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Supporting Information for

## Efficient Stabilization of Copper(III) in Tetraaza Pseudo-macrocyclic Oxime-and-Hydrazide Ligands with adjustable cavity size

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**Materials.** All starting materials were purchased from Aldrich or Fluka and used as received.

**Instrumentation.** Electrospray (ESI) mass spectra were collected on a Finigan TSQ 700 mass spectrometer. Complexes were dissolved in methanol, methanol : water(1:2) or methanol : DMSO (1:2) solutions with concentration of  $10^{-4}$ - $10^{-6}$  M. The interpretation of mass spectra of mono- and polynuclear complexes as well as calculation of isotope patterns distribution for positive ion clusters was made with the help of program "Isopro 3.0". <sup>1</sup>H (400 MHz) NMR spectra were recorded on a Bruker AC-400 spectrometer at 293 K. Elemental analysis was done on a Perkin-Elmer 2400 CHN. IR spectra (KBr pellets) were recorded on a Perkin-Elmer 180 spectrometer in the range of 200-4000  $\text{cm}^{-1}$ . X-ray data of **2a** was collected on a Nonius KappaCCD diffractometer<sup>i</sup> with graphite-monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using the  $\phi$ - $\omega$ - $\kappa$  technique at 100 K and COLLECT data collection program.<sup>i</sup> The data collection of **1**, **3b**, and **5** were made using Oxford diffraction programs.<sup>ii,iii</sup> The structures were solved by direct methods (SHELXS-97)<sup>iv</sup>, and refined by full-matrix least-squares on all  $F_o^2$  (SHELXL-97)<sup>v</sup> anisotropically for all non-hydrogen atoms. In **5**, two solvate water molecules (O3W and O4W) were found to be disordered between two positions. All the H atoms were located in difference maps (except those of the solvate water molecules in **5**, then the C-H atoms were refined using a riding model [Uiso(H) = 1.2 eq(C) for the methylene and aromatic H-atoms and 1.5 eq(C) for the methyl groups], the O-H and N-H hydrogen atoms were refined freely. Cyclic voltammograms were obtained with an Autolab PGSTAT 12 electrochemical analyzer with GPES 4.9 software, using  $2 \cdot 10^{-3}$  M solutions in methanol or

acetonitrile at 6 different sweep rates ranging from 50 to 1000 mV/s. The working electrode was a Pt or C electrode (2-mm diameter) with an Ag/AgCl reference electrode. The redox potential of the ferrocene/ferrocenium redox couple under these conditions was found to be equal to +0.410 V in methanol and +0.441 V in acetonitrile solutions containing 0.1 M (Bu<sub>4</sub>N)PF<sub>6</sub>. The measurements were performed at 298 K under nitrogen. XPS spectra were recorded on SPECS UHV/XPS/AES system using MgK $\alpha$  source for excitation and equipped with a hemispherical analyzer operating in fixed analyzer transmission mode with pass energy of 10 or 20 eV. A power setting of 10 kV and 150 W was applied. The working pressure in an analyzing chamber was less than 5·10<sup>-10</sup> mbar. The binding energy (BE) scale was calibrated by taking the Au 4f<sub>7/2</sub> peak at 84 eV. Correction of the energy shift due to the static charging of the samples was accomplished using as reference the C1s peak at 284.8 eV. The accuracy of the reported BE was  $\pm$ 0.1 eV. For the XPS analysis, all sample specimens were obtained by pressing sample powders into thin disks which were mounted on sample holders and placed in a prechamber, outgassed to less than 10<sup>-8</sup> mbar at room temperature, and then transferred to the analysis chamber.

### Synthesis and characterisation of copper complexes.

All the syntheses were performed in the air without use of inert atmosphere.

