Supporting Information

Crystal Engineering Applied to Modulate the Structure and Magnetic Properties of Oxamate Complexes Containing the $[Cu(bpca)]^+$ Cation

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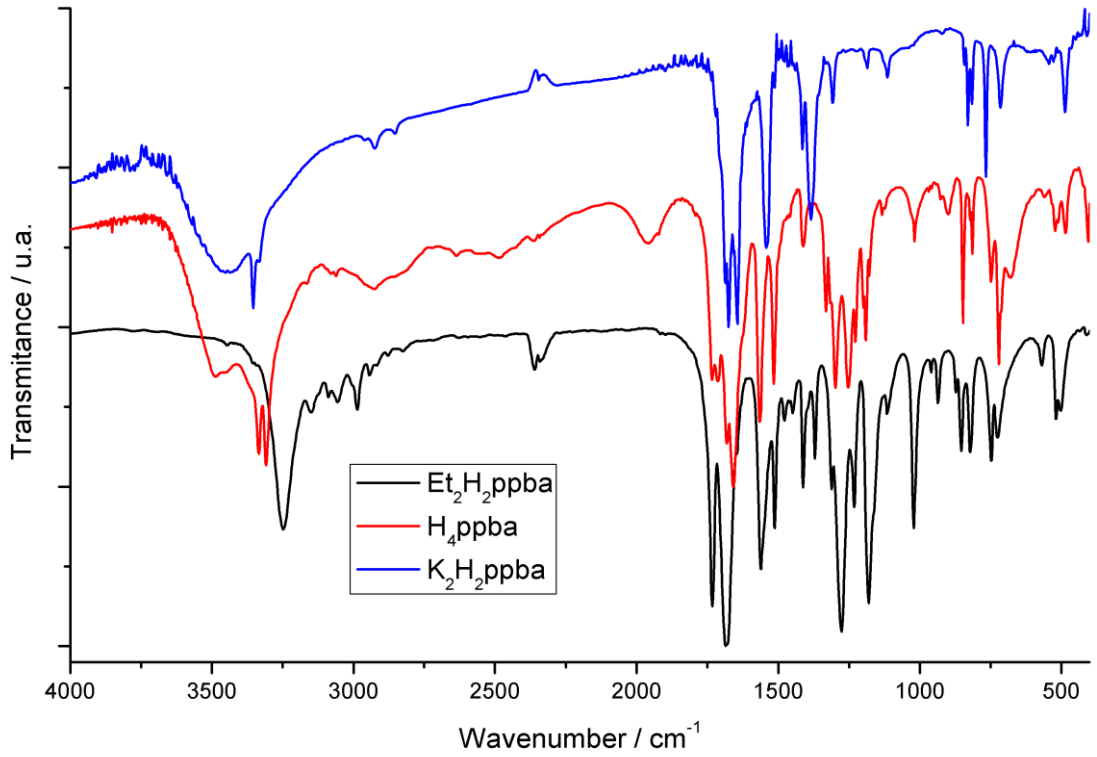


Figure S1. Infrared spectra for Et_2H_2ppba (–), H_4ppba (–) and K_2H_2ppba (–).

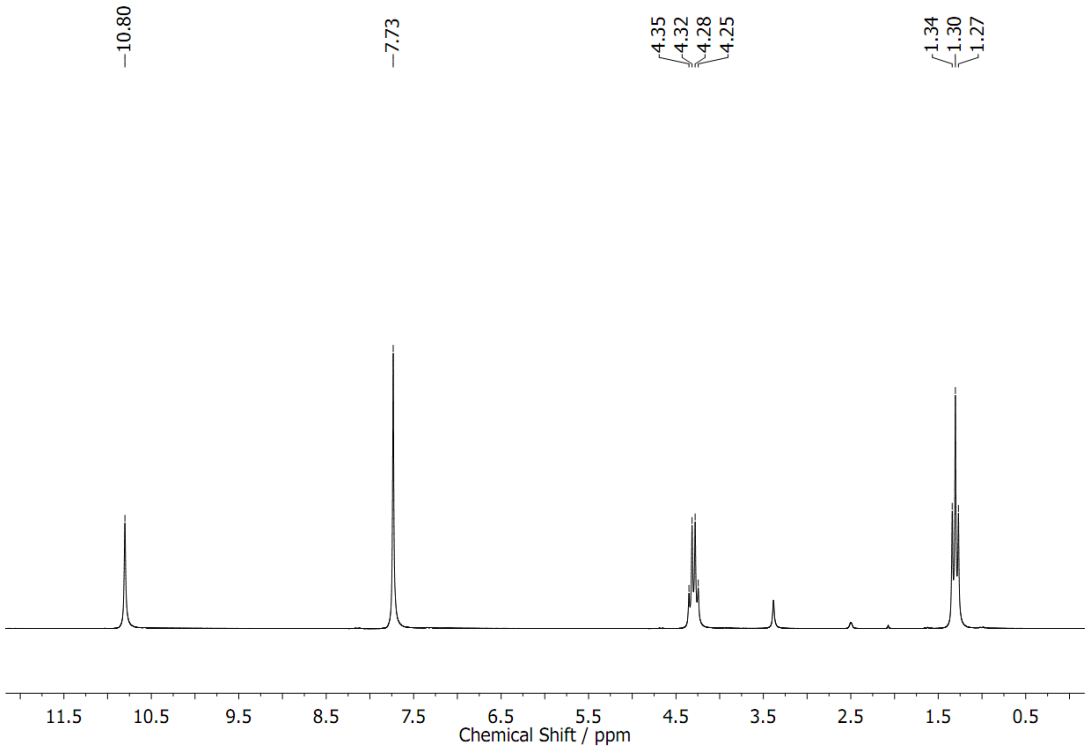


Figure S2. ^{1}H NMR spectrum for Et_2H_2ppba, in dmso-d_6, at 200 MHz.

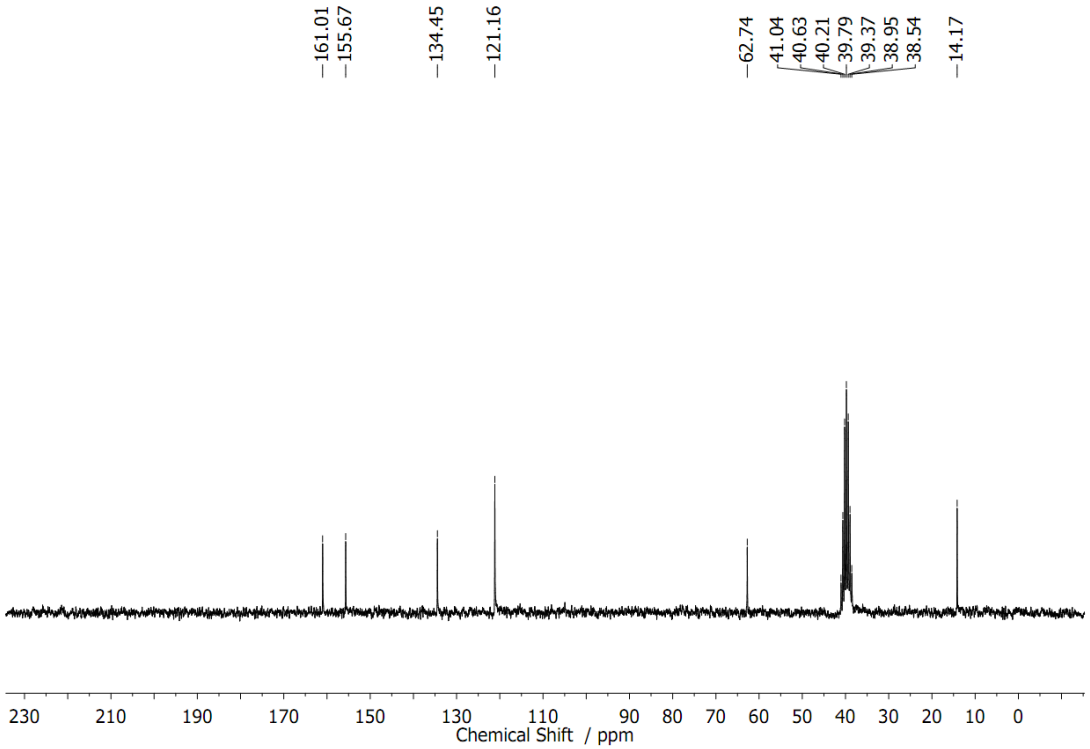


Figure S3. ^{13}C NMR spectrum for Et_2H_2ppba, in dmso-d_6, at 50 MHz.

