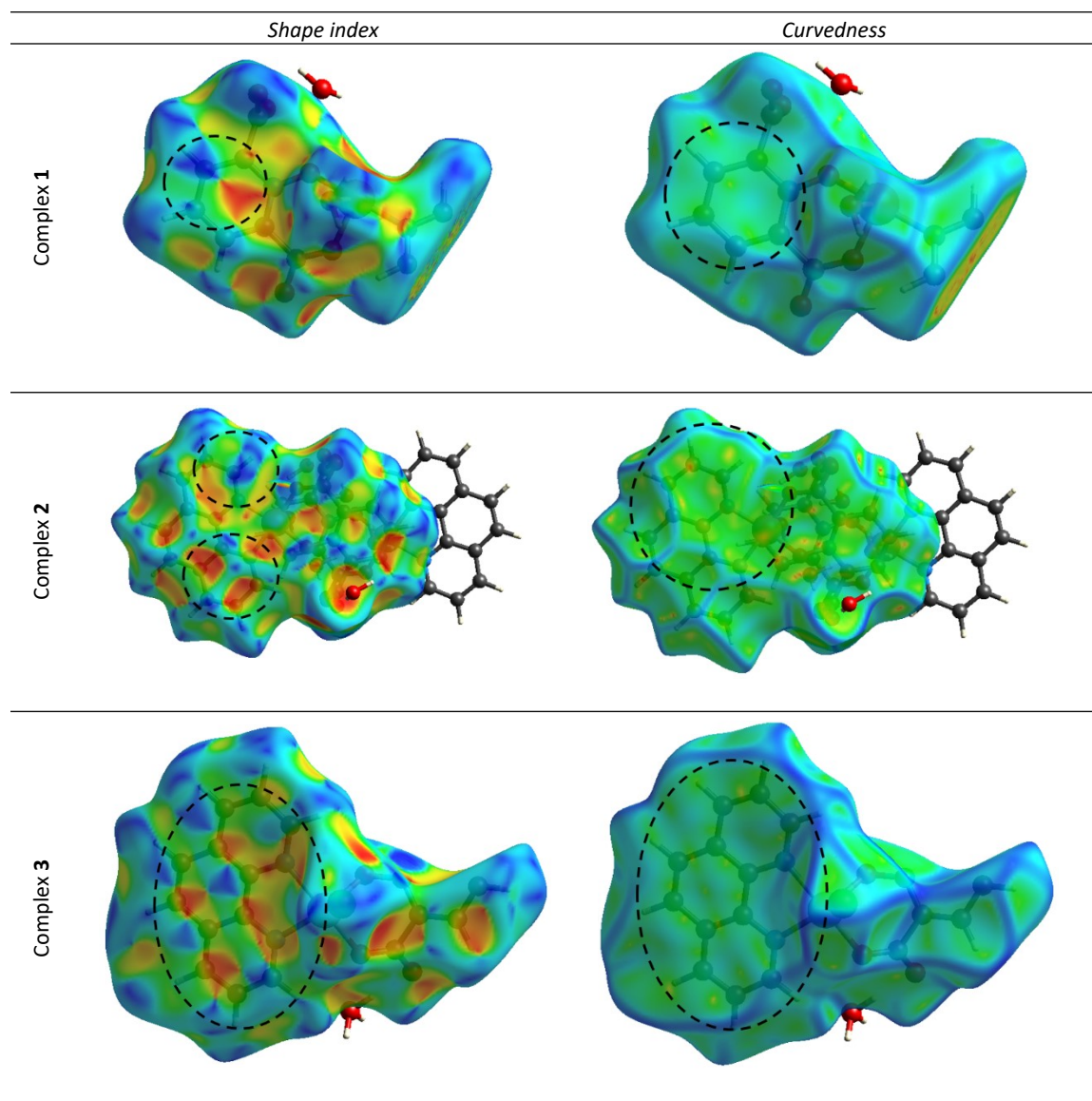
**Fig. S13.** Representation of the H-bond motifs in **2**. Color code: Cu, orange; C, grey; N, blue; O, red; H, white.



**Fig. S14.** Packing of **3** viewed along the [1-10] direction with O–H···O and C–H···Cl hydrogen bonds actively, and C–H··· $\pi$  interactions by orange dashed lines.



**Fig. S15.** Representation of the H-bond motifs in **3**. Color code: Zn, green; Cl, dark green; C, grey; N, blue; O, red; H, white.



**Fig. S16.** Hirshfeld surfaces of **1-3** mapped over shape index and curvedness properties. The regions highlighted in black dashed circles correspond to regions involved in  $\pi \cdots \pi$  stacking interactions.