**PPh<sub>4</sub>[Cu(PAP-3H)]·4.5H<sub>2</sub>O (1):** This complex was synthesized according to ref.<sup>vi</sup>

**Li<sub>2</sub>[Cu(fpoh-3H)]<sub>2</sub>·H<sub>2</sub>O·CH<sub>2</sub>O (2a):** The suspension of the compound CuCO<sub>3</sub> (0.0648 g, 0.5 mmol), H<sub>2</sub>poh (0.117 g, 1.0 mmol) was dissolved in methyl alcohol (5 ml) and LiOH·H<sub>2</sub>O (0.084 g; 2 mmol) dissolved in water (5 ml). Paraformaldehyde (0.120 g, 4 mmol), depolymerised in 10 ml methanol was added to the mixture. The obtaining mixture was heated under reflux with continuous stirring for 30 min, then the solvent was removed on a rotary evaporator. The residue was treated by methanol (30 ml), and then the obtained dark brown solution was filtered and reduced to 5ml on a rotary evaporator, filtered, and diethyl ether (10 ml) was added. In 10 h the product was obtained as a clear brown crystalline precipitate, which was filtered and washed with diethyl ether and dried over CaCl<sub>2</sub>. Needle shaped dark brown single crystals suitable for X-ray analysis were obtained by slow diffusion of by vapor of the diethyl ether to the mother liquor at room temperature. Complex 2a is soluble in water and methanol, insoluble in diethyl ether and acetone. Yield 0.205 g (54%).

Calc. for Cu<sub>2</sub>N<sub>12</sub>O<sub>12</sub>C<sub>19</sub>H<sub>30</sub>Li<sub>2</sub> (759.49): C, 30.05; H, 3.98; N, 22.13 Cu, 16.73. Found: C, 29.92; H, 4.08; N, 21.63; Cu, 16.64%. – ESI-MS: *m/z* (%): 347.7 (100) [<sup>65</sup>Cu<sup>63</sup>Cu{Cu(fpoh-3H)}<sup>-</sup>]. – IR (KBr pellet, v/cm<sup>-1</sup>): 1130 [ν(N-O)]; 1600 [ν(C=N), Amide II]; 1640 [ν(C=O), Amide I]; 3460 [ν(O-H)]. – Absorption spectrum (methanol): λ<sub>max</sub> (ε, mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>) 493 (770) nm. – EPR (DMSO:H<sub>2</sub>O: ethylene glycol, G): g<sub>||</sub>=2,149; g<sub>⊥</sub>=2,04; A<sub>||</sub>=209·10<sup>-4</sup>; A<sub>⊥</sub><sup>N</sup>=18,5; A<sub>||</sub><sup>N</sup>=16,3.

**PPh<sub>4</sub>[Cu(fpoh-3H)]·H<sub>2</sub>O (2b):** The complex has been prepared by template procedure analogously to **2a**, with use of solution of tetraphenylphosphine hydroxide in hot water:

a) To the compound AgNO<sub>3</sub> (0.3397 g, 2 mmol) dissolved in water (5 ml), an excess of an aqueous solution NaOH (0.12 g, 3 mmol) was added. Dark grey precipitate of AgOH was washed several times with water and added to the hot solution of tetraphenylphosphonium bromide (0.6285 g, 1.5 mmol) in water (10 ml). The precipitate (AgBr) was filtered off, a hot filtrate (solution of PPh<sub>4</sub>OH) was used as alkaline solution in the syntheses of the complex.

b) The product of the template procedure was extracted with chloroform. The organic phase was separated and dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated and the solvent was removed on a rotary evaporator. The residue was treated by chloroform (10 ml) and added diethyl ether (10 ml). In 10 h the product was obtained as a clear brown crystalline precipitate, which was filtered and washed with diethyl ether and dried over CaCl<sub>2</sub>. Complex **2b** is soluble in methanol and chloroform, insoluble in diethyl ether and acetone. Yield 0.169 g (48%).

