Electronic Supplementary Information (ESI)

Copper(II) hydrazone complexes with different nuclearities and geometries: synthetic methods and ligand substituent effects

Višnja Vrdoljak*, Gordana Pavlović, Nadica Maltar-Strmečki, and Marina Cindrić

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Powder X-ray diffraction patterns

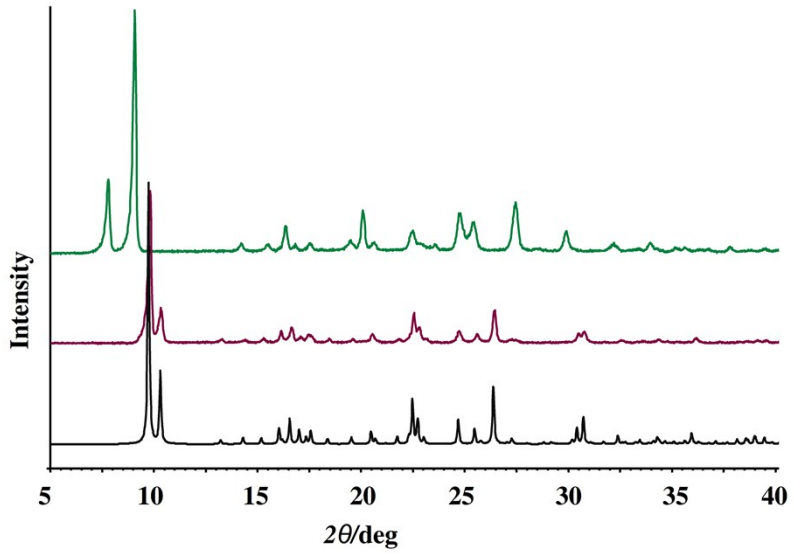


Fig. S1 PXRD patterns of: **1α** obtained upon reaction in methanol at room temperature (top); **1β** obtained upon thermally induced transformation in the solid state (middle); and **1β** calculated from the X-ray single-crystal structure (bottom).

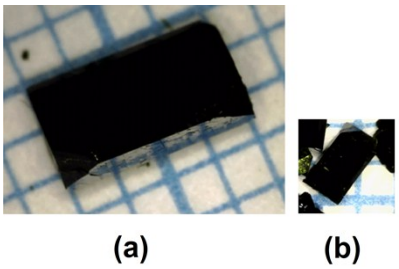


Fig. S2 Photos of single crystals of **2MeOH** synthesized by (a) the solvothermal synthesis , (b) the conventional solution-based method at reflux temperature.

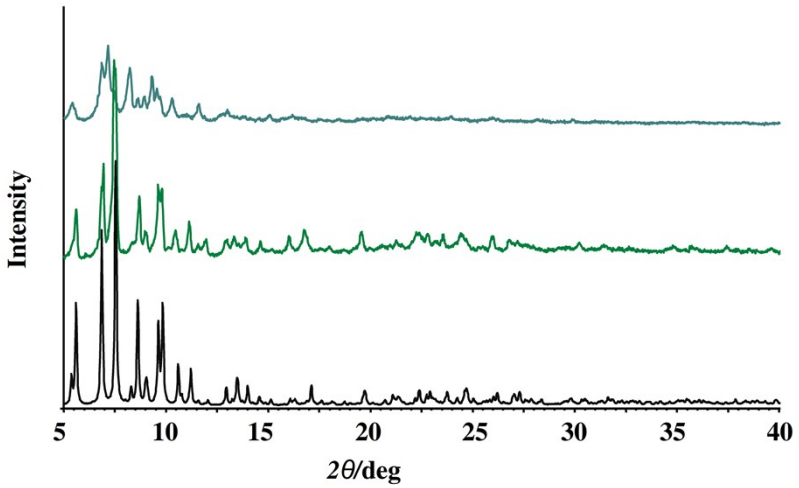


Fig. S3 PXRD patterns of sample obtained upon standing of **2MeOH** at room temperature for 12 h (top); sample obtained upon standing of **2MeOH** at room temperature for 5 min (middle); and PXRD pattern of **2MeOH** calculated from the X-ray single-crystal structure (bottom).