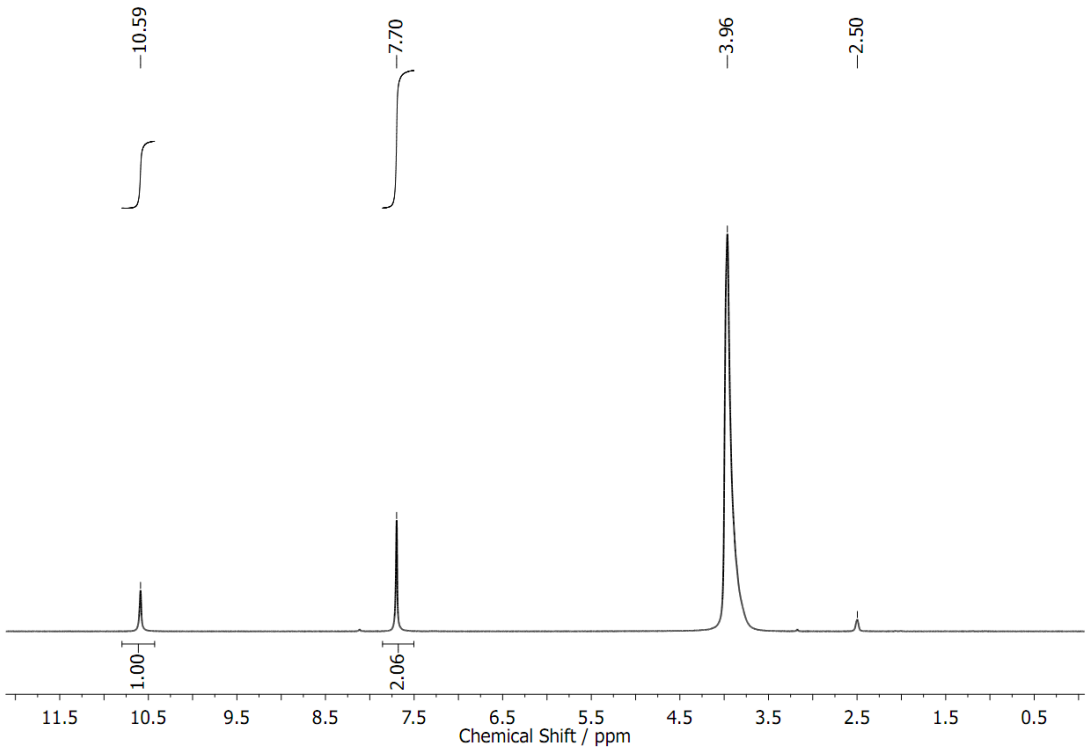


Figure S4. ^{1}H NMR spectrum for H_4ppba, in dmso-d_6/$CDCl_3$, at 200 MHz.

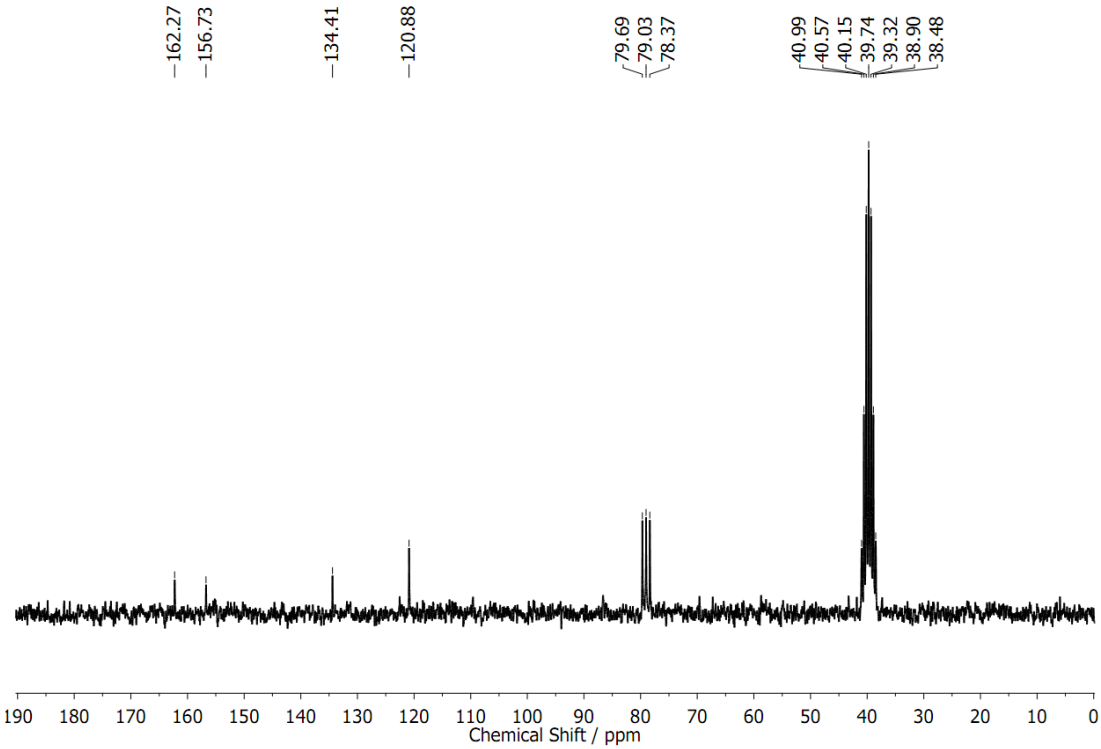


Figure S5. ^{13}C NMR spectrum for Et_2H_2ppba, in dmso-d_6/$CDCl_3$, at 50 MHz.

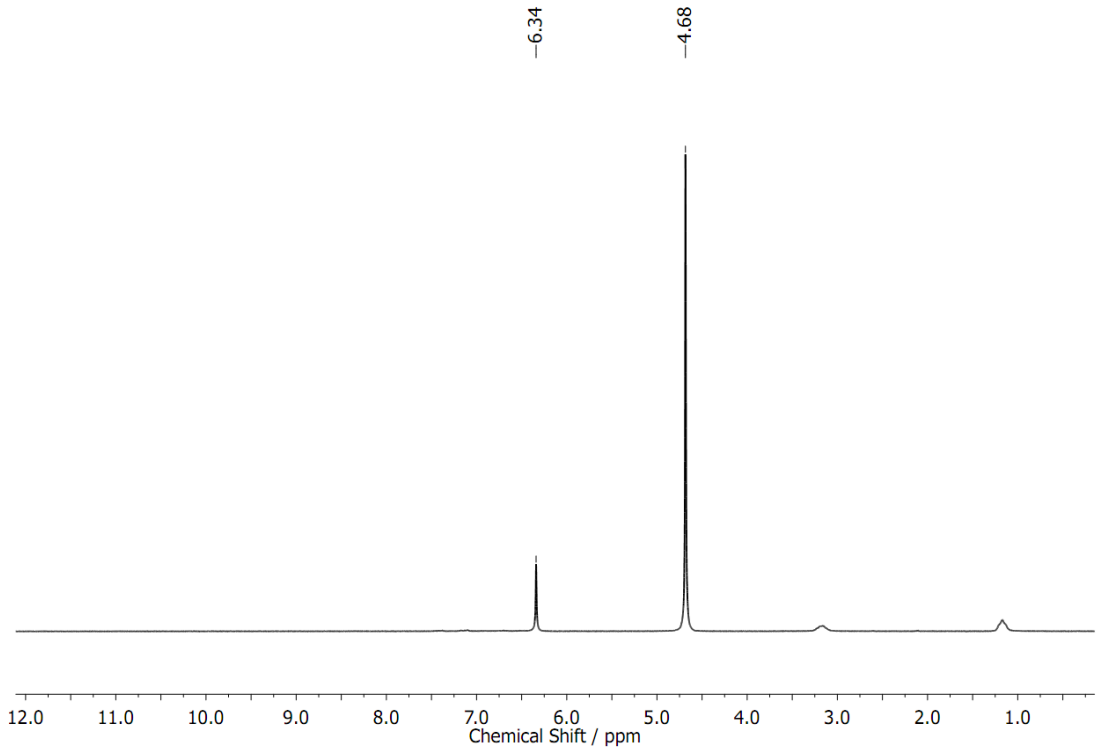


Figure S6. ^{1}H NMR spectrum for **1**, in D_2O, at 200 MHz.