Calc. for CuN<sub>6</sub>O<sub>6</sub>C<sub>33</sub>H<sub>35</sub>P (706.2): C, 56.13; H, 5.00; N, 11.90 Cu, 9.00. Found: C, 55.76; H, 5.10; N, 12.20; Cu, 9.08%. – ESI-MS: *m/z* (%): 347.7 (100) [<sup>65</sup>Cu<sup>63</sup>Cu[ {Cu(fpoh-3H)} ]]. – IR (KBr pellet, v/cm<sup>-1</sup>): 1120 [ν(N-O)]; 1580 [ν(C=N), Amide II]; 1620 [ν(C=O), Amide I]; 3515 [ν(O-H)]. – Absorption spectrum (methanol): λ<sub>max</sub> (ε<sub>mol</sub><sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) 486(562) nm. – EPR (DMSO:H<sub>2</sub>O: ethylene glycol, G): g<sub>||</sub>=2,150; g<sub>⊥</sub>=2,04; A<sub>||</sub>=207·10<sup>-4</sup>; A<sub>⊥</sub><sup>N</sup>=18,5; A<sub>||</sub><sup>N</sup>=16,3.

**Cu(fpoh-3H)·H<sub>2</sub>O (3a):** Solution of complex **2a** in water was cooled off to a room temperature, and solution of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6184 g, 2 mmol) in water (10 ml) was added. The obtained black solution was filtered, the filtrate was extracted with chloroform (30 ml). The combined extracts organic was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed on a rotary evaporator. The residue was treated by chloroform (10 ml), and diethyl ether (10 ml) was added. In 6 h the product was obtained as a clear black crystalline precipitate, which was filtered and washed with diethyl ether and dried over CaCl<sub>2</sub>. Complex **3a** is soluble in methanol, acetone and chloroform, insoluble in diethyl ether. Yield 0.090 g (49%).

Calc. for CuN<sub>6</sub>O<sub>6</sub>C<sub>9</sub>H<sub>15</sub> (366.80): C, 29.47; H, 4.12; N, 22.91; Cu, 17.32. Found: C, 29.69; H, 3.72; N, 22.64; Cu, 17.08%. – ESI-MS: *m/z* (%): 347.6 (78) [<sup>65</sup>Cu<sup>63</sup>Cu[ {Cu(fpoh-4H)} ]]. – IR (KBr pellet, v/cm<sup>-1</sup>): 1150 [ν(N-O)]; 1650 [ν(C=N), Amide II]; 1660 [ν(C=O), Amide I]; 3485 [ν(O-H)]. <sup>1</sup>H NMR (CDCl<sub>3</sub>-d<sub>1</sub>):– δ 1.24 (s; 2H, H<sub>2</sub>O), 2.22 (s; 6H, CH<sub>3</sub>), 3.258 (d.tr., 1H, <sup>2</sup>J<sub>H5A,5B</sub> = 13.1 Hz, <sup>4</sup>J<sub>H5A,H6A,7A</sub> = 1.8 Hz H5A), 4.43 (d.d.; 2H, <sup>2</sup>J<sub>H6A,6B</sub> = <sup>2</sup>J<sub>H7A,7B</sub> = 10.66 Hz, <sup>4</sup>J<sub>H7A,H6A,5A</sub> = 2.1 Hz H6A, 7A), 4.86 (d; 2H, H6B, H7B), 5,85 (d; 1H, <sup>2</sup>J<sub>H5B,5A</sub> = 13.1 Hz, H5B), 18.75 (s; 1H, NOH). – Absorption spectrum (methanol): λ<sub>max</sub> (ε<sub>mol</sub><sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) 701 (4195), 543 (5515), 442 (7715), 332 (10198) nm.