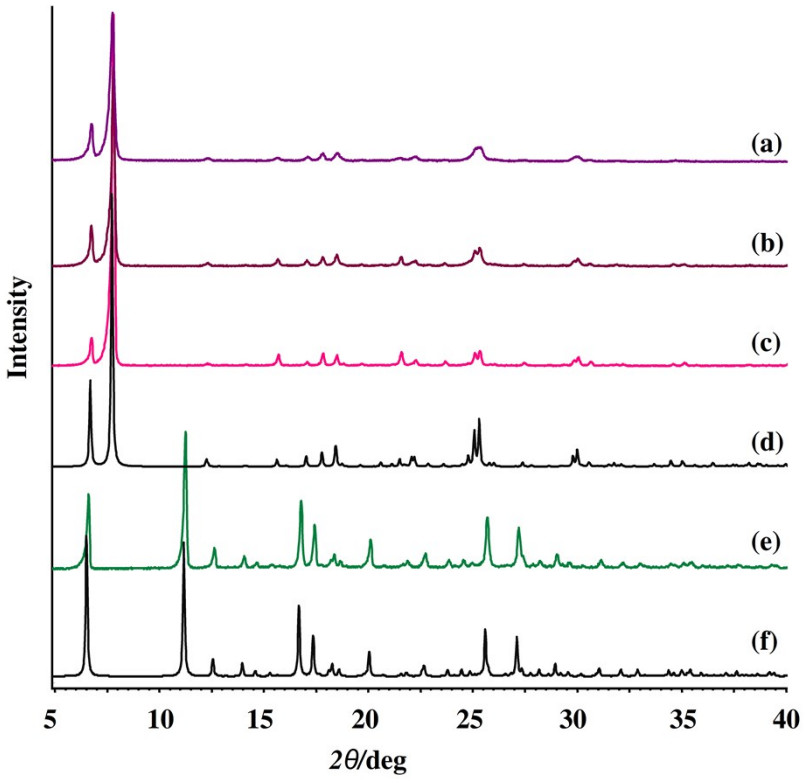


Fig. S4 PXRD patterns of (a) **3** obtained by the solid state thermally induced synthesis, (b) **3** obtained by the solvothermal method in MeOH and (c) **3** obtained by the conventional solution-based method in EtOH; (e) PXRD patterns of **3MeOH** obtained by the electrochemical synthesis in MeOH. The black lines (d) and (f) indicate patterns of **3** and **3MeOH**, respectively, calculated from the X-ray single-crystal structures.

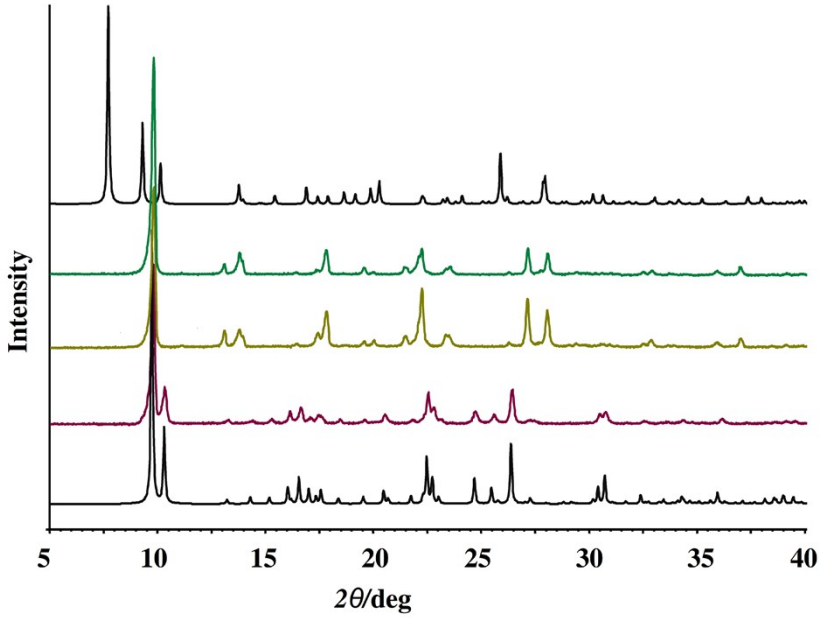


Fig. S5 PXRD patterns (form top to bottom) for: the polinuclear complex **1py*** calculated from the X-ray single-crystal structure; the dinuclear complex **1py** obtained by the conventional solution-based method; **1py** obtained upon an exposure of **1β** to pyridine vapours; the dinuclear complex **1β** obtained by the solid state thermally induced synthesis form **1py**; and **1β** calculated from the X-ray single-crystal structure.

