*Supporting Information for*

# Novel Supramolecular Thixotropic Metallo-Hydrogels Consisting of Rare Metal-Organic Nanoparticles: Synthesis, Characterization, and Mechanism of Aggregation

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## 1. General.

All commercial reagents and solvents were used directly without further purification. $^{1}H$ and $^{13}C$ NMR were recorded on Jeol ECA-400 and Bruker 500 DRX spectrometers. ESI-MS spectra were recorded on a Bruker micrOTOF II instrument. Powder X-ray diffraction (PXRD) patterns were measured using a Bruker D8 powder diffractometer with Cu Kα radiation (λ = 1.5406 Å). Data collections were carried out on a Bruker Smart APEX diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation, λ= 0.71073 Å) operating at 50 kV and 30 mA at 293 K. SEM experiments were carried out on a Philips XL30 microscope operated at 20 kV. Transmission electron microscopy (TEM) experiments were carried out on a JEOL JEM-2010 transmission electron microscope. Dynamic light scattering (DSL) was measured on a Zetasizer Nano Serie ZS apparatus from Malvern. AFM images were performed by using Veeco Multimode Nanoscope (Bruker) with tapping mode. UV-Vis absorption was recorded on a UV-Vis 2550 spectroscope (Shimadzu). All reactions were carried out under air unless otherwise noted. Rheological measurements were carried out on freshly prepared gels using a controlled stress rheometer (Malvern Bohlin Gemini HR nano).

## 2. Experimental techniques.

### [2.1] **Gelation test.**

For the preparation of the metallogel samples, the solvents were used as purchased. For 1 wt% gel: 5 mg Cu(II)-pincer complex **2a** or **2b** was filled into a screw-cap tube and then solvent (0.5 mL) was added by syringe. The exact concentration was determined by differential weighting. The Cu(II)- pincer complex was dissolved by heating with a heat-gun or continuous shaking. Then, the samples were allowed to cool down slowly or rest at room temperature to form a gel.

### [2.2] **Determination of gel-to-solution phase-transition temperatures $T_g$ by using a test-tube-inversion method.**[1]

A test tube containing the gel sample was immersed inversely in a thermostat controlled oil bath and the temperature was raised at a rate of 0.5 ℃ per minute. The $T_g$ was defined as the temperature at which the gel

collapsed.

[2.3] **Scanning electron microscopy (SEM).**

SEM experiments were carried out on a Philips XL30 microscope operated at 20 kV. All pictures were taken digitally. For preparation of the samples, a silicon sheet was placed on the surface of the gel for a short time. The gel samples were partly destroyed by knocking the test tube on the table to provide a "print" of the inner volume of the gel.

[2.4] **Transmission electron microscopy (TEM).**

Transmission electron microscopy (TEM) experiments were carried out on a JEOL JEM-2010 transmission electron microscope. All pictures were taken digitally. For preparation of the samples, carbon-coated copper grids (mesh 200 or 150) were placed on the surface of the gels for a short time. The gel samples were partly destroyed by knocking the test tube on the table to provide a "print" of the inner volume of the gel.

[2.5] **Rheology**

Rheological measurements were carried out on freshly prepared gels using a controlled stress rheometer (Malvern Bohlin Gemini HR nano). Cone and plate geometry of 40 mm diameter was employed throughout the dynamic oscillatory work. The following tests were performed: increasing amplitude of oscillation up to 100% apparent strain shear (kept at a frequency of 6.283 rad $s^{-1}$) and frequency sweeps at 25 $^{o}$C (from 100– 0.005 rad $s^{-1}$, 0.5% strain).