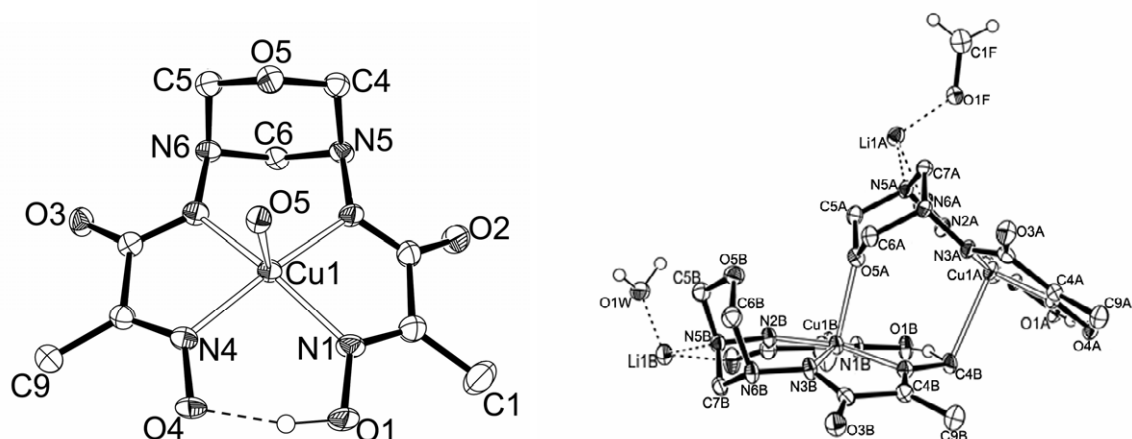
**[Cu(fpoh-3H)]·DMSO (3b):** The synthesis of the complex was performed in mixture of DMSO, acetone and chloroform (5 ml, of each) using **3a** (0.183 g, 0.5 mmol) as initial compound, which was dissolved, filtered off and the filtrate was set aside for evaporation at the room temperature in a test-tube. Needle prismatic shaped black single crystals suitable for X-ray analysis were obtained in 36 h. The crystalline product was separated by filtration, washed with diethyl ether and dried in the air. Complex **3b** is soluble in methanol, acetone and chloroform, insoluble in diethyl ether. Yield 0.189 g (89%).

Calc. for  $\text{CuN}_6\text{O}_6\text{C}_{11}\text{H}_{19}\text{S}$  (426.91): C, 30.95; H, 4.49; N, 19.69; Cu, 14.88. Found: C, 30.69; H, 4.72; N, 19.64; Cu, 15.08%.

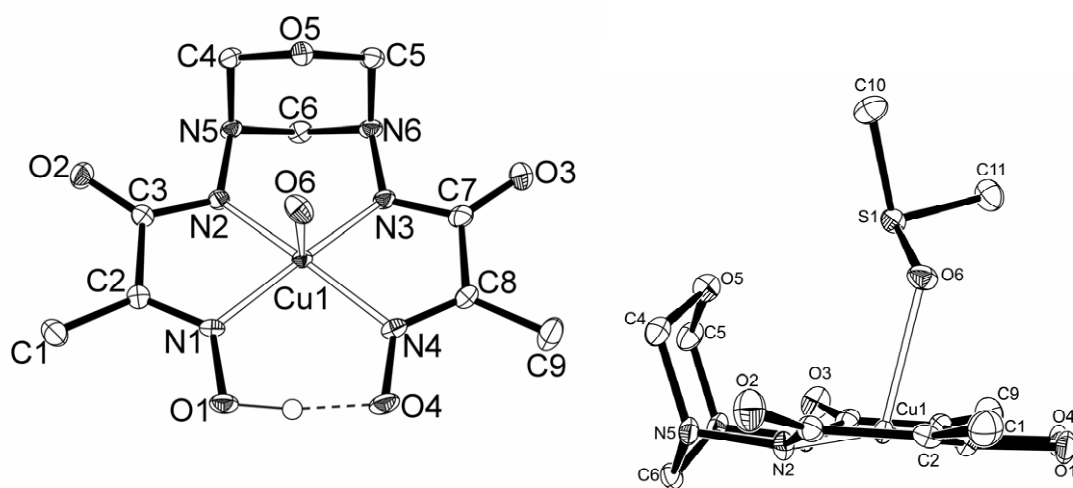
**[{Cu(dipy)Cu(PAP-4H)(H<sub>2</sub>O)<sub>2</sub>}]<sub>2</sub> (4)** and **[{Cu(dipy)Cu(fpoh-4H)}<sub>2</sub>] 5H<sub>2</sub>O (5):** A solutions of  $\text{Cu(dipy)Cl}_2$  (0.097 g, 0.33 mmol) were added to a solution of  $[\text{Li(H}_2\text{O)}_4][\text{Cu(PAP-3H)}]\cdot 2\text{H}_2\text{O}$  (0.140 g, 0.33 mmol) (synthesised according to <sup>vi</sup>) and **2a** ( 0.125 g, 0.33 mmol) in 5 mL of water, respectively. The resulting solutions turned red-purple, and in 2-5 min yielded dark red-purple precipitates, which were filtered, washed consequently with water, acetone and dried in vacuum under  $\text{CaCl}_2$ . The products are fairly soluble in DMFA and DMSO, slightly soluble in methanol and ethanol on heating, but insoluble in water. Yield 0.138 g (75%) and 0.172(85%).