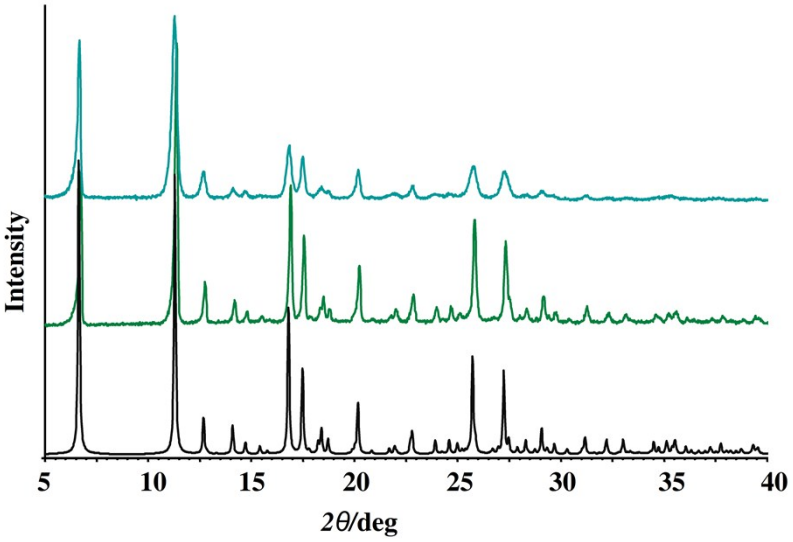


Fig. S6 PXRD patterns of: **3MeOH** obtained upon an exposure of the unsolvated complex $[Cu_2(L^{4OMe})_2]$ to methanol vapours (top); **3MeOH** obtained by the electrochemical synthesis in MeOH (middle); and **3MeOH** calculated from the X-ray single-crystal structure (bottom).

X-Ray Crystallography. Single crystal diffraction.

Table S1. Selected bond lengths [Å] and angles [°] for complexes: **1β**, **1py***, **2py**, **3** and **3MeOH**

Complex	**1β**	**1py***	**2py**	**3**	**3MeOH**
Bond length					
Cu1–N1	1.9140 (18)	1.928 (3)	1.921 (3)	1.905(2)	1.9127 (16)
Cu1–O1	1.9226 (16)	1.943 (3)	1.927 (3)	1.918(2)	1.9469 (14)
Cu1–O2	1.9376 (16)	1.905 (3)	1.883 (3)	1.944(2)	1.9574 (13)
Cu1–N3		2.011 (3)	2.001 (3)		
Cu1–O2^{i}	1.9540 (15)	2.870(4)		1.968(2)	1.9724 (13)
Cu1–O5					2.501(2)
Cu1···Cu1^{i}	2.9827 (11)			3.0052 (7)	3.0316 (5)
N1–C8	1.284 (3)	1.279 (5)	1.293 (5)	1.275(4)	1.281 (2)
N1–N2	1.404 (2)	1.397 (4)	1.401 (4)	1.397(3)	1.395 (2)
N2–C1	1.327 (3)	1.320 (5)	1.322 (5)	1.306(4)	1.314 (2)
O1–C1	1.294 (2)	1.284 (4)	1.299 (4)	1.297(3)	1.296 (2)
O2–C10	1.362 (2)	1.316 (5)	1.305 (5)	1.352(3)	1.350 (2)
Bond angles					
N1–Cu1–O1	81.50 (7)	80.83 (11)	81.17 (13)	81.54(9)	81.37 (6)
N1–Cu1–O2	92.95 (7)	92.13 (12)	93.06 (13)	93.96(9)	93.10 (6)
O1–Cu1–O2	170.49 (6)	170.61 (13)	174.19 (12)	175.49(8)	173.81 (6)
N1–Cu1–O2^{i}	172.33 (7)	91.21(12)		172.66(9)	168.11 (6)
O1–Cu1–O2^{i}	105.94 (6)	87.08(12)		104.85(8)	105.98 (5)
O2–Cu1–O2^{i}	79.93 (7)	99.35(12)		79.62(8)	79.03 (6)
O2–Cu1–N3		93.70 (13)	92.38 (14)		
N1–Cu1–N3		173.86 (12)	174.39 (16)		
O1–Cu1–N3		93.16 (12)	93.41 (13)		
N1–Cu1–Cu1^{i}	133.06 (6)			133.97 (8)	132.19 (5)
O1–Cu1–Cu1^{i}	145.14 (5)			144.36 (6)	145.18 (4)
O2–Cu1–Cu1^{i}	40.17 (4)			40.11 (5)	39.70 (4)
O2^{i}–Cu1–Cu1^{i}	39.76 (5)			39.52 (5)	39.33 (4)

Symmetry code: (i) −*x*+1, −*y*, −*z*+2 for **1β**, x,−y, −1/2+z for **1py***, i= –x+1, –y, –z for 3, i= –x+1, –y, –z+1 for **3MeOH**.