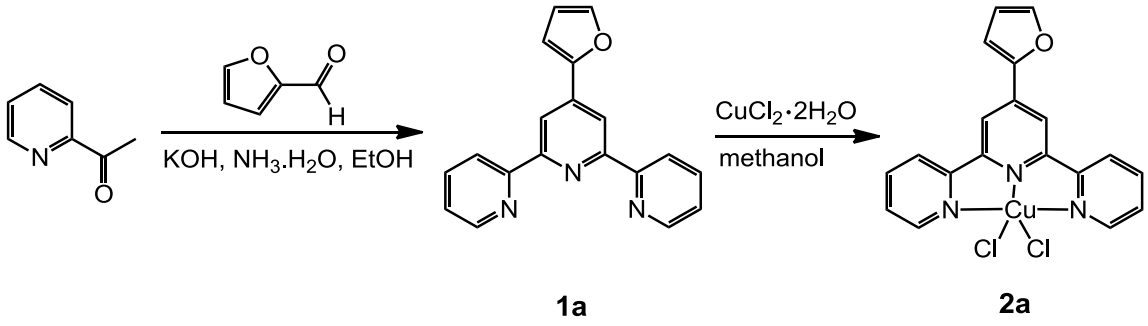
[2.6] **X-ray scattering (SAXS)**

Characterization with *X-rays* was performed using a pinhole camera with a rotating anode generator (Cu Kα radiation from crossed Göbel mirrors by using Bruker AXS D8 with a power of 40 kV and 50 mA). All X-ray patterns were radially averaged and corrected for background scattering from the solvent to obtain the scattering intensity in dependence on the scattering vector $q = (4/\pi)\sin\theta$ , with $2\theta$ being the scattering angle and $\lambda = 0.15406$ nm the X-ray wavelength**.**

[2.7] **Single-crystal X-ray structure determination**

Crystal structure determination of complexes **2a**•MeOH and **3** was performed on a Bruker Smart APEX diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation, λ= 0.71073 Å) operating at 50 kV and 30 mA at 293 K. A hemisphere of intensity data was collected at room temperature with a scan width of 0.60° in ω. Empirical absorption corrections were based on SADABS program.[2] The structures were solved by direct methods and refined by full-matrix least-squares refinement using the SHELXTL-97 program.[3] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors.

## 3. Synthesis of Cu(II)-pincer complexes 2a-c, and 3.

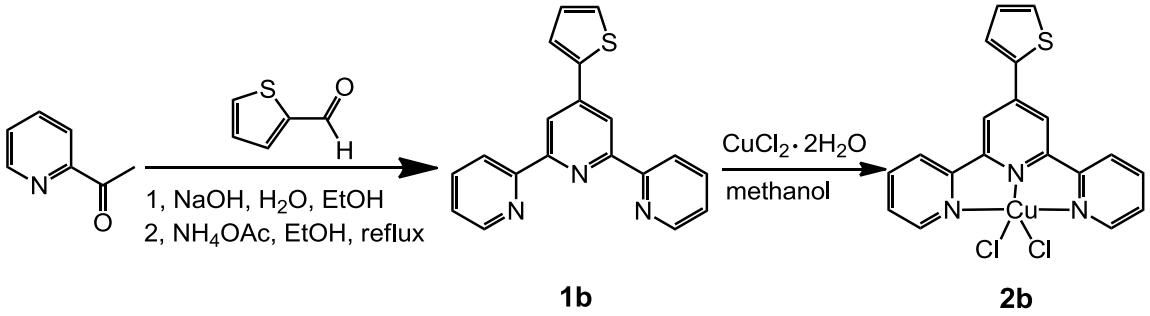



***Scheme S1.*** Synthesis of Cu(II)-pincer complex **2a**.

**4'-(2-Furyl)-2,2':6',2''-terpyridine (1a)**:[4] 2-Furaldehyde (1.92 g, 40 mmol) and 2-acetylpyridine (4.84 g, 80 mmol) were dissolved in EtOH (200 mL). KOH (3.08 g, 110 mmol) was added and the reaction mixture was stirred for several minutes, then aqueous ammonia solution (120 mL, 25%−28%) was added. The solution was stirred at 60 °C for 24 h. Then the solution was cooled to r.t. and filtered to yield an off-white solid. Recrystallization from EtOH/MeOH gave **1a** (5.17 g, 42%) as white needles. $^{1}$H NMR (DMSO-$D_6$, 400 MHz, 298 K): δ = 8.75 (d, *J* = 4.0 Hz, 2H), 8.68 (s, 2H), 8.63 (d, *J* = 8.0 Hz, 2H), 8.02 (t, *J* = 7.6 Hz, 2H), 7.96 (bs, 1H), 7.52 (t, *J* = 6.0 Hz, 2H), 7.46 (d, *J* = 3.2 Hz, 1H), 6.73 – 6.74 (m, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 155.90, 155.75, 151.80, 148.96, 143.53, 139.33, 136.67, 123.71, 121.11, 114.94, 111.99, 109.01.