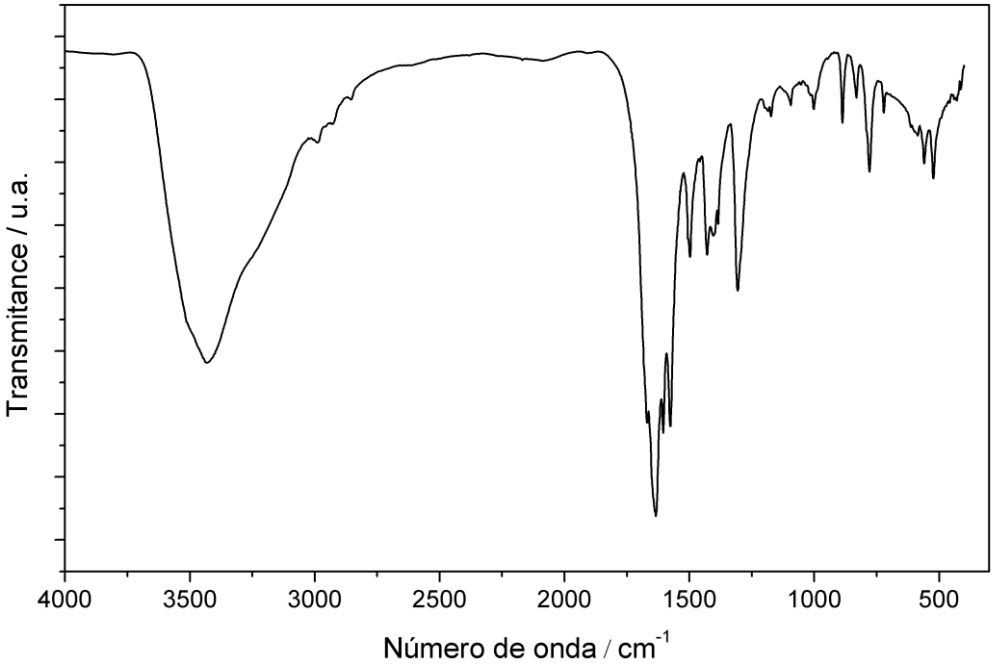


Figure S7. Infrared spectrum for **1**.

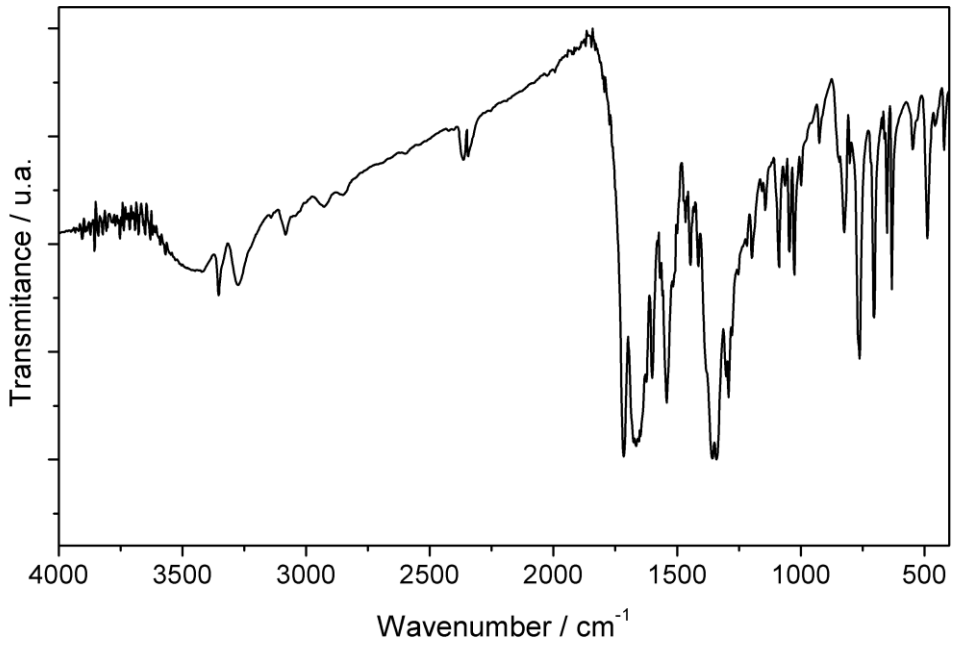


Figure S8. Infrared spectrum for **2**.

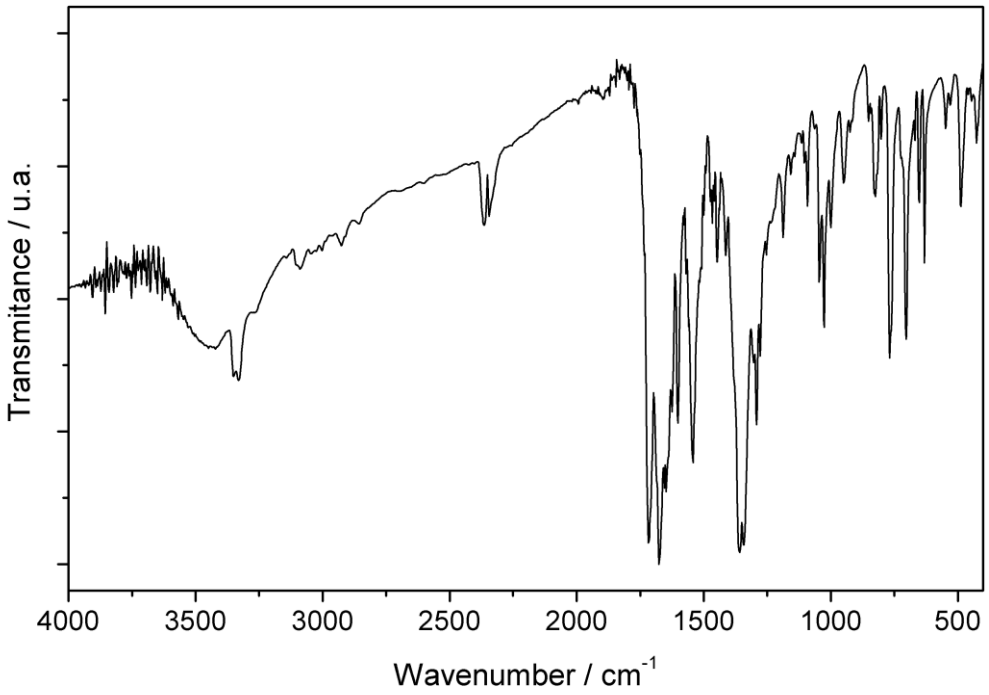


Figure S9. Infrared spectrum for **4**.

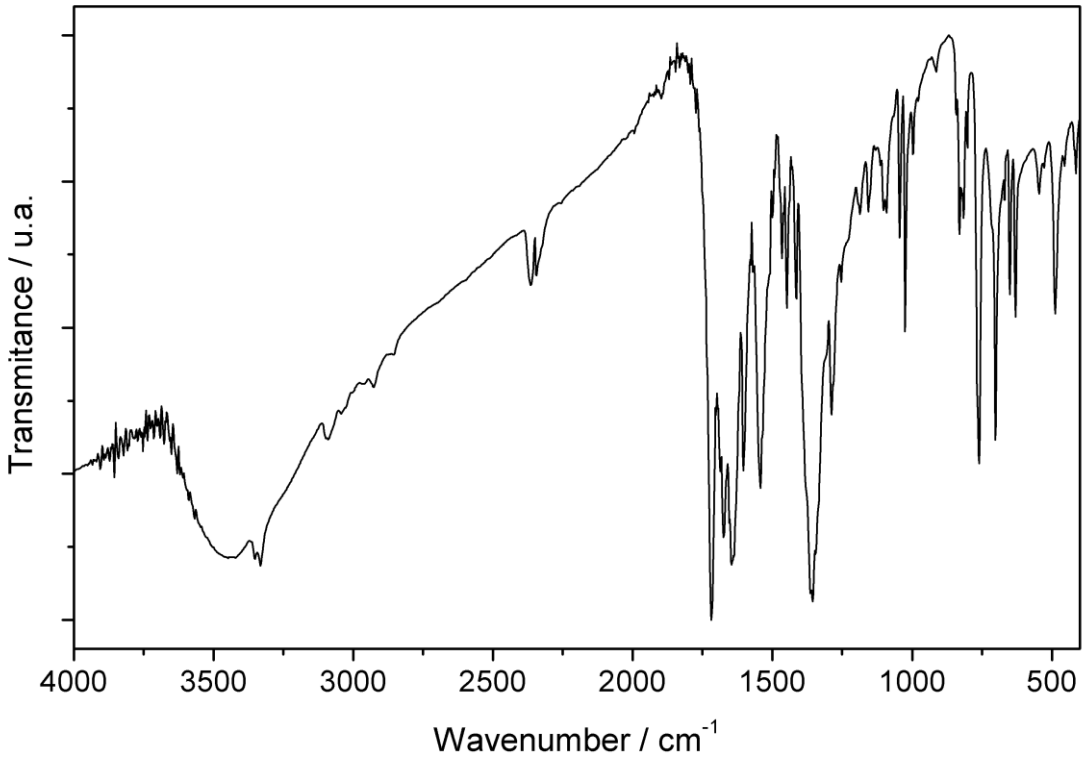


Figure S10. Infrared spectrum for **5**.