**Table S1.** Selected bond lengths (Å) and angles (°) of **1-3**.

<b>1</b>				
Cu1–O1	1.918(10)	Cu1–O3	1.932(13)	
Cu1–N2	2.039(12)	Cu1–O5	1.955(12)	
O3–Cu1–N2	167.87(5)	O1–Cu1–O5	171.64(4)	
O3–Cu1–O6	95.28(4)	O5–Cu1–O6	100.52(5)	
O1–Cu1–O6	87.81(4)	N2–Cu1–O6	96.05(5)	
O1–Cu1–O3	91.13(5)	O3–Cu1–O5	87.56(5)	
O5–Cu1–N2	92.43(5)	N2–Cu1–O1	87.13(4)	
<b>2</b>				
Cu1–O3	1.903(13)	Cu1–O1	1.912(11)	
Cu1–N2	1.976(12)	Cu1–N1	2.079(10)	
Cu1–O6	2.322(12)	Cu2–O9	1.904(11)	
Cu2–O7	1.921(10)	Cu2–N4	1.966(7)	
Cu2–N5	1.967(7)	Cu2–O12	2.326(12)	
O3–Cu1–O1	92.4(5)	O3–Cu1–N2	88.4(5)	
O1–Cu1–N2	171.1(5)	O3–Cu1–N1	166.4(5)	
O1–Cu1–N1	90.5(4)	N2–Cu1–N1	86.7(5)	
O3–Cu1–O6	96.6(5)	O1–Cu1–O6	92.5(5)	
N2–Cu1–O6	96.2(5)	N1–Cu1–O6	96.5(4)	
N5–Cu2–O12	92.2(4)	O9–Cu2–O7	91.3(4)	
O9–Cu2–N4	91.3(4)	O7–Cu2–N4	170.9(5)	
O9–Cu2–N5	169.6(4)	O7–Cu2–N5	93.3(4)	
N4–Cu2–N5	82.8(3)	O9–Cu2–O12	96.9(4)	
O7–Cu2–O12	92.1(4)	N4–Cu2–O12	96.3(4)	
<b>3</b>				
Zn1–O1	2.0548 (12)	Zn1–N1	2.1268 (13)	
Zn1–N2	2.0846 (14)	Zn1–Cl1	2.2241 (5)	
Zn1–O3	2.1158 (6)			
O1–Zn1–N2	90.46 (5)	O3–Zn1–N1	85.89 (5)	
O1–Zn1–O3	81.35 (4)	O1–Zn1–Cl1	105.00 (4)	
N2–Zn1–O3	127.50 (5)	N2–Zn1–Cl1	125.94 (4)	
O1–Zn1–N1	153.55 (5)	O3–Zn1–Cl1	106.15 (3)	
N2–Zn1–N1	79.10 (5)	N1–Zn1–Cl1	100.76 (4)	



**Table S2.** Selected Hydrogen bond geometry, lengths (Å), and angles (°) for **1-3**.

D-H···A	D-H	H···A	D···A	D-H···A
<b>1</b>				
C3-H3···O2 <sup>i</sup>	0.95	2.35	3.2545 (19)	160
O6-H6A···O7 <sup>ii</sup>	0.87	1.90	2.7389 (17)	162
O6-H6B···O4 <sup>iii</sup>	0.87	1.97	2.7294 (17)	146
O7-H7A···O2 <sup>iv</sup>	0.87	2.08	2.9449 (18)	178
O7-H7B···O4 <sup>iii</sup>	0.87	2.04	2.8327 (17)	150
Symmetry codes: (i) -x, -y+1, -z; (ii) -x+1, -y, -z+1; (iii) -x+1, -y+1, -z+1; (iv) x, y, z+1.				
<b>2</b>				
O6-H6B···O15 <sup>i</sup>	0.91	2.14	2.949 (18)	149
C15-H15···O2 <sup>ii</sup>	0.95	2.46	3.200 (20)	134
O12-H12A···O16	0.87	1.96	2.818 (18)	171
O12-H12B···O16 <sup>iii</sup>	0.87	2.23	2.994 (19)	147
C34-H34···O8 <sup>iv</sup>	0.95	2.51	3.212 (19)	131
O13-H13A···O11	0.87	1.89	2.755 (16)	174
O13-H13B···O10 <sup>v</sup>	0.87	2.12	2.953 (17)	160
O14-H14A···O5	0.87	2.08	2.732 (17)	131
O14-H14B···O4 <sup>vi</sup>	0.87	2.10	2.967 (17)	178
O15-H15B···O4	0.87	1.84	2.707 (17)	172
O16-H16A···O10	0.87	1.86	2.630 (18)	147
Symmetry codes: (i) x+1, -y+1, -z+1; (ii) -x+1, -y+1, -z; (iii) -x, -y+1, -z+2; (iv) -x, -y+1, -z+1; (v) x, -y+1/2, z-1/2; (vi) x, -y+3/2, z-1/2.				
<b>3</b>				
C15-H15···O2 <sup>i</sup>	0.95	2.29	3.183 (2)	156
O4-H4A···O2	0.87	1.97	2.836 (2)	178
O4-H4B···O4 <sup>ii</sup>	0.87	1.88	2.723 (4)	162
O4-H4BA···O4 <sup>iii</sup>	0.87	1.89	2.757 (4)	171
Symmetry codes: (i) -x+1, -y+1, -z+1; (ii) x, -y+3/4, -z+3/4; (iii) -x+3/4, y, -z+3/4.169.5				