Crystal structure and chemical bonds in [Cu^{II}_2(Tolf)$_4$(MeOH)$_2$]·2MeOH

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Supplementary Materials

Table S1. Geometry of C–H···π interactions in [Cu$^{II}_2$(Tolf)$_4$(MeOH)$_2$]·2MeOH.

C–H···π	H···Cg (Å)	C···Cg (Å)	<(C–H···Cg) (°)
C2M–H2MC···Cg3	2.99	3.61	122
C11B–H11B···Cg1[ii]	2.93	3.77	147

Symmetry code: ii = 1-x,-y,2-z

Table S2. Geometry of C–Cl···π interaction in [Cu$^{II}_2$(Tolf)$_4$(MeOH)$_2$]·2MeOH.

| C–Cl···π	Cl···Cg (Å)	C···Cg (Å)	<(C–Cl···Cg) (°)
C10B–Cl2···Cg2[ii]	3.43	4.86	137
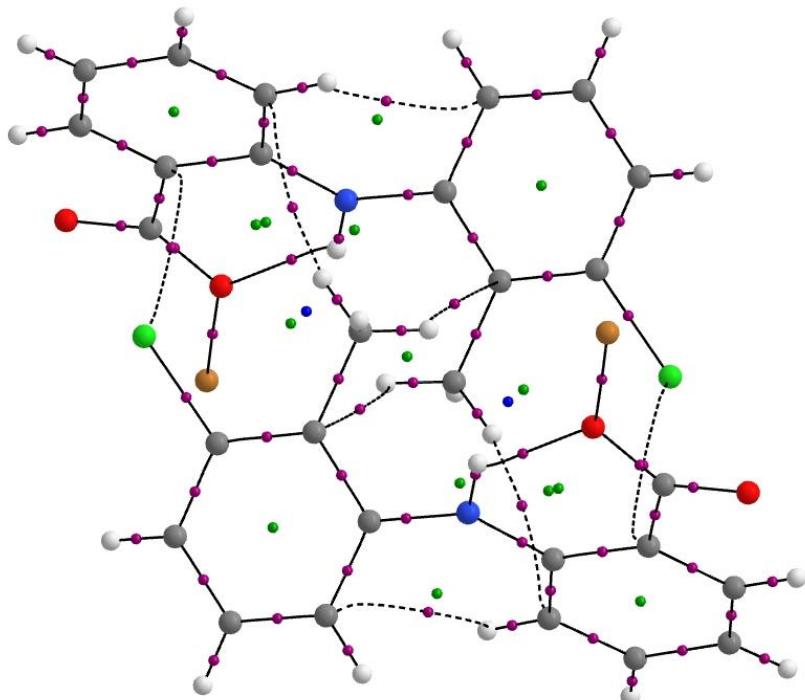
Symmetry code: iii = 1-x, -y, 2-z

Centres of aromatic rings:

Cg1 [C2A/C3A/C4A/C5A/C6A/C7A],

Cg2 [C2B/C3B/C4B/C5B/C6B/C7B],

Cg3 [C8A/C9A/C10A/C11A/C12A/C13A]