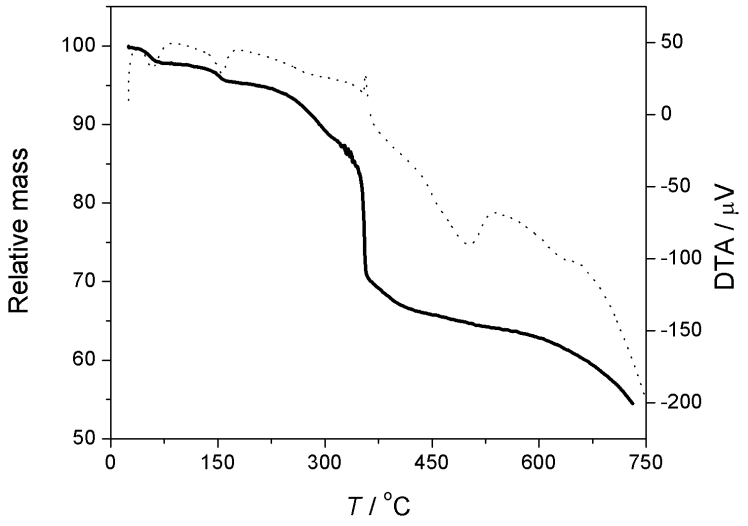


Figure S11. TG (–) and DTA (···) curves for **1**.

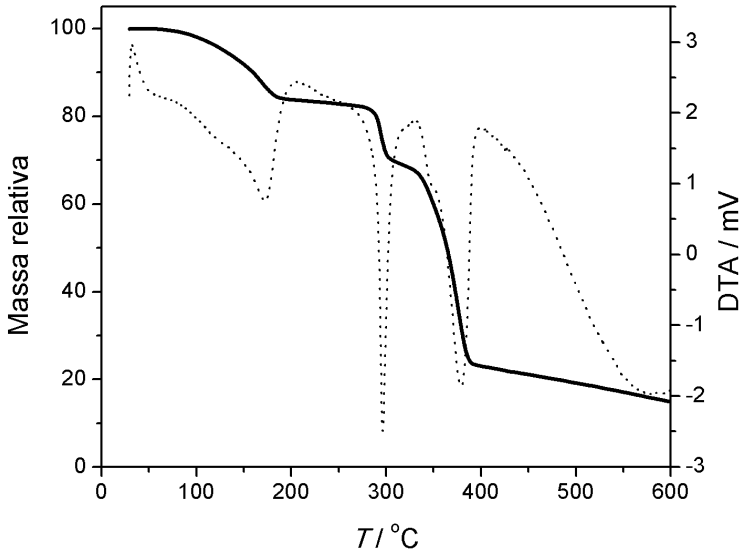


Figure S12. TG (–) and DTA (···) curves for **2**.

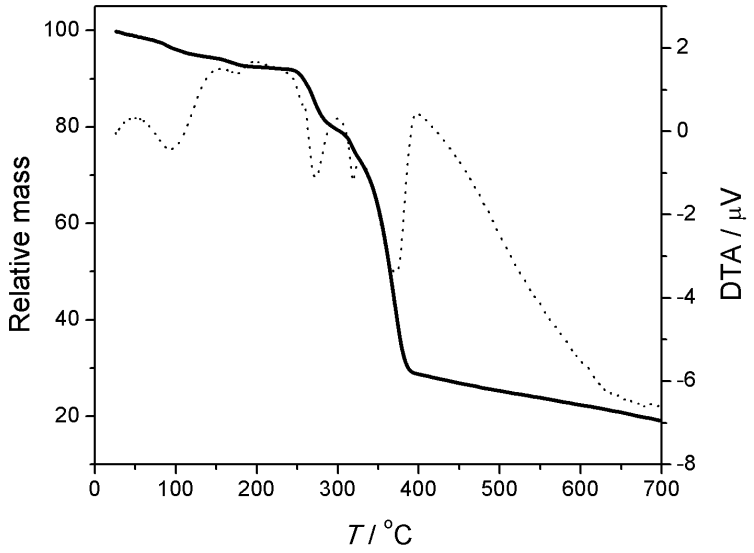


Figure S13. TG (–) and DTA (···) curves for **4**.

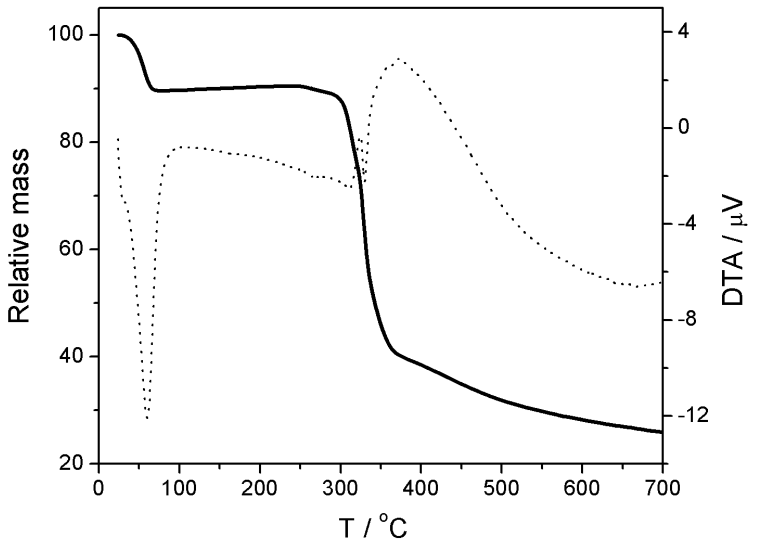


Figure S14. TG (–) and DTA (···) curves for **5**.

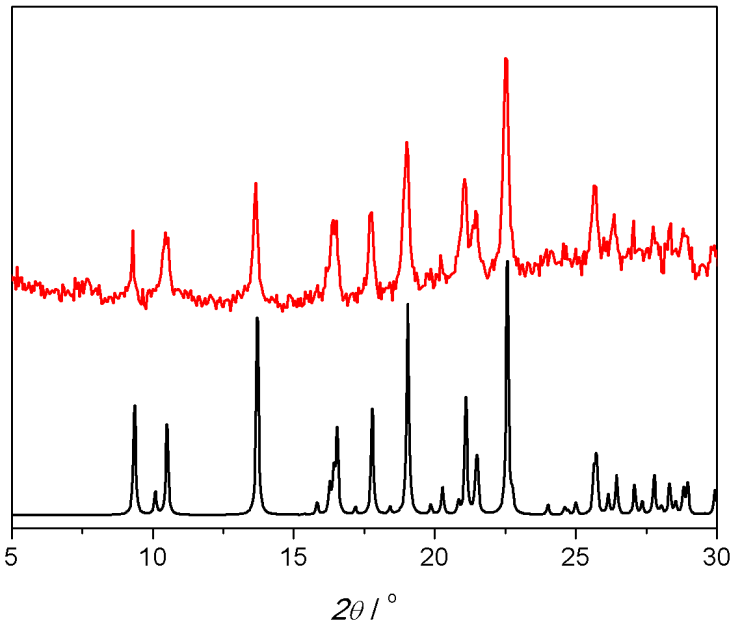


Figure S15. Comparison between the experimental (–) and calculated (–) X-ray patterns for **1**.

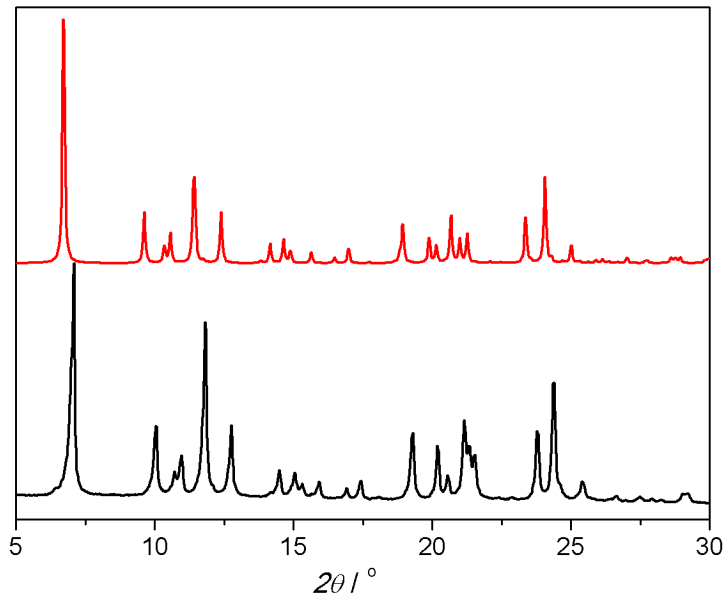


Figure S16. Comparison between the experimental (–) and calculated (–) X-ray patterns for **2**.