**Cu(II)-pincer complexes 2a:** Ligand **1a** (2.99 g, 10 mmol) and $CuCl_2$•$2H_2O$ (2.05 g, 12 mmol) were added to $CH_3OH$ (200 mL) and stirred at r.t. for 24h. The green solid was collected after filtration, washed with $CH_3OH$ (3 ×

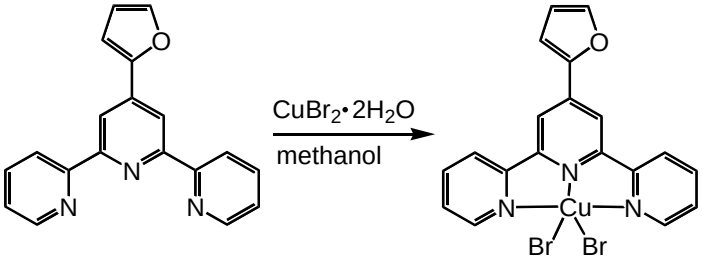
30 mL) three times and then dried under vacuum to give complex **2a** as a green solid (4.31 g, 99%). $^1$H NMR ($D_2O$, 400 MHz, 353 K): δ = 10.68 (bs, 6H), 10.24 (bs, 2H), 10.06 (bs, 3H), 6.91 (bs, 3H); HR-MS (ESI): m/z 397.0043 (Calcd. $[M\text{-}Cl]^+$), 397.0078 (Found. $[M\text{-}Cl]^+$).




***Scheme S2.*** Synthesis of Cu(II)-pincer complex **2b**.

**4'-(2-Thienyl)-2,2':6',2''-terpyridine** (**1b**):[5] A solution of 2-acetylpyridine (3.34 mL, 0.03 mol) in EtOH (250 mL) was added over 2 h to a stirred solution of 2-thiophenecarbaldehyde (1.4 mL, 0.015 mol) and NaOH (4.0 g) in the mixture of $H_2O$ (25 mL) and EtOH (250 mL). Then the reaction mixture was stirred for 20 h at r.t. and the solvent was removed *in vacuo*. The residue was redissolved in $CH_2Cl_2$ (300 mL), washed with $H_2O$ (3 × 250 mL) and dried over $MgSO_4$. The remaining solvent was removed to give orange oil. This oil was dissolved in EtOH (100 mL), $NH_4OAc$ (2.00 g, 0.03 mol) was added and the mixture was refluxed for 4 h. The solvent was removed *in vacuo* and the residue dissolved in toluene (250 mL) and was then washed with $H_2O$ (3 × 100 mL). The toluene was then removed and the residue was dissolved in HCl (150 mL, 0.5 M), and washed with $CH_2Cl_2$ (5 × 100 mL). The aqueous layer was neutralized with NaOH giving the precipitate of **1b** as an off-white solid (0.584 g, 12%). $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.30 – 8.74 (m, 2H), 8.69 (s, 2H), 8.64 (d, *J* = 7.6 Hz, 2H), 7.87 (t, *J* = 7.6 Hz, 2H), 7.78 (m, 1H), 7.44 (d, *J* = 4.0 Hz, 1H), 7.35 (m, 2H), 7.17 (m, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 156.00, 149.07, 143.35, 141.84, 136.78, 128.22, 127.04, 125.76, 123.83, 121.27, 117.08.