Figure S1. QTAIM diagram shoving C–Cl···π interactions in [Cu$^{II}_2$(Tolf)$_4$(MeOH)$_2$]·2MeOH.
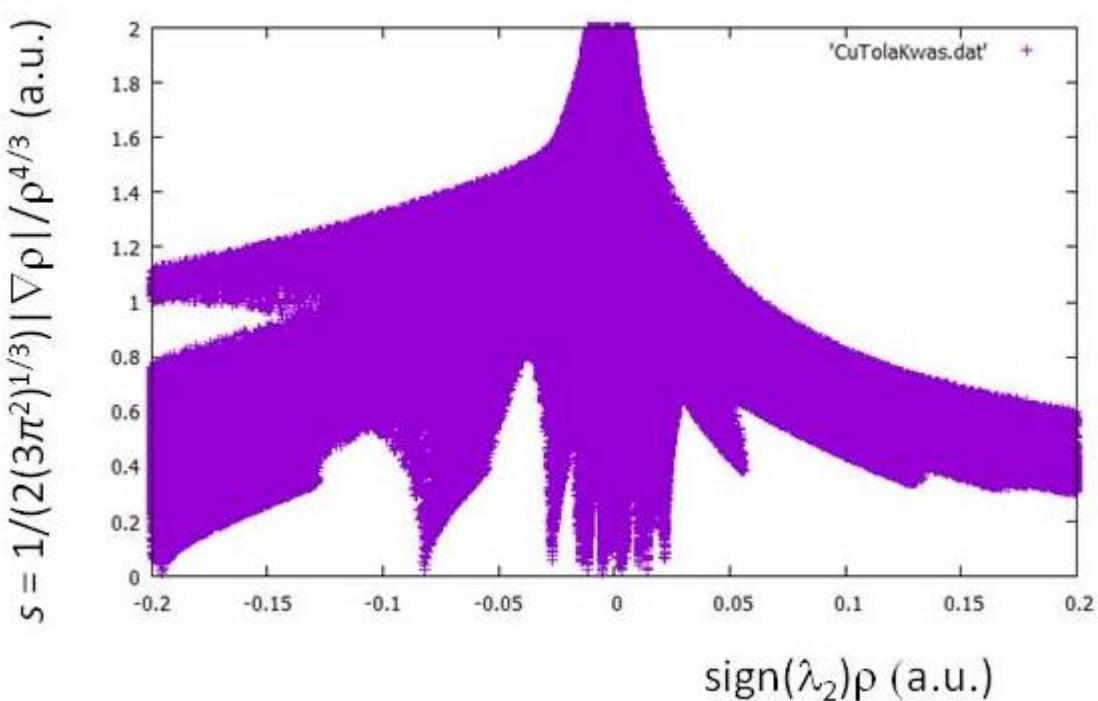
Figure S2. NCI diagram shoving C–Cl⋯π interactions in [Cu$^{II}_2$(Tolf)$_4$(MeOH)$_2$]·2MeOH.
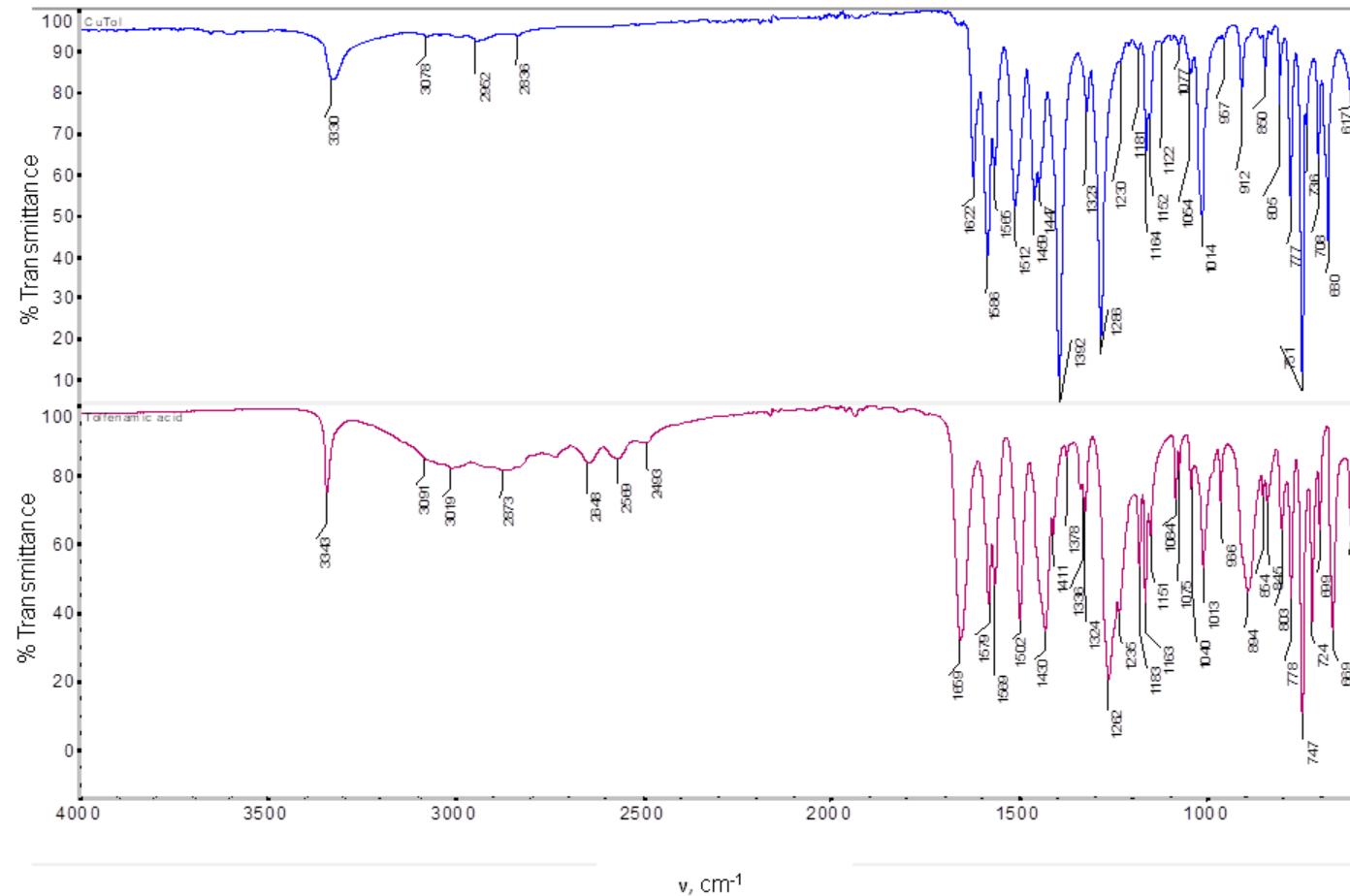