Table S2. Dihedral angles (°) and atoms defining planes in complexes **1β**, **1py***, **2py**, **3** and **3MeOH**

Complex	Dihedral angle, ∠/° C1, C2, C3, C4 C5, C6, C7 and C9, C10, C11, C12, C13 and C14	Dihedral angle, ∠/° O1,C1,N2,N1 and N1,C8,C9,C10, O2
1β	9.29(12)	3.32(2)
1py*	7.48(21)	16.31(21)
2py	4.79(20)	7.58(26)
3	25.77(12)	2.36(2)
3MeOH	27.59(8)	2.01(1)

Table S3. Hydrogen bonds and interactions for complexes: **1β**, **1py***, **2py**, **3**, **3MeOH**, **2EtOH**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)	Symmetry code
1β					
O3–H3O···N1	0.81 (1)	2.75(2)	3.450(4)	151(2)	x+1/2, −y+1/2,+z+1/2
O3–H3O···N2	0.81 (1)	1.95 (1)	2.758 (2)	179 (3)	*x*+1/2, −*y*+1/2, *z*+1/2
C7–H7···O3	0.93	2.82	3.472(3)	128	x−1/2, −y+1/2,+z−1/2
C8–H8···O3	0.93	2.93	3.469(3)	118	x-1/2,-y+1/2,+z-1/2
C11–H11···O1	0.93	2.21	3.031 (3)	147	−*x*+1, −*y*, −*z*+2
C4–H4···N1	0.93	2.91	3.619(3)	135	x+1/2,-y+1/2,+z+1/2
C4–H4···N2	0.93	2.78	3.434(3)	128	x+1/2,-y+1/2,+z+1/2
C13–H13···O3	0.93	2.57	3.316(3)	137	−x+1/2+2,+y−1/2, −z+3/2
1py*					
O3–H3O···N1	0.80(4)	2.76(4)	3.450(4)	146(3)	−x+1/2, −y−1/2,+z−1/2
O3–H3O···N2	0.80(4)	1.93(4)	2.725(4)	172(3)	1/2−x, −1/2−y, −1/2+z
C8–H8···O3	0.93	2.76	3.368(4)	124	−x+1/2, −y−1/2,+z+1/2
C16–H16···O3	0.93	2.97	3.594(5)	126	−x+1/2, −y+1/2,+z+1/2
C16–H16···O3	0.93	2.91	3.488(6)	121	−x+1/2,+y+1/2,+z
C15–H15···O1	0.93	2.33	2.910(5)	120	-
C6–H6···N2	0.93	2.96	3.579(4)	126	−x+1/2, −y−1/2,+z−1/2
2py					
O3–H3O···N1	0.78(5)	2.90(5)	3.617(5)	155(4)	−x+1/2+1,+y+1/2, −z+5/2
O3–H13O···N2	0.78(5)	2.02(5)	2.800(5)	178(5)	−x+1/2+1,+y+1/2, −z+5/2
C3–H3···O3	0.93	2.58	3.475(5)	162	−x+1/2+1,+y−1/2, −z+5/2
C4–H4···O4	0.93	2.94	3.750(5)	146	x−1/2, −y+1/2,+z+1/2
C4–H4···N2	0.93	2.75(1)	3.417(6)	130(1)	−x+1/2+1,+y+1/2, −z+5/2
C8–H8···O3	0.93	2.77	3.493(6)	136	−x+1/2+1,+y−1/2, −z+5/2
C16–H16···O1	0.93	2.33	2.908(5)	120	-
C20–H20···O2	0.93	2.33	2.882(5)	118	-
3					
O3–H3O···N1	0.80(3)	2.96(3)	3.618(3)	141(2)	−x+1/2+1, −y+1/2,+z+1/2
O3–H3O···N2	0.80(3)	1.97(3)	2.756(3)	165(4)	3/2−x,1/2−y,1/2+z
C7–H7···O3	0.93	2.79	3.466(4)	130	−x+1/2+1, −y+1/2,+z−1/2
C8–H8···O3	0.93	2.79	3.518(4)	136	−x+1/2+1, −y+1/2,+z−1/2
C11–H11···O1	0.93	2.180	3.011(3)	148	1−x, −y, −z
C15–H15B···O4	0.96	2.72	3.521(5)	142	−x, −y, −z−1
3MeOH					
O5–H5O···O3	0.81(2)	2.14(3)	2.907(2)	161(2)	x+1/2, −y+1/2,+z−1/2
O3–H3O···N1	0.82(2)	2.843(2)	3.532(2)	144(2)	x+1/2, −y+1/2,+z+1/2
O3–H3O···N2	0.83(2)	1.88(2)	2.685(2)	166(2)	x+1/2, −y+1/2,+z+1/2
C3–H3···O3	0.93	2.94	3.766(3)	149	x+1/2, −y+1/2,+z−1/2
C4–H4···N2	0.93	2.93	3.540(3)	125	x+1/2, −y+1/2,+z−1/2
C7–H7···O3	0.93	2.67	3.352(3)	131	x−1/2, −y+1/2,+z−1/2
C8–H8···O3	0.93	2.71	3.428(2)	135	x−1/2, −y+1/2,+z−1/2
C8–H8···O4	0.93	2.66	3.548(3)	159	x−1,+y,+z
C14–H14···O4	0.93	2.72	3.588(3)	156	x−1,+y,+z
C11–H11···O1	0.93	2.19	3.023(2)	149	−x+1, −y, −z+1
C15–H15B···O4	0.96	2.92	3.709(3)	141	−x+1, −y, −z
C16–H16B···O5	0.96	2.61	3.307(3)	130	−x, −y, −z
2MeOH					
O34–H34O···O2W	0.84 (1)	1.83 (1)	2.660 (7)	170 (1)	-
O44–H44O···O5W	0.84 (1)	1.90 (1)	2.711 (8)	162 (1)	-
O54–H54O···O1W	0.84 (1)	1.82 (1)	2.641 (7)	167 (1)	-
O1W–H1WB···N41	0.86(1)	2.86(9)	3.617(7)	148(5)	-
O1W–H1WB···N42	0.86(1)	1.89(7)	2.732(7)	165(6)	-
O2W–H2WA···O10W	0.86(1)	2.20(10)	2.88(13)	135(3)	-
O3W–H3WA···N62	0.86(1)	2.18(9)	2.910(7)	143(6)	-
O4W–H4WA···O10W	0.86(1)	2.06(11)	2.87(13)	157(10)	-
O14–H14O···O31	0.84(1)	1.897(4)	2.698(6)	159(1)	x, −y+1/2,+z+1/2
O24–H24O···N52	0.84(1)	1.960(5)	2.795(7)	172(1)	−x+1,+y−1/2, −z+1/2