Calc. for  $\text{C}_{38}\text{H}_{48}\text{N}_{12}\text{O}_{12}\text{Cu}_4$  (1119.06): C, 19.00; H, 4.32; N, 15.02; Cu, 22.71. Found: C, 19.09; H, 4.22; N, 15.14; Cu, 23.08%. ESI-MS:  $m/z$  (%): 1069.1 (100)  $[\text{}^{65}\text{Cu}^{63}\text{Cu}_3\{\text{Cu(dipy)Cu(PAP-4H)}\}_2 + \text{Na}]^+$ , 545.0 (57)  $[\text{}^{63}\text{Cu}_2\{\text{Cu(dipy)Cu(PAP-4H)}\} + \text{Na}]^+$ , 1593.1 (15)  $[\text{}^{65}\text{Cu}_2\text{}^{63}\text{Cu}_4\{\text{Cu(dipy)Cu(PAP-4H)}\}_3 + \text{Na}]^+$ . IR (KBr pellet,  $\text{v}/\text{cm}^{-1}$ ): 1150  $[\nu(\text{N-O})]$ ; 1590  $[\nu(\text{C=O})]$ , Amide I; 3600  $[\nu(\text{O-H})]$ . – Absorption spectrum (methanol):  $\lambda_{\text{max}}$  ( $\epsilon_{\text{mol}}^{-1} \text{dm}^3 \text{cm}^{-1}$ ) 525(296) nm. – EPR (DMSO:H<sub>2</sub>O: ethylene glycol, G):  $g_{\text{iso}}=2.116$ .

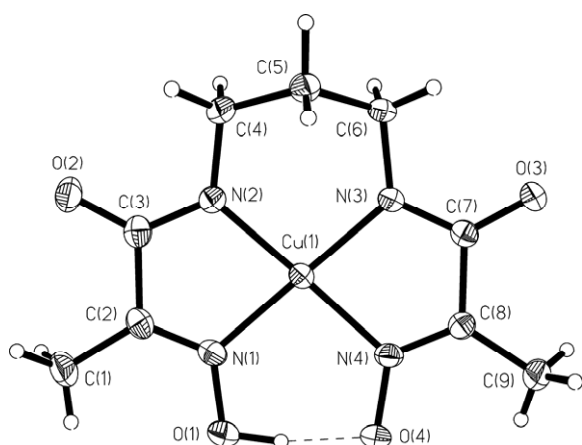
Calc. for  $\text{C}_{38}\text{H}_{50}\text{N}_{16}\text{O}_{15}\text{Cu}_4$  (1225.10): C, 37.26; H, 4.11; N, 18.29; Cu, 20.75. Found: C, 37.09; H, 4.22; N, 18.14; Cu, 21.08%. ESI-MS:  $m/z$  (%): 1158.01 (100)  $[\text{}^{65}\text{Cu}^{63}\text{Cu}_3\{\text{Cu(dipy)Cu(fpoh-4H)}\}_2 + \text{Na}]^+$ ,  $[\text{}^{65}\text{Cu}^{63}\text{Cu}[\{\text{Cu(dipy)Cu(fpoh-4H)(H}_2\text{O)}_2\}] + \text{H}^+]$  (567.3). IR (KBr pellet,  $\text{v}/\text{cm}^{-1}$ ): 1160  $[\nu(\text{N-O})]$ ; 1590  $[\nu(\text{C=O})]$ , Amide I; 3450  $[\nu(\text{O-H})]$ . – Absorption spectrum (methanol):  $\lambda_{\text{max}}$  ( $\epsilon_{\text{mol}}^{-1} \text{dm}^3 \text{cm}^{-1}$ ) 539(360) nm. – EPR (DMSO:H<sub>2</sub>O: ethylene glycol, G):  $g_{\text{iso}}=2.10$ .