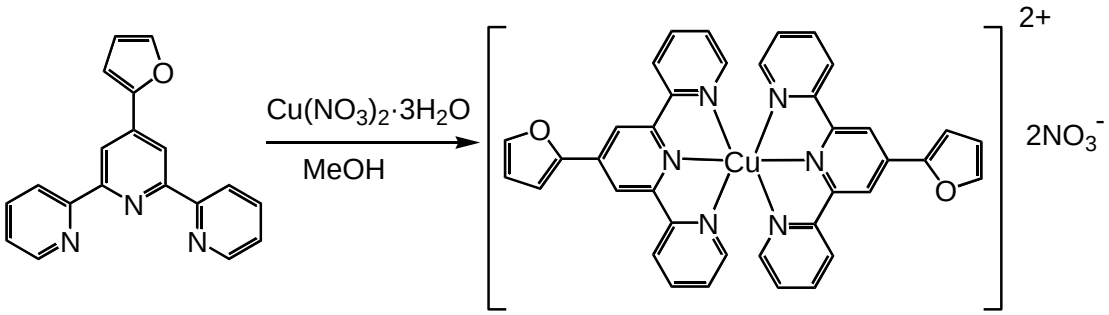
**Cu(II)-pincer complexes 2b:** A similar synthetic protocol for complex **2a** was applied, complex **2b** was provided as a green solid (0.408 g, 91%). HR-MS (ESI): m/z 412.9815 (Calcd. $[M\text{-}Cl]^+$), 412.9827 (Found. $[M\text{-}Cl]^+$). Due to the poor solubility and paramagnetic property of complex **2b**, it is hard to get satisfied NMR spectra.




**1a** **2c**

***Scheme S3.*** Synthesis of Cu(II)-pincer complex **2c**.

**Cu(II)-pincer complexes 2c:** A similar synthetic protocol for complex **2a** was applied, complex **2c** was obtained as a green solid (0.435 g, 83%). HR-MS (ESI): m/z 442.9518 (Calcd. $[M\text{-}Br]^+$), 442.9551 (Found. $[M\text{-}Br]^+$).




**1a** **3**

***Scheme S4.*** Synthesis of Cu(II)-pincer complex **3**.

**Cu(II)-pincer complex 3:**[6] To a solution of complex **1a** (120 mg, 0.4 mmol) in 100 mL methanol, a solution of 0.05 mmol of $Cu(NO_3)_2$ $3H_2O$ (48 mg, 0.2 mmol) in 8 mL of methanol was added. The mixture was then heated to reflux for 1 h and allowed to cool at room temperature. The product was isolated after filtration upon precipitation by addition of diethyl ether. The solid was washed three times with diethyl ether and dried under vacuum to afford the complex **3** as a light-green solid powder. (134 mg, 85%). HR-MS (ESI): m/z 330.5707 (Calcd. $[M\text{-}2NO_3]^{2+}$), 330.5728 (Found. $[M\text{-}2NO_3]^{2+}$).