Figure S3. IR spectra: Top: for [Cu$^{II}_2$(Tolf)$_4$(MeOH)$_2$]·2MeOH in the range of 4000 – 400 cm^{-1}; Down: for tolfenamic acid.
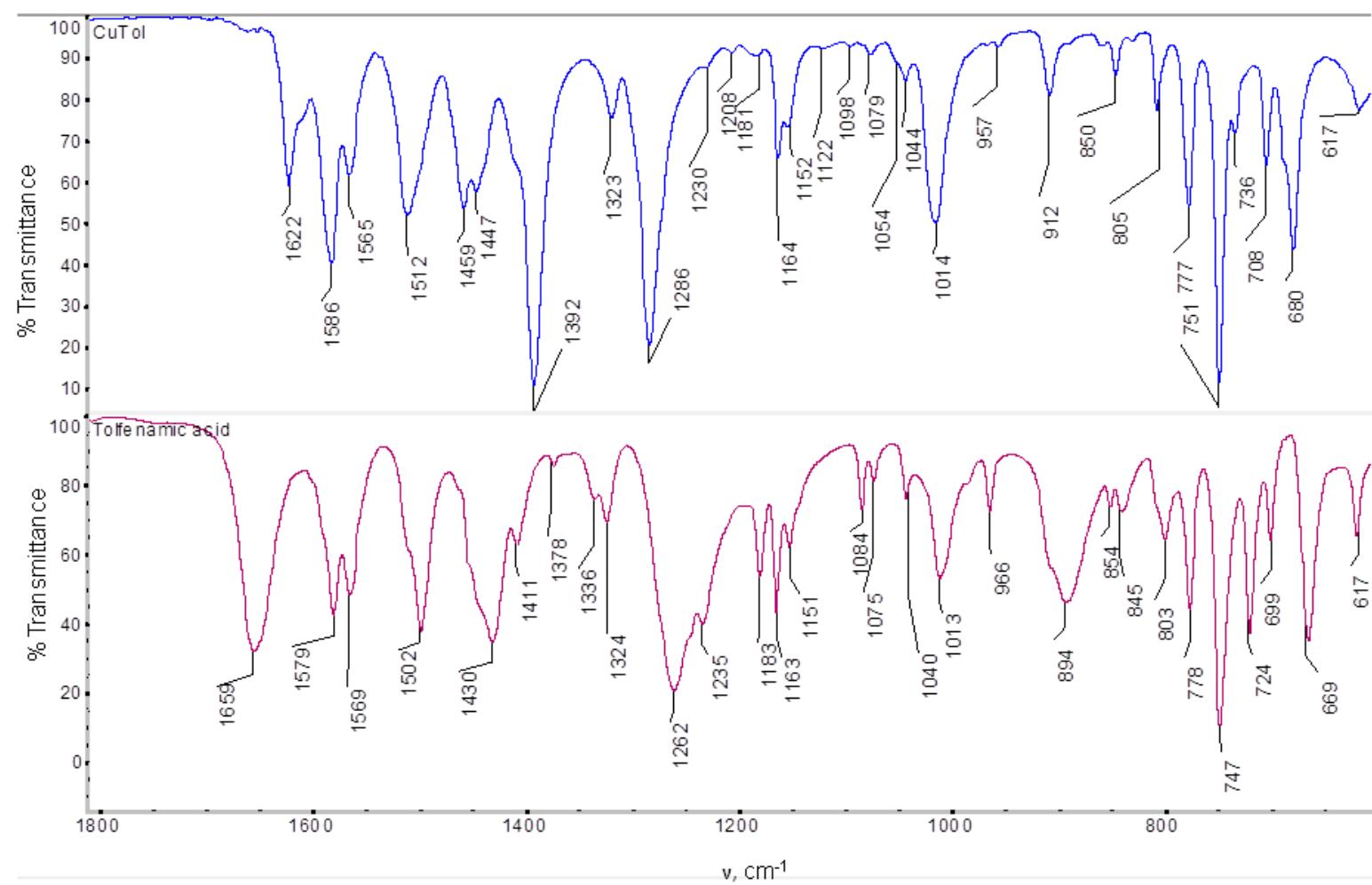
Figure S4. IR spectra: Top: for [Cu$^{II}_2$(Tolf)$_4$(MeOH)$_2$]·2MeOH in the range of 1800 – 400 cm^{-1} Down: for tolfenamic acid.
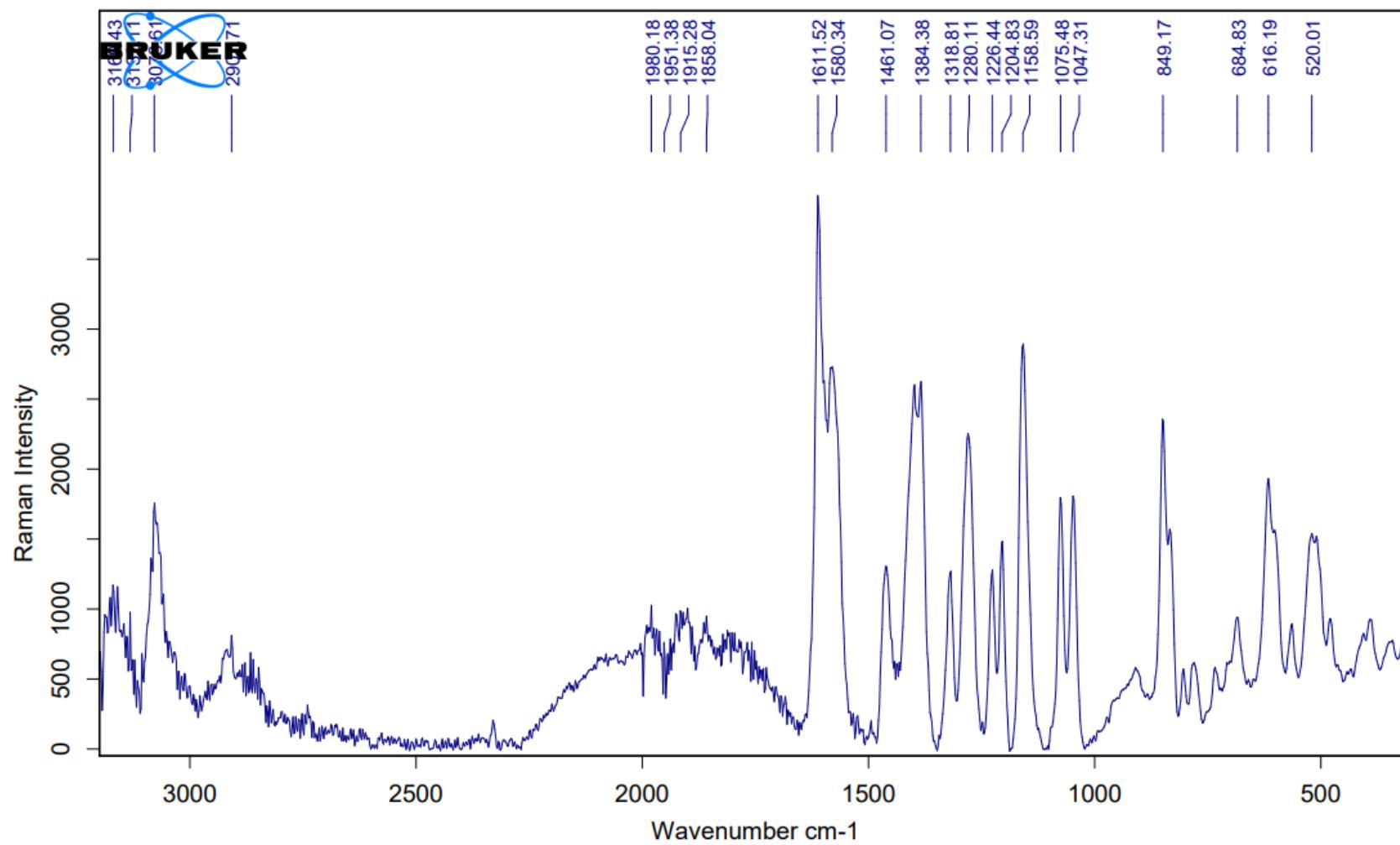