O24–H24O···N51	0.84(1)	2.903(5)	3.664(7)	152(1)	−x+1,+y−1/2,−z+1/2
O64–H64O···O51	0.84(1)	1.822(4)	2.655(6)	172(1)	x,−y+1/2,+z−1/2
O4W–H4WB···O1W	0.86(7)	2.03(11)	2.809(8)	151(5)	x,−y+1/2,+z−1/2
O84–H84O···N31	0.84(1)	2.806(5)	3.642(6)	174(1)	−x,+y+1/2,−z+1/2
O1W–H1WA···N81	0.86(7)	2.75(7)	3.475(6)	143(6)	−x+1,+y+1/2,−z+1/2
O1W–H1WA···N82	0.86(7)	1.93(7)	2.773(6)	169(7)	−x+1,+y+1/2,−z+1/2
O2W–H2WB···N21	0.86(7)	2.73(7)	3.494(6)	150(5)	−x+1,+y+1/2,−z+1/2
O2W–H2WB···N22	0.86(7)	1.97(8)	2.801(7)	163(7)	−x+1,+y+1/2,−z+1/2
O7M–H7M···O5W	0.84(1)	1.957(6)	2.65(11)	139(1)	x,−y−1/2,+z−1/2
Contact distances formed by solvent molecules of crystallization in 2MeOH complex indicating possible hydrogen bonds					
O1W···O4W			2.808(8)		
O2W···N72			2.740(7)		
O2W···O34			2.660(6)		
O3W···O7W			2.641(9)		
O3W···N62			2.910(8)		
O3W···O4W			2.754(9)		
O4W···O3W			2.754(9)		
O5W···O44			2.711(9)		
O6W···O7M			2.598(14)		
O6W···O74			2.900(8)		
O6W···N12			2.885(8)		
O7M···O6W			2.598(14)		
O7M···O5W			2.653(11)		
O7W···O3W			2.641(9)		
O7W···O74			2.677(9)		
O9W···O8W			3.031(15)		
O10W···O2W			2.873(12)		
O34···O2W			2.660(6)		
O54···O10W			3.015(12)		
O74···O7W			2.677(9)		
O74···O6W			2.900(8)		
2EtOH					
O14–H14O···O14	0.83 (8)	1.93 (9)	2.663 (7)	148 (8)	1−x,y,3/2−z
O34–H34O···N12	0.84(1)	1.930(4)	2.769 (5)	176 (1)	−x+1/2,+y−1/2,−z+3/2
O24–H24O···O31	0.84 (10)	1.95 (10)	2.757 (7)	161 (8)	x−1/2,−y+3/2,+z−1/2
Contact distances formed by solvent molecules of crystallization in 2EtOH complex indicating possible hydrogen bonds					
O2E···O1W			2.96(3)		-
O1E···O14			2.570(8)		-