## 4. Gelation tests of Cu(II)-pincer complexes 2a,b in various solvents.

***Table S1***. Gelation ability of Cu(II)-pincer complexes **2a,b** in various organic solvents[a]

| Solvent | **2a** | $T_g$/°C | **2b** | $T_g$/ °C | Solvent | **2a** | $T_g$/ °C | **2b** | $T_g$/ °C |
|---|---|---|---|---|---|---|---|---|---|
| Ethanol | I | / | / | / | Cyclohexane | I | / | / | / |
| DCE | I | / | / | / | 1,2-Ethanediamine | S | / | / | / |
| Methanol | C | / | I | / | HOAc | P | / | / | / |
| DCM | I | / | / | / | *i*-PrOH | I | / | / | / |
| TCM | I | / | / | / | *n*-BuOH | I | / | / | / |
| DMSO | P | / | I | / | *n*-PrOH | I | / | / | / |
| DMF | I | / | / | / | *t*-BuOH | I | / | / | / |
| DMA | I | / | / | / | 1,2-Ethanediol | G/S[b] | 33.5 | I | / |
| THF | I | / | / | / | 1,3-Propanediol | G/S[b] | 32 | I | / |
| Dioxane | I | / | / | / | 1,4-Butanediol | G[c] | / | / | / |
| Toluene | I | / | / | / | Glycerin | G | 36.6 | G | 53.5 |
| Benzene | I | / | / | / | Triglycol | I | / | I | / |
| PhCl | I | / | / | / | Polyethylene glycol | I | / | I | / |
| Pyridine | I | / | / | / | $H_2O$ (0.1 wt%) | S | / | / | / |
| NMP | I | / | / | / | $H_2O$ (0.2 wt%) | PG[d] | / | / | / |
| PhCN | I | / | / | / | $H_2O$ (0.25 wt%) | G[e] | / | / | / |
| ACN | I | / | / | / | $H_2O$ (0.3 wt%) | G | / | / | / |
| EtOAc | I | / | / | / | $H_2O$ (0.5 wt%) | G | 51.6 | / | / |
| Acetone | I | / | / | / | $H_2O$ (1.0 wt%) | G | 72.9 | I | / |

[a] Gelator concentration: 1 wt%; C: crystal, G: gel, I: insoluble, PG: partial gel, P: precipitate, S: soluble. [b] Gelator concentration: 0.4 wt%. [c] The gel was only stable for 2 hours. [d] Resting for 3 days. [e] Resting for 14 days.

***Table S2***. Gelation ability of Cu(II)-pincer complexes **2a** in various aqueous mixtures[a]

| Solvent | **2a** | $T_g$/ °C [a] | Solvent | **2a** | $T_g$/ °C [a] |
|---|---|---|---|---|---|
| $H_2O$/Methanol | G/G[b]/G[c] | 58.4 | $H_2O$/DME | G[c] | r.t. |
| $H_2O$/Ethanol | G/G[b]/G[c] | 54.9 | $H_2O$/HOAc | G[c] | 42.7 |
| $H_2O$/*n*-PrOH | G/G[b]/G[c] | 57.8 | $H_2O$/DMSO | G/S[b]/G[c] | r.t. |
| $H_2O$/*i*-PrOH | G/G[b]/G[c] | 41.9 | $H_2O$/DMF | S/S[b]/S[c] | /[d] |
| $H_2O$/*t*-BuOH | G/G[b]/G[c] | 78.2 | $H_2O$/DMA | G/S[b]/S[c] | /[d] |
| $H_2O$/Diethylene glycol | G/S[b]/G[c] | 51.4 | $H_2O$/Pyridine | S[c] | /[d] |
| $H_2O$/Triethylene glycol | G/S[b]/G[c] | r.t. | $H_2O$/NMP | G[c] | 35.5 |
| $H_2O$/Polyethylene glycol | G/WG[b]/WG[c] | /[d] | $H_2O$/ACN | S/S[b]/S[c] | /[d] |
| $H_2O$/2-Methoxyethanol | G[c] | 43.8 | $H_2O$/ Acetone | G/WG[b]/PG[c] | /[d] |

[a] Gelator concentration: 0.67 wt% (5 mg/0.75 mL); G: gel, PG: partial gel, S: soluble, WG: weak gel. $H_2O$ : X = 1:1 (volume ratio), X = methanol, ethanol, *n*-PrOH, *i*-PrOH, *t*-BuOH, diethylene glycol, triethylene glycol, polyethylene glycol, DMSO, DMF, DMA, ACN, and acetone. [b] Gelator concentration: 0.5 wt% (5 mg/1 mL), $H_2O$ : X = 1:1 (volume ratio), X = methanol, ethanol, *n*-PrOH, *i*-PrOH, *t*-BuOH, diethylene glycol, triethylene glycol, polyethylene glycol, DMSO, DMF, DMA, ACN, and acetone. [c] Gelator concentration: 1.0 wt% (10 mg/1 mL), $H_2O$ : X = 1:1 (volume ratio), X = methanol, ethanol, *n*-PrOH, *i*-PrOH, *t*-BuOH, diethylene glycol, triethylene glycol, polyethylene glycol, 2-methoxyethanol, DME, HOAc, DMSO, DMF, DMA, pyridine, NMP, ACN, and acetone. [d] The gelation tests for mixtures of solvents were not carried out.