**Figure S1.** Molecular structure of  $2a \cdot Li^+ \cdot H_2O$  (left- a monomeric complex anion; right- a dimeric molecule).



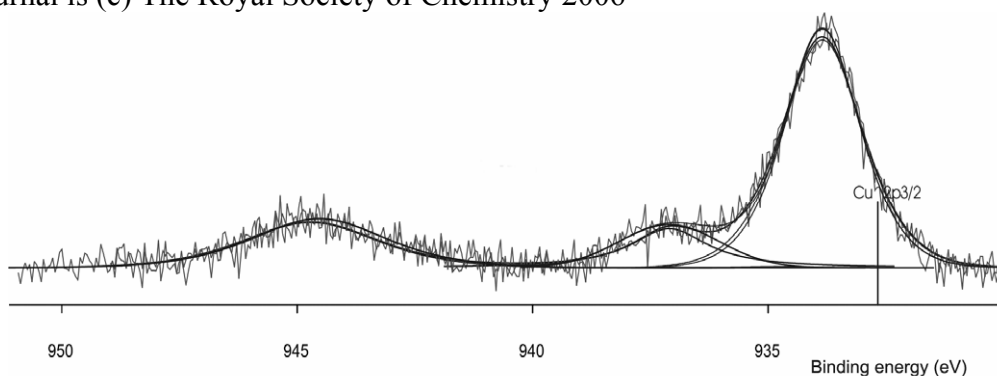
**Figure S2** Structure and numbering scheme for **3b**



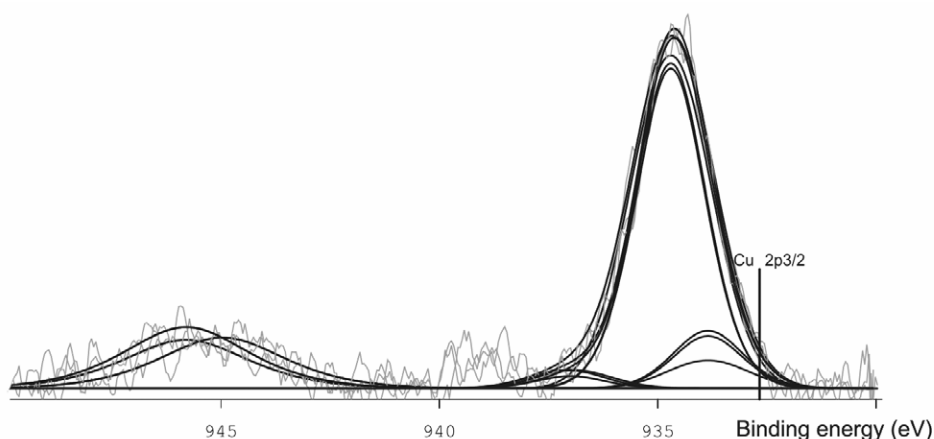
**Figure S3** Molecular structure of  $[Cu(PAP-3H)]^-$  anion in **1**