Table S4. Selected bond lengths [Å] for complex **2MeOH**

	Bond length		Bond length
Cu1–O11	1.899 (5)	Cu5–O51	1.925 (4)
Cu1–N11	1.913 (4)	Cu5–O52	1.932 (4)
Cu1–O12	1.921 (4)	Cu5–O62	1.982 (4)
Cu1–O42	1.979 (4)	Cu5–O63	2.360 (4)
Cu1–O43	2.306 (4)	Cu5–O72	2.539(4)
Cu1–O22	2.745(4)	Cu6–O61	1.881 (4)
Cu2–N21	1.898 (5)	Cu6–O62	1.916 (4)
Cu2–O21	1.916 (4)	Cu6–N61	1.916 (5)
Cu2–O22	1.947 (4)	Cu6–O72	1.994 (4)
Cu2–O32	1.992 (4)	Cu6–O73	2.335 (4)
Cu2–O33	2.276 (4)	Cu7–N71	1.910 (5)
Cu2–O12	2.663(4)	Cu7–O71	1.927 (4)
Cu3–N31	1.918 (5)	Cu7–O82	1.952 (4)
Cu3–O31	1.920 (4)	Cu7–O72	1.965 (4)
Cu3–O32	1.934 (4)	Cu7–O83	2.277 (4)
Cu3–O12	1.983 (4)	Cu7–O52	2.701(4)
Cu3–O13	2.329 (4)	Cu8–N81	1.912 (5)
Cu3–O42	2.578(4)	Cu8–O81	1.936 (4)
Cu4–N41	1.909 (4)	Cu8–O82	1.952 (4)
Cu4–O41	1.947 (4)	Cu8–O52	1.995 (4)
Cu4–O22	1.961 (4)	Cu8–O53	2.245 (4)
Cu4–O42	1.980 (4)	Cu8–O62	2.688(4)
Cu4–O23	2.278 (4)		
Cu4–O32	2.683(4)		
Cu5–N51	1.915 (5)		

Table S5. Selected bond lengths [Å] for complex **2EtOH**

	Bond length
Cu1–O11	1.911 (3)
Cu1–N11	1.921 (3)
Cu1–O12	1.929 (3)
Cu1–O32	1.981 (3)
Cu1–O33	2.361 (3)
Cu1–O22	2.734(3)
Cu2–N21	1.932(3)
Cu2–O21	1.916(3)
Cu2–O22	1.941(3)
Cu2–O42	1.993(3)
Cu2–O43	2.343(3)
Cu2–O12	2.713(3)
Cu3–N31	1.918(3)
Cu3–O31	1.943(3)
Cu3–O32	1.964(3)
Cu3–O22	1.996(3)
Cu3–O23	2.350(3)
Cu3–O42	2.585(3)
Cu4–N41	1.906(3)
Cu4–O41	1.926(3)
Cu4–O12	1.976(3)
Cu4–O42	1.991(3)
Cu4–O13	2.303(3)
Cu4–O32	2.641(3)