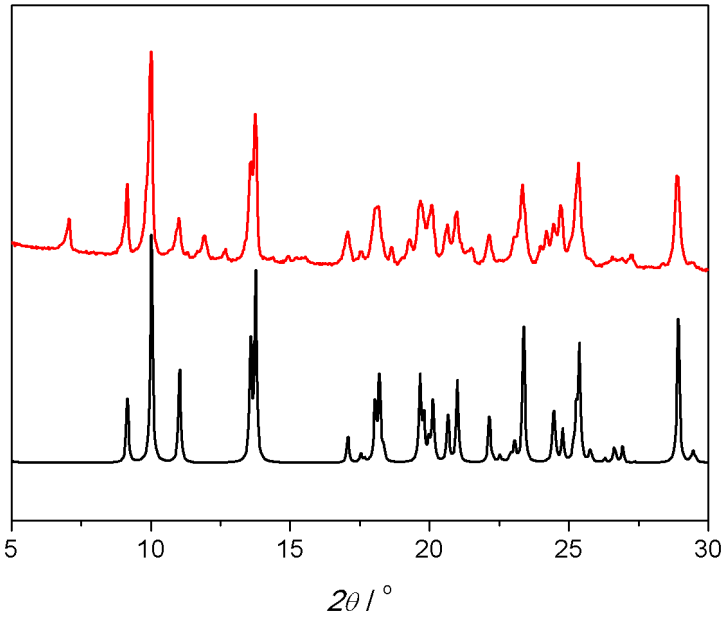


Figure S17. Comparison between the experimental (–) and calculated (–) X-ray patterns for **4**.

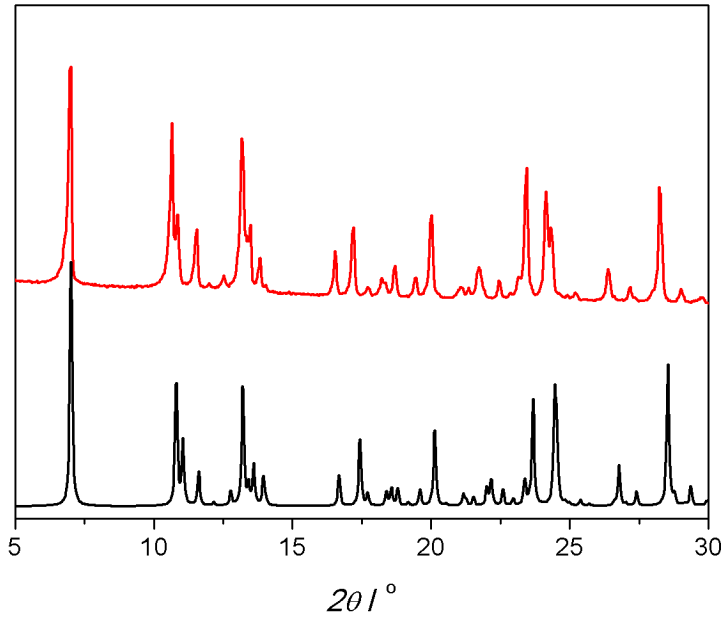


Figure S18. Comparison between the experimental (–) and calculated (–) X-ray patterns for **5**.

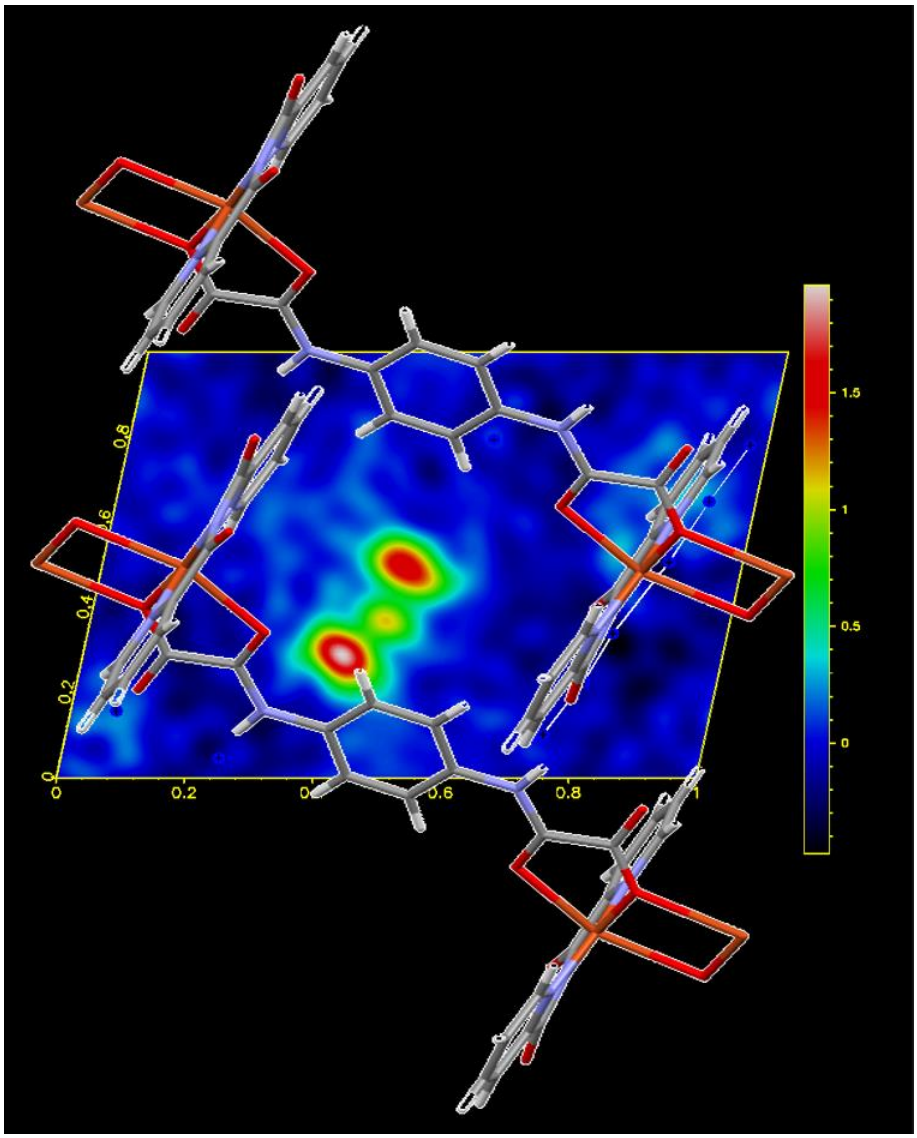


Figure S19. Cut-off of electronic density map of **2** parallel to *bc* plane at *a* = 0.5. The structure of the [{Cu(bpca)}$_2$(H$_2$ppba)] units present in the unit cell are overlaped for a better understanding of the residual eletron density.