Figure S5. Raman spectrum for [Cu$^{II}_2$(Tolf)$_4$(MeOH)$_2$]·2MeOH.
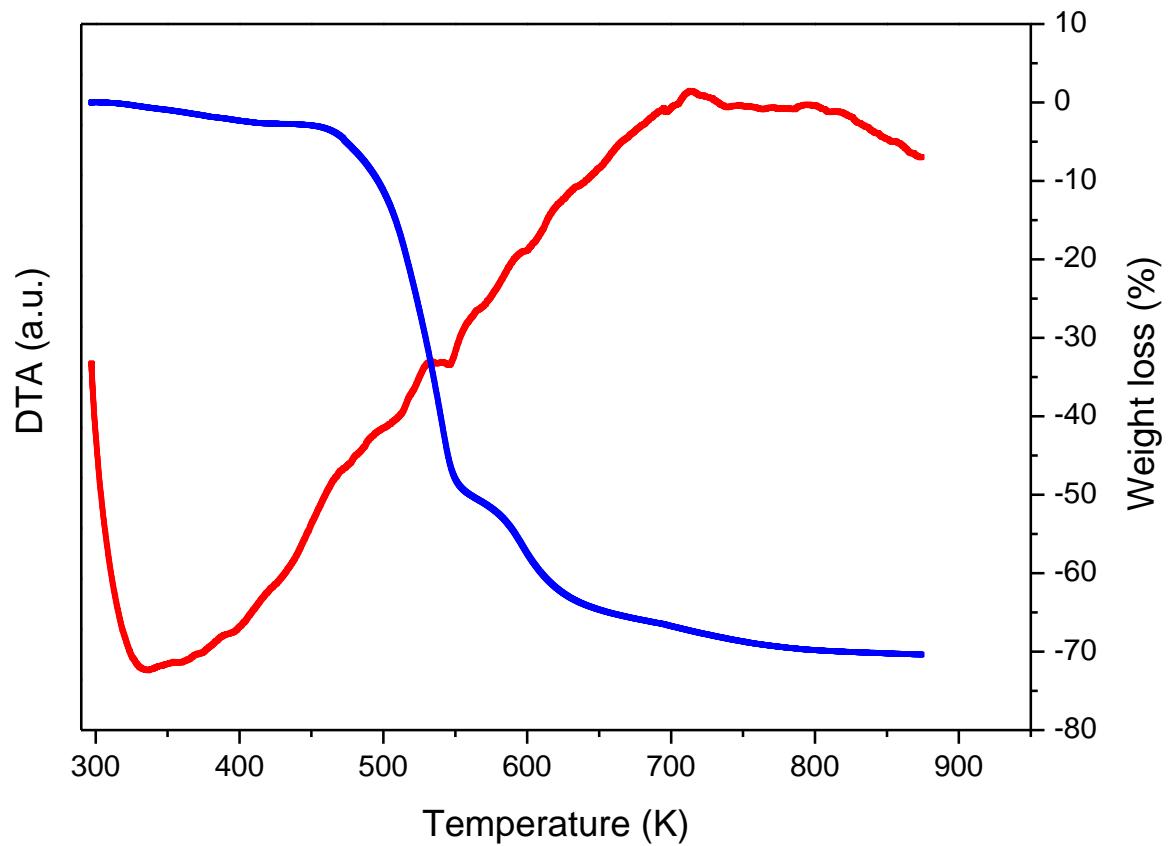
Figure S6. DTA (red) and DTG (blue) curves upon heating run for the $Cu^{II}_2(Tolf)_4(MeOH)_2]\cdot 2MeOH$ crystal.
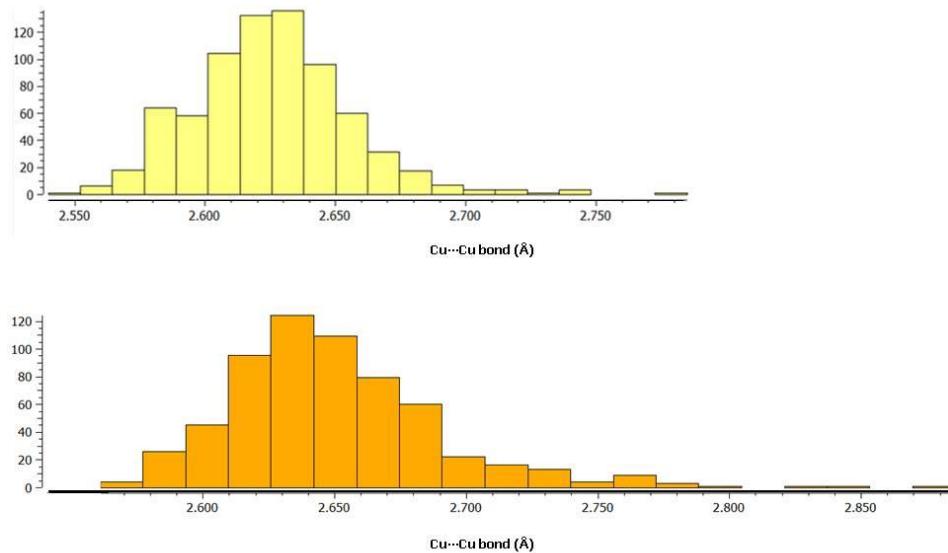
Figure S7. Histograms from CSD showing the tendency of Cu(II)···Cu(II) bond lengths (in the range of the sum of van der Waals radii) in paddle-wheel-like double-core Cu(II) compounds with carboxylate ligands. **Top**: yellow plot for structures with only O-donor ligands; **Down**: orange plot – for structures with N-donor ligands apart from carboxylates.

The adopted criterion for the distances Cu(II)···Cu(II): distances in the range of the sum of van der Waals radii, where the value of the van der Waals radius for Cu was determined by Bondi (Bondi, A. "van der Waals Volumes and Radii". *J. Phys. Chem.* **1964**, *68 (3)* 441–451. *doi*:*10.1021/j100785a001*.)