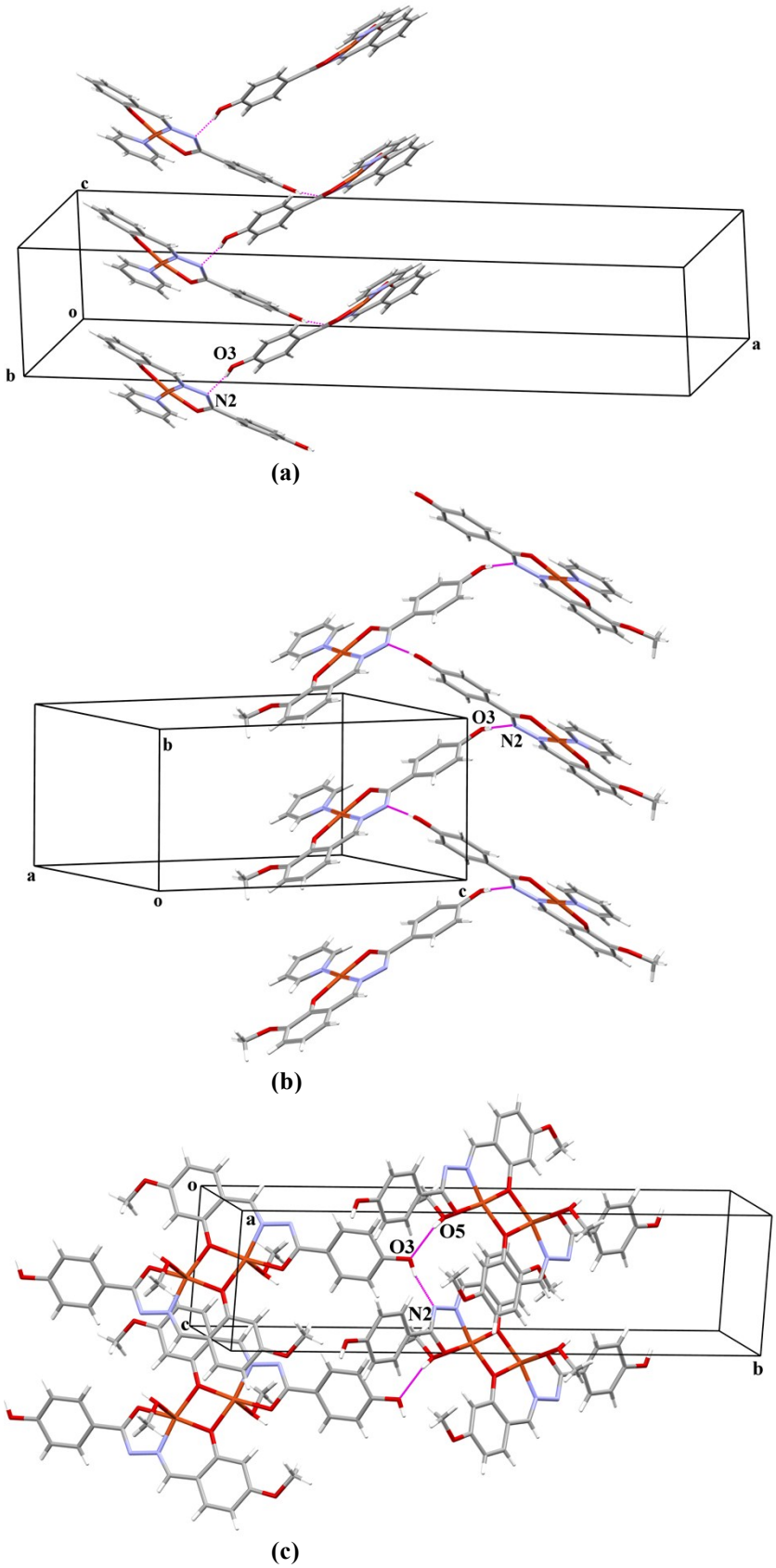
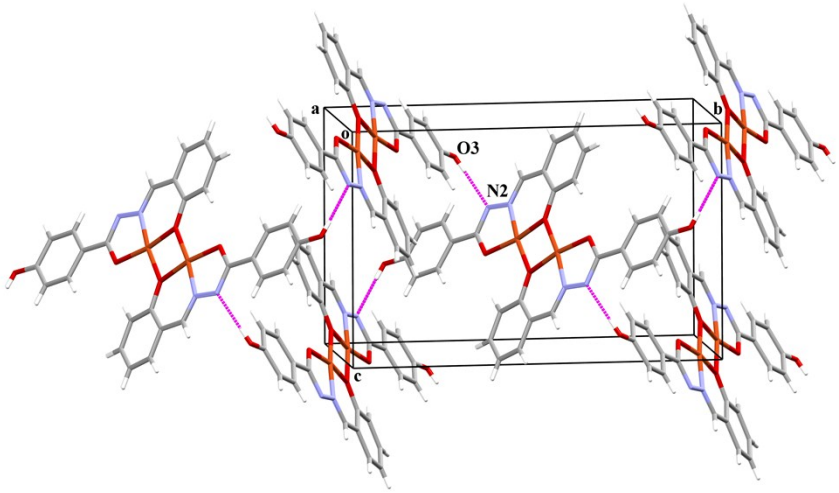
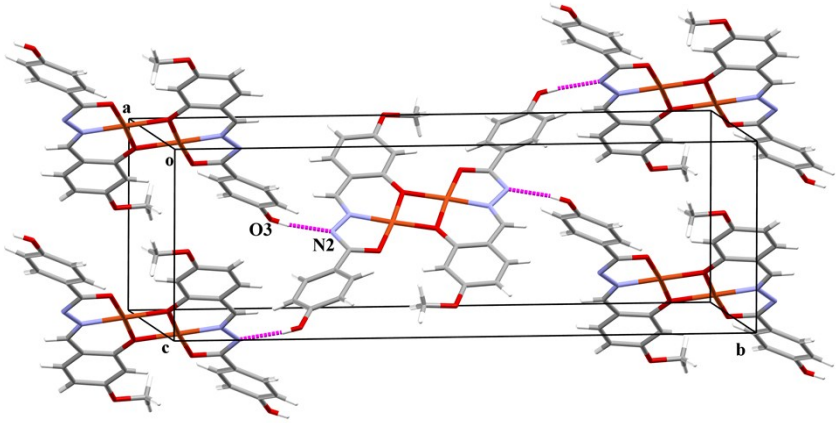


Fig. S7 Fraction of crystal structure of complex (a) **1py***, (b) **2py** and (c) **3MeOH** showing assembling of complex molecules *via* O3–H3O···N2 and O3–H3O···O5 (in **3MeOH**) intermolecular hydrogen bond (denoted as magenta dashed line) into *zig-zag* 1D infinite chain along *b* axis (a and b) and *a* axis (c).