## 5. Anion selective metallo-hydrogel formation by various cooper salts via stirring in water.

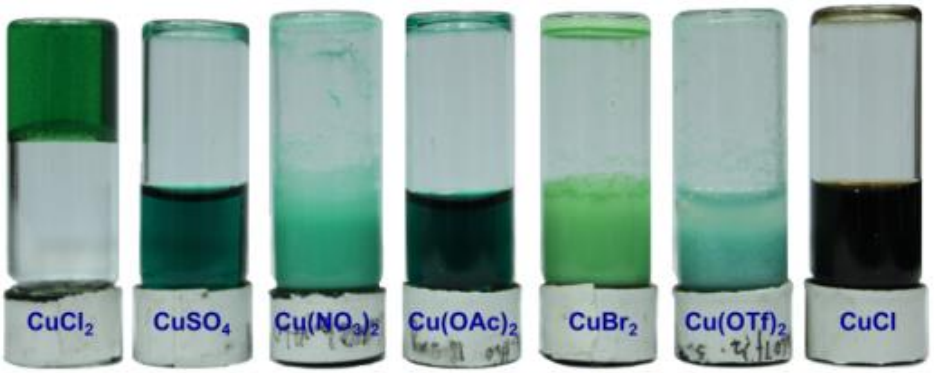



***Figure S1.*** Anion selective metallo-hydrogel formation by complex **1a** and various cooper salts via stirring in water.