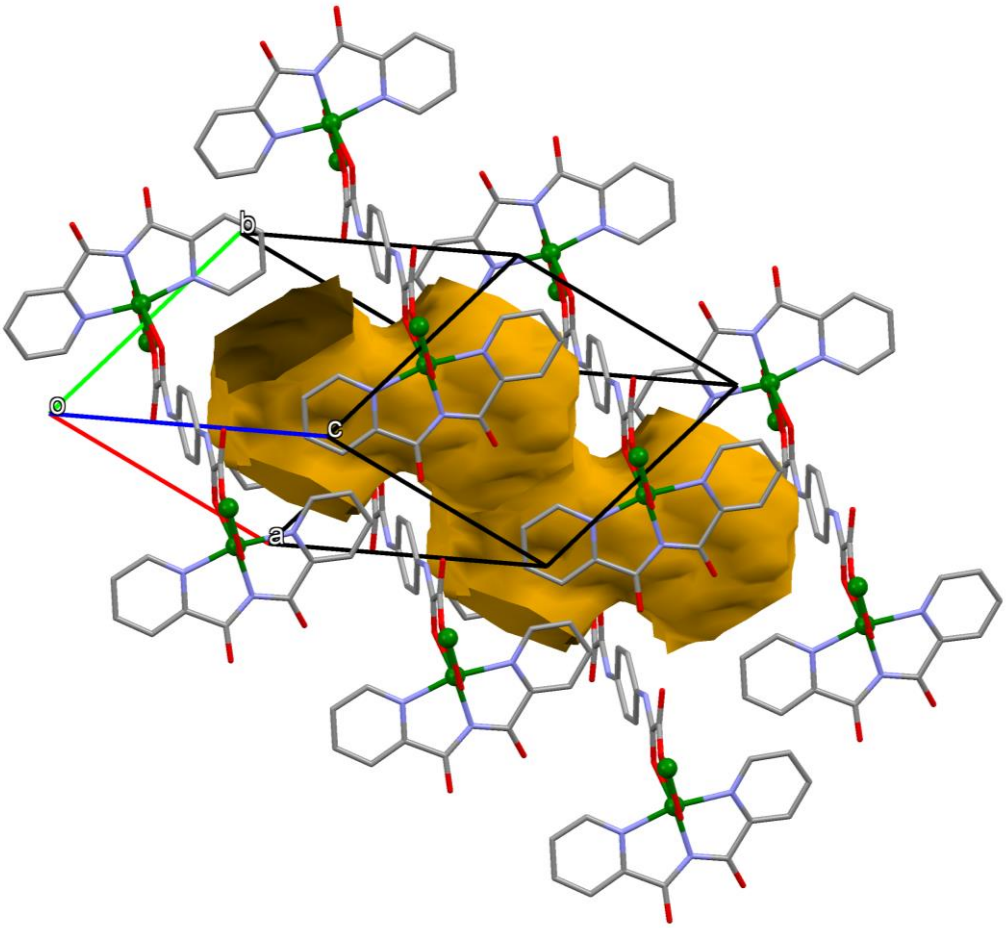


Figure S11. Void projection (golden surface) on structure of **2**, using two cell unit along crystallographic *a* axis, featuring the extended nature of the accessible voids in this structure.

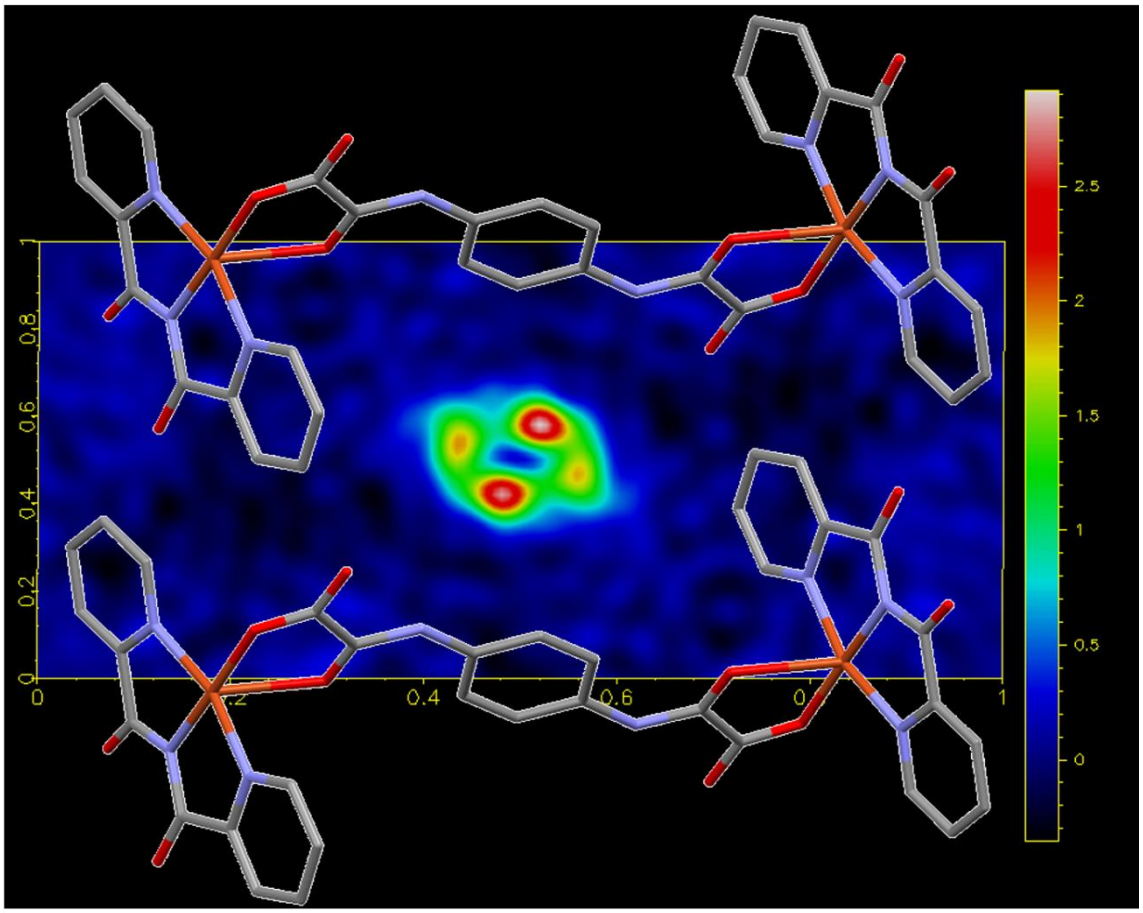


Figure S21. Cut-off of electronic density map of **4** parallel to *bc* plane at *a* = 0.5. The structure of the [{Cu(bpca)}$_2$(H$_2$ppba)] units present in the unit cell are overlapped for a better understanding of the residual electron density.

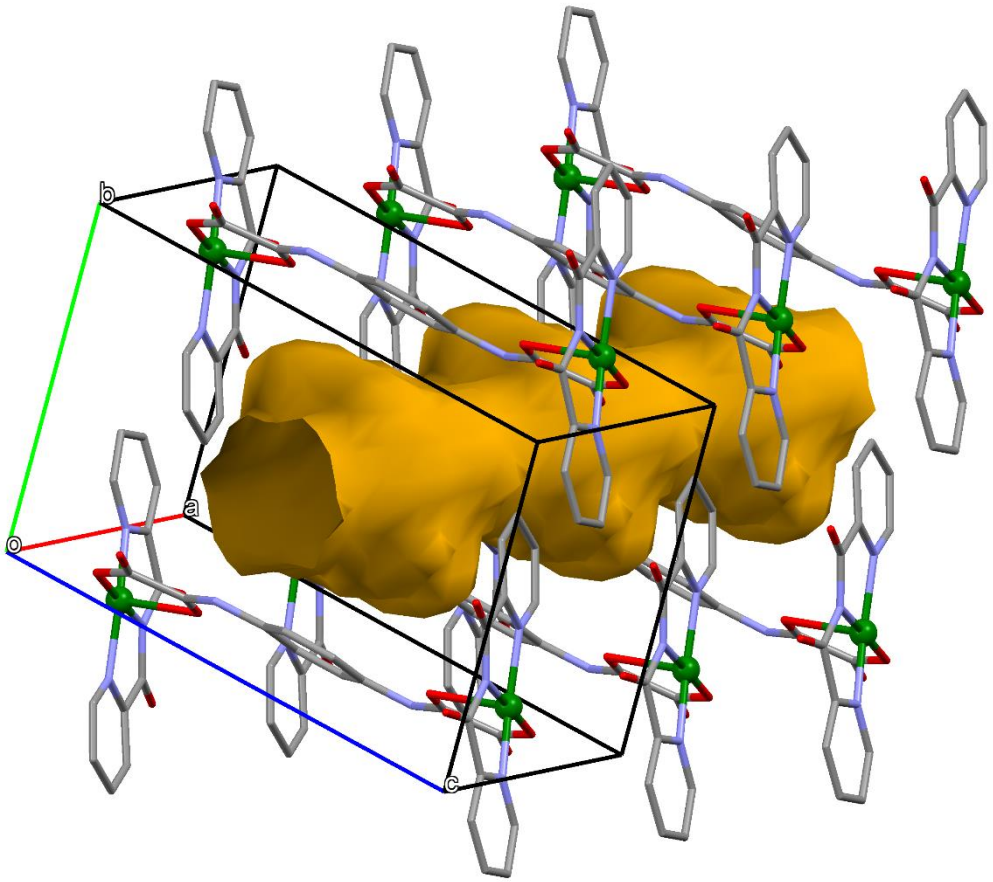


Figure S12. Void projection (golden surface) on structure of **4**, using three cell unit along crystallographic *a* axis, featuring the extended nature of the accessible voids in this structure.