(a)



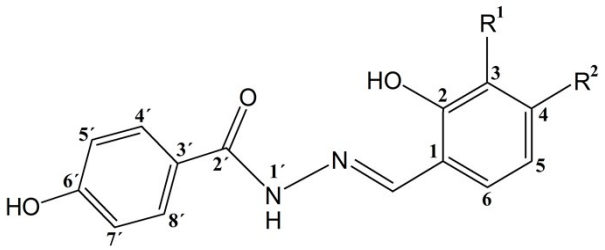
(b)

Fig. S8 (a) Fraction of crystal structure of complex **1β** showing assembling of complex molecules *via* O3–H3O···N2 intermolecular hydrogen bond (denoted as magenta dashed line). (b) Fraction of crystal structure of complex **3** showing assembling of complex molecules *via* O3–H3O···N2 intermolecular hydrogen bond (denoted as magenta dashed line) into 3D network.

Ligands

Table S6.[1]H and [13]C chemical shifts (ppm) of compounds **H_2L^H**, **H_2L^{3OMe}**·H_2O and **H_2L^{4OMe}**·H_2O

Atom	**H_2L^H**		**H_2L^{3OMe}**·H_2O		**H_2L^{4OMe}**·H_2O	
	δ/ppm (^{1}H)	δ/ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{1}H)	δ / ppm (^{1}H)	δ / ppm (^{13}C)
α	8.63	147.72	8.64	8.55	8.55	148.21
1	–	118.66	–	–	–	111.81
2	–	157.45	–	–	–	159.41
3	6.91	119.23	–	6.52	6.52	106.29
4	7.30	131.08	7.12	–	–	161.88
5	6.94	116.37	6.87	6.53	6.53	106.29
6		131.08	7.02	7.39	7.39	131.17
1'	11.94	–	11.92	11.81	11.81	–
2'	–	162.48	–	–	–	162.31
3'	–	123.21	–	–	–	123.33
4', 8'	7.87	129.70	7.87	7.87	7.87	129.61
5', 7'	6.91	115.11	6.92	6.92	6.92	115.09
6'	10.18	160.91		–	–	160.81
OH-2	11.47	–	11.20	11.83	11.83	–
OH-6'	7.51	–	10.19	10.16	10.16	–
OMe			3.83	3.79	3.79	55.21



R^1	**R^2**	**ligand**
H	H	**H_2L^H**
OCH_3	H	**H_2L^{3OMe}**·H_2O
H	OCH_3	**H_2L^{4OMe}**·H_2O

Scheme S1 The structural formula of H_2L with the NMR numbering scheme

Reaction conditions for solution based synthetic methods and yields

Table S7. Reaction conditions and yields

	solvent	**RT**[a]	**R**[a]	**ST**[a]	**E**[a]
1α					
	MeOH	✓ (82%)	✹	✹	✓ (23%)
	EtOH	✓ (70%)	✓(89%)	✹	✓ (17%)
	ACN	✹	✹	✹	
1β					
	MeOH	×	✹	✹	×
	EtOH	×	×	✹	×
	ACN	✹	✹	✹	
1py	MeOH	✓ (79%)	✓ (84%)	✹	✓ (35%)
2MeOH	MeOH	✓ (35%)	✓ (65 %)	✓ (70%)	✓ (29%)
2EtOH	EtOH	✓ (41%)	✓ (47%)	✓ (52%)	✓ (18%)
2py	MeOH	✓ (76%)	✓ (81%)	✓ (52%)	✹
3					
	MeOH	×	×	✓ (88%)	×
	EtOH	×	✓ (88%)	✓ (94%)	
	ACN	✓ (76%)	✓ (88%)	✓ (88%)	
3MeOH	MeOH	✓ (79%)	✓ (84%)	×	✓ (22%)
3EtOH	EtOH	✓ (87%)	×	×	✹
3py	MeOH	✓ (81%)	✓ (90%)	✓ (90%)	✓ (36%)

[a] **RT** = Room Temperature; **R** = Reflux; **ST** = Solvothermal synthesis; **E** = Electrochemical synthesis; ✓ successful synthetic route; ◆ mixture of products; × compound was not obtainable *via* this method