**Table S1** Crystal data and structure refinement for complexes **1**, **2a**, **3b** and **5**

Molecular formula	PPh <sub>4</sub> [Cu(PAP-3H)]·4.5H <sub>2</sub> O ( <b>1</b> )	Li <sub>2</sub> [Cu(fpoh-3H)] <sub>2</sub> ·H <sub>2</sub> O·CH <sub>2</sub> O ( <b>2a</b> )	[Cu(fpoh-3H)·DMSO] ( <b>3b</b> )	[{Cu(dipy)Cu(fpoh-4H)} <sub>2</sub> ]·5H <sub>2</sub> O ( <b>5</b> )
Empirical formula	C <sub>33</sub> H <sub>42</sub> CuN <sub>4</sub> O <sub>8.5</sub> P	C <sub>19</sub> H <sub>30</sub> Cu <sub>2</sub> Li <sub>2</sub> N <sub>12</sub> O <sub>12</sub>	C <sub>11</sub> H <sub>19</sub> CuN <sub>6</sub> O <sub>6</sub> S	C <sub>19</sub> H <sub>30</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>10</sub>
M	725.22	759.51	426.92	657.59
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P-1	P 2 <sub>1</sub> /c	P-1	P 2 <sub>1</sub> /c
<i>a</i> /(Å)	11.241(6)	15.024(6)	8.144(2)	12.859(1)
<i>b</i> /(Å)	12.652(7)	11.629(6)	9.362(2)	7.043(1)
<i>c</i> /(Å)	13.020(7)	18.2082(8)	11.394(2)	27.665(2)
$\alpha$ /(°)	78.28(1)	90°	91.83(3)	90°
$\beta$ /(°)	85.76(1)	107.669(3)	91.08(3)	93.603(2)
$\gamma$ /(°)	68.63(1)	90	111.53(3)	90°
<i>V</i> /(Å <sup>3</sup> )	1688.56	3031.5(2)	807.3(3)	2500.7(4)
<i>Z</i>	2	4	2	4
<i>D<sub>c</sub></i> /(mg m <sup>3</sup> )	1.426	1.664	1.756	1.747
$\mu$ (mm <sup>-1</sup> )	0.752	1.481	1.527	1.772
<i>F</i> (000)	760	1552	440.0	1352.0
$\theta$ Range for data collection <sup>o</sup>	1.76 - 30.51	3.78 - 25.67	3.28 - 28.43	7.30-27.48
Number of reflections collected	9960	18356	6554	11475
Unique reflections/parameters	9960 /469	5717 / 428	3596 / 234	5490/372
G.O.F.	1.064	1.049	1.076	1.054
Final indices	<i>R</i> 1 = 0.0414,	<i>R</i> 1 = 0.0422,	<i>R</i> 1 = 0.0328,	<i>R</i> 1 = 0.0534,
<i>R</i> 1 and <i>wR</i> 2 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>wR</i> 2 = 0.0978	<i>wR</i> 2 = 0.0943	<i>wR</i> 2 = 0.0822	<i>wR</i> 2 = 0.1397
Final indices	<i>R</i> 1 = 0.0590,	<i>R</i> 1 = 0.0719,	<i>R</i> 1 = 0.040,	<i>R</i> 1 = 0.0755,
<i>R</i> 1 and <i>wR</i> 2 (all data)	<i>wR</i> 2 = 0.1078	<i>wR</i> 2 = 0.1071	<i>wR</i> 2 = 0.0843	<i>wR</i> 2 = 0.1489
Max., min. residual	0.520, -0.562	0.688, -0.462	0.567, -0.374	0.692, -0.716
Electron density /e Å <sup>-3</sup>				



**Figure S4** XPS spectra of  $\text{Li}_2[\text{Cu}(\text{fpoh-3H})]_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_2\text{O}$  (**2a**) with its deconvolution



**Figure S5** XPS spectra of  $\text{Cu}(\text{fpoh-3H}) \cdot \text{H}_2\text{O}$  (**3a**) with its deconvolution

**Table S2.** The binding energy  $\text{Cu } 2p_{3/2}$  for **2a** and **3a** complexes

	Determined $E_b$	Intensity %	
<b>Li[Cu(fpoh-3H)]·H<sub>2</sub>O (2a)</b>	933.85	65.4	10eV; 120W
	933.85	62.8	5eV; 150W
<b>[Cu(fpoh-3H)]·H<sub>2</sub>O (3a)</b>	934.7	72.8	10eV; 120W
	934.7	65.7	5eV; 150W
	934.7	64.2	5eV; 200W

<sup>i</sup> COLLECT data collection software, Bruker AXS, Delft, The Netherlands, 2004.

<sup>ii</sup> Cryp Alin Red 166, Oxford Diffraction Wroclaw.

<sup>iii</sup> Cryp alin CCD, Oxford Diffraction Wroclaw.

<sup>iv</sup> G.M.Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Germany, **1997**.

<sup>v</sup> G.M.Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

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<sup>vi</sup> O. M. Kanderl, H. Kozłowski, A. Dobosz, J. Swiatek-Kozłowska, F. Meyer and I. O. Fritsky,  
Dalton Trans., 2005, 1428-1437.