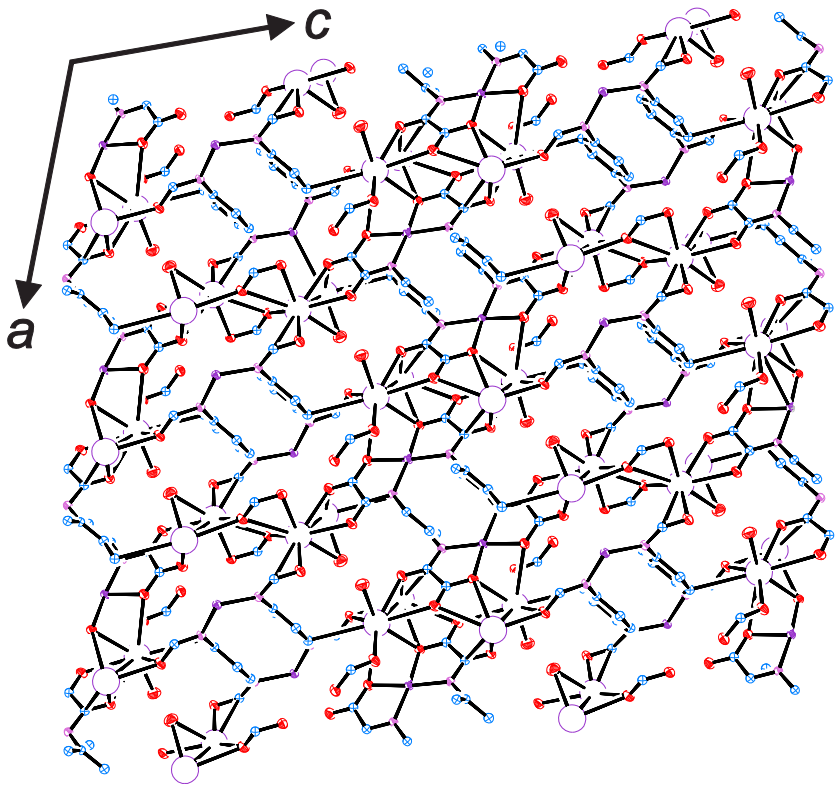


Figure S23. A view of the packing of **1** down crystallographic *b* axis. Color scheme follows the one in Figure 1. The potassium(I) atoms are drawn as purple circles for the sake of clarity.

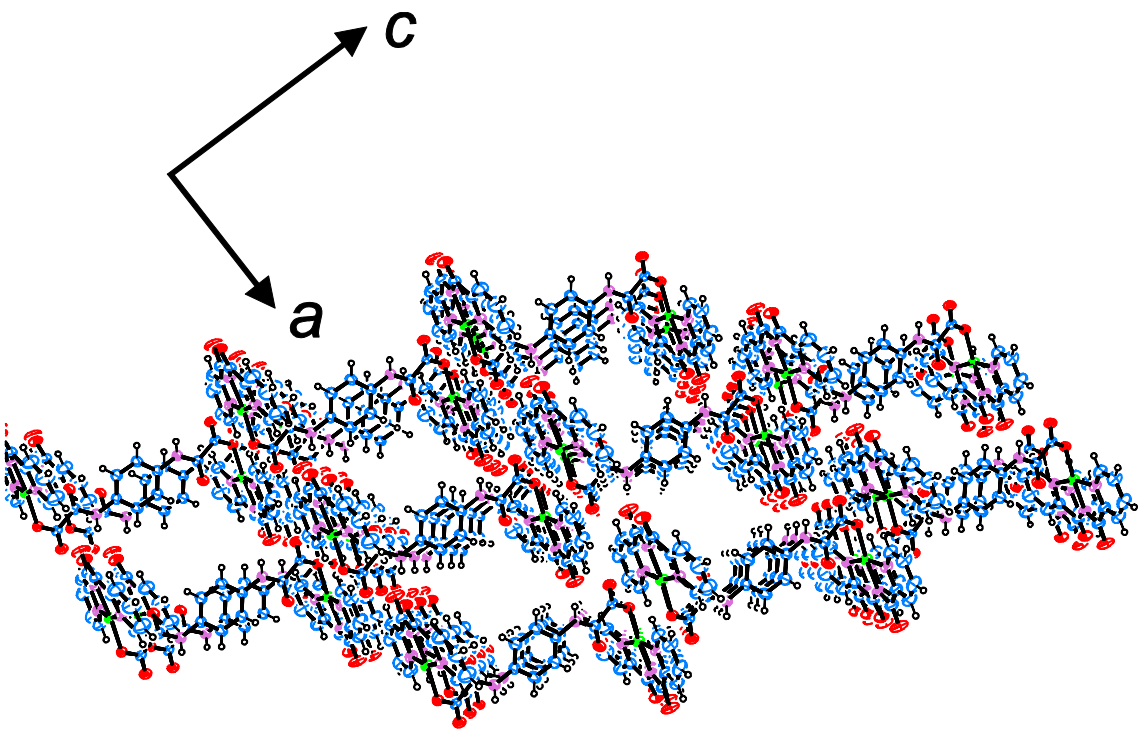


Figure S24. A view of the packing of **2** down crystallographic *b* axis. Color scheme follows the one in Figure 4 of the manuscript.

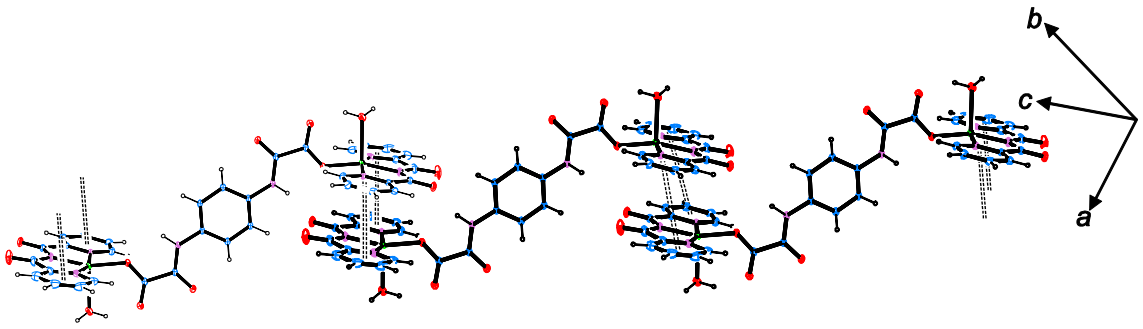
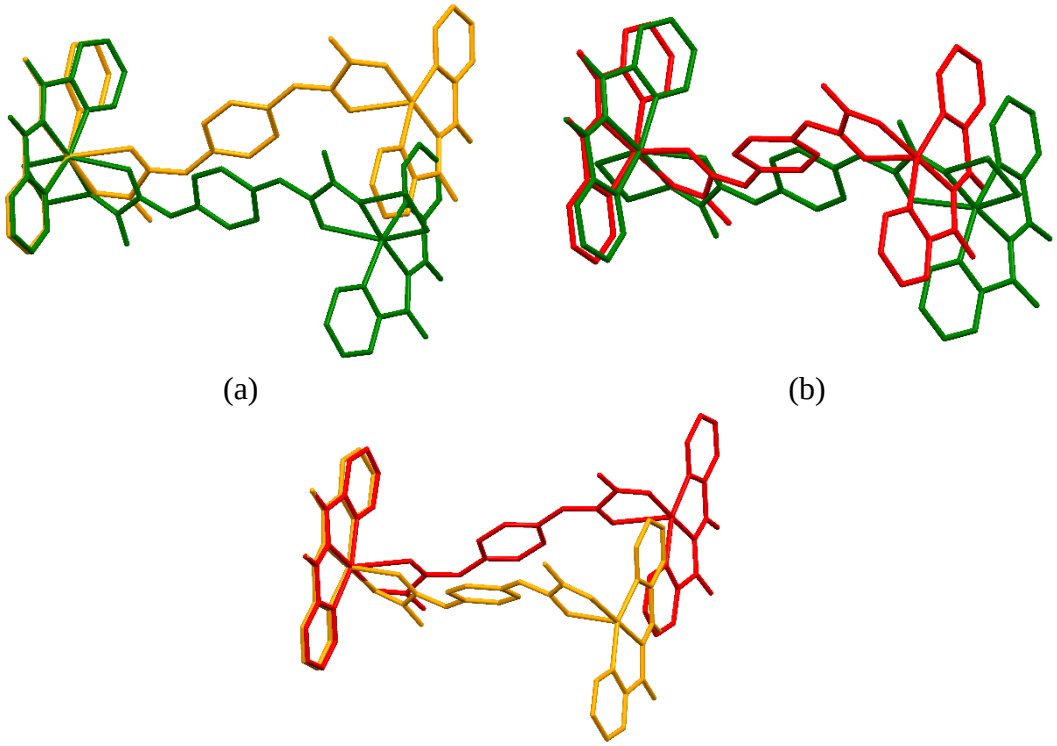


Figure S25. The supramolecular 3D network emphasizing the π-π stacking interactions in **3**.



(a) (b)

(c)

Figure S26 – Superimposition of crystal structure of **2** (in green), **4** (in yellow) and **5** (in red), using one [Cu(bpca)] moiety as anchor.

Table S1. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Pd1				K1				K2			
Bond length		Bond Angle		Bond length		Bond Angle		Bond length		Bond Angle	
Pd1–N2^{i}	2.010 (3)	N2^{i}–Pd1–N	105.70 (1	K1–O2^{ii}	2.709 (3	O2^{iii}–K1–O3^{iii}	60.56 (8	K2–O6^{i}	2.654 (3)	O6^{iv}–K2–O3^{vi}	77.54 (8)
Pd1–O1	2.014 (2)	O1–Pd1–N1	81.63 (11	K1–O3^{ii}	2.745 (3	O2^{iii}–K1–O6	134.05 (	K2–O3^{v}	2.696 (3)	O6^{iv}–K2–O2^{iii}	143.81 (9)
Pd1–N1	2.017 (3)	N2^{i}–Pd1–O4	81.36 (11	K1–O6	2.751 (3	O3^{iii}–K1–O6	75.13 (8	K2–O2^{i}	2.733 (3)	O3^{vi}–K2–O2^{iii}	138.63 (8)
Pd1–O4^{i}	2.040 (2)	O1–Pd1–O4	91.32 (10	K1–O7	2.813 (3	O2^{iii}–K1–O7	77.23 (1	K2–O7	2.776 (4)	O6^{iv}–K2–O7	82.14 (9)
				K1–O5^{iv}	2.842 (3	O3^{iii}–K1–O7	74.25 (9	K2–O4^{v}	2.880 (3)	O3^{vi}–K2–O7	119.17 (9)
				K1–O4^{v}	3.050 (3	O6–K1–O7	103.16 (	K2–O5^{i}	2.931 (3)	O2^{iii}–K2–O7	77.48 (9)
				K1–O5^{v}	3.073 (3	O2^{iii}–K1–O5^{iv}	89.60 (8	K2–O1^{v}	3.172 (3)	O6^{iv}–K2–O4^{vii}	79.77 (8)
						O3^{iii}–K1–O5^{iv}	143.78 (			O3^{vi}–K2–O4^{vii}	80.70 (8)
						O6–K1–O5^{iv}	136.18 (			O2^{iii}–K2–O4^{vii}	103.59 (8)
						O7–K1–O5^{iv}	79.71 (9			O7–K2–O4^{vii}	149.28 (9)
						O2^{iii}–K1–O4^{v}	83.05 (8			O6^{iv}–K2–O5^{iv}	59.34 (8)
						O3^{iii}–K1–O4^{v}	76.94 (8			O3^{vi}–K2–O5^{iv}	131.14 (8)
						O6–K1–O4^{v}	75.33 (7			O2^{iii}–K2–O5^{iv}	87.33 (8)
						O7–K1–O4^{v}	150.45 (			O7–K2–O5^{iv}	78.80 (9)
						O5^{iv}–K1–O4^{v}	122.28 (			O4^{vii}–K2–O5^{iv}	70.64 (7)
						O2^{iii}–K1–O5^{v}	113.09 (			O6^{iv}–K2–O1^{viii}	128.98 (8)
						O3^{iii}–K1–O5^{v}	117.46 (			O3^{vi}–K2–O1^{viii}	70.45 (7)
						O6–K1–O5^{v}	75.86 (7			O2^{iii}–K2–O1^{viii}	77.72 (8)
						O7–K1–O5^{v}	166.88 (			O7–K2–O1^{viii}	148.42 (9)

$O5^{iv}$–K1–$O5^{v}$	91.94 (7	$O4^{vii}$–K2–$O1^{viii}$	57.00 (7)
$O4^{v}$–K1–$O5^{v}$	42.45 (6	$O5^{iv}$–K2–$O1^{viii}$	119.13 (7)

[a]Symmetry code: (*i*) = –*x*+1, –*y*+1, –*z*+1; (*ii*) = *x*–1, *y*, *z*; (*iii*) = –*x*+3/2, *y*+1/2, –*z*+1/2; (*iv*) = *x*, *y*–1, *z*; (*v*)= –*x*+2, –*y*+2, –*z*+1; (*vi*) = –*x*+3/2, *y*–1/2, –*z*+1/2; (*vii*) = –*x*+2, –*y*+1, –*z*+1; (*viii*) = *x*+1, *y*, *z*; (*ix*) = *x*, *y*+1, *z*.

Table S2. Selected Bond Lengths (Å) and Angles (deg) for **2** and **3**[a]

2				**3**			
Bond length		Bond Angle		Bond length		Bond Angle	
Cu1–N2	2.023 (2)	N2–Cu1–O2^{i}	97.26 (7)	Cu1–N2	2.001 (2)	N2–Cu1–O6	94.98 (7)
Cu1–N3	1.939 (2)	N2–Cu1–O3	90.68 (8)	Cu1–N3	1.9320 (18)	N3–Cu1–N2	82.58 (9)
Cu1–N4	2.007 (2)	N3–Cu1–N2	81.71 (9)	Cu1–N4	1.9991 (19)	N3–Cu1–N4	82.03 (8)
Cu1–O2	1.9813 (16)	N3–Cu1–N4	82.17 (9)	Cu1–O1	1.9355 (15)	N3–Cu1–O1	162.77 (7)
Cu1–O2^{i}	2.5421 (16)	N3–Cu1–O2	174.66 (8)	Cu1–O6	2.3519 (19)	N3–Cu1–O6	101.20 (7)
		N3–Cu1–O2^{i}	102.77 (7)			N4–Cu1–N2	163.82 (8)
		N3–Cu1–O3	110.07 (8)			N4–Cu1–O6	92.90 (7)
		N4–Cu1–N2	163.39 (9)			O1–Cu1–N2	99.51 (8)
		N4–Cu1–O2^{i}	90.19 (7)			O1–Cu1–N4	93.74 (7)
		N4–Cu1–O3	91.09 (8)			O1–Cu1–O6	95.67 (7)
		O2–Cu1–N2	96.40 (8)				
		O2–Cu1–N4	100.01 (8)				
		O2–Cu1–O2^{i}	72.44 (7)				
		O2–Cu1–O3	74.87 (6)				
		O3–Cu1–O2^{i}	147.00 (6)				

[a]Symmetry code: (i) = –*x*+2, –*y*+1, –*z*.

Table S3. Selected Bond lengths (Å) and Angles (deg) for **4** and **5**

4				**5**			
Bond length		Bond Angle		Bond length		Bond Angle	
Cu1–O1	2.394 (2)	N2–Cu1–O1	83.24 (10)	Cu1–N2	2.009 (4)	N2–Cu1–O3	91.30 (15)
Cu1–O3	1.952 (2)	N3–Cu1–N4	82.45 (11)	Cu1–N3	1.943 (4)	N3–Cu1–N2	82.13 (18)
Cu1–N2	2.010 (3)	N3–Cu1–N4	82.45 (11)	Cu1–N4	1.995 (4)	N3–Cu1–N4	81.58 (18)
Cu1–N3	1.927 (3)	N3–Cu1–O3	178.20 (11)	Cu1–O2	1.959 (3)	N3–Cu1–O2	177.72 (15)
Cu1–N4	1.989 (3)	N3–Cu1–O1	102.73 (10)	Cu1–O3	2.242 (4)	N3–Cu1–O3	98.57 (16)
		N4–Cu1–N2	163.05 (12)			N4–Cu1–N2	160.36 (18)
		N4–Cu1–O1	107.78 (10)			N4–Cu1–O3	101.90 (16)
		O3–Cu1–N2	99.24 (11)			O2–Cu1–N2	96.65 (17)
		O3–Cu1–N4	95.80 (11)			O2–Cu1–N4	99.98 (17)
		O3–Cu1–O1	77.41 (9)			O2–Cu1–O3	79.51 (14)