## 6. Crystal grownth from metallogels in situ.

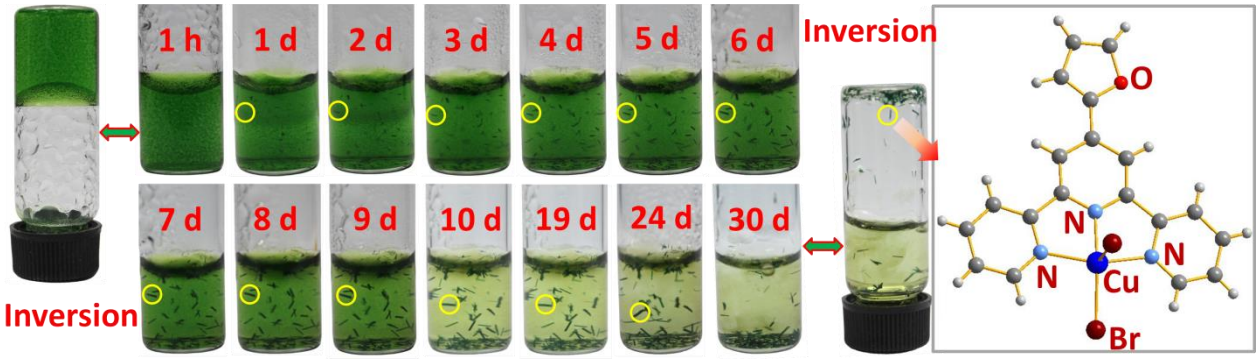



***Figure S2.*** Crystal grownth from hydrogel **2c**/$H_2O$ (1 wt%) in situ.

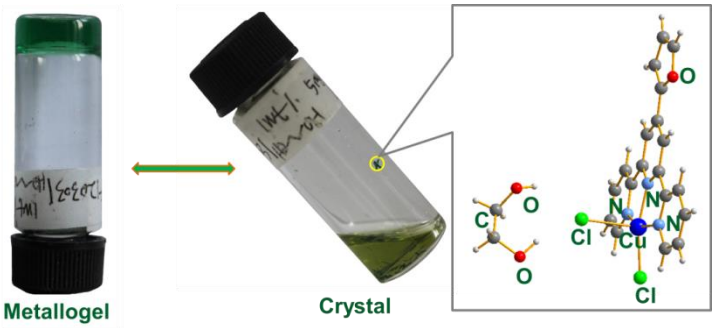



***Figure S3.*** Crystal grownth from metallogel **2a**/ethylene glycol (1 wt%) in situ.

## 7. Sol-gel transition temperatures ($T_g$) for metallogels of 2a/$H_2O$ as a function of gelator concentrations.

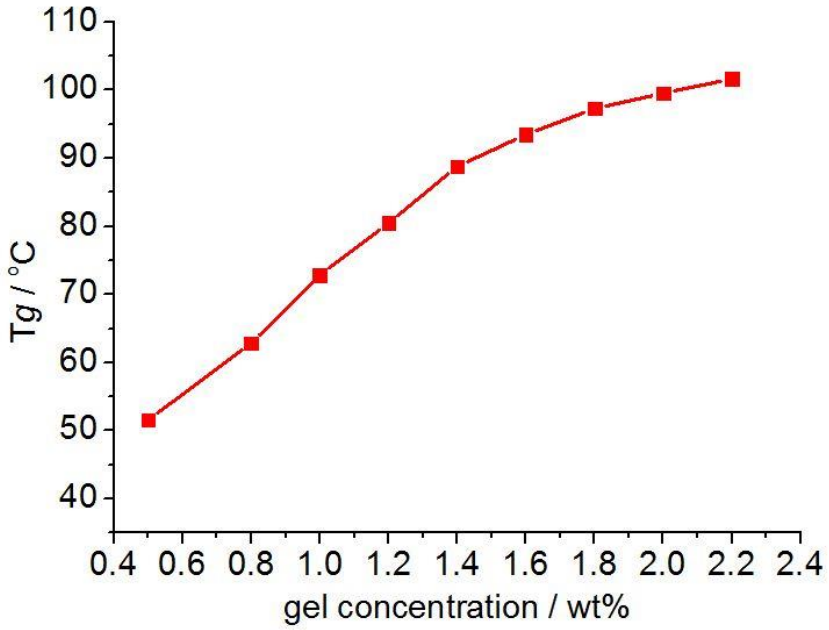



***Figure S4.*** Sol-gel transition temperatures ($T_g$) for metallogels of **2a**/$H_2O$ as a function of gelator concentrations.

## 8. Phase-selective gelation by metallogelator 2a.


***Figure S5.*** Phase-selective gelation by metallogelator **2a** with a variety of aqueous mixtures.

## 9. EDX analysis

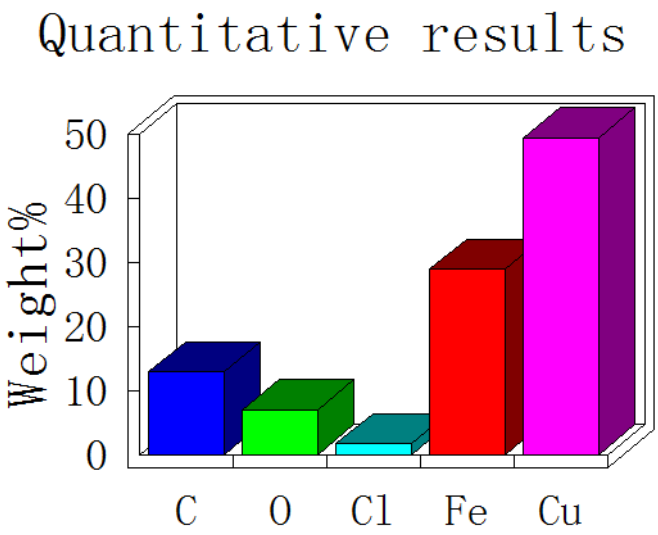



***Figure S6.*** EDX analysis of the NMPs in the xerogel **2a** (0.5 wt%) during the TEM study. (Fe element exists in the carbon-coated copper grids)

## 10. SEM Morphologies of gels formed by Cu(II)-pincer complexes 2a-2c with different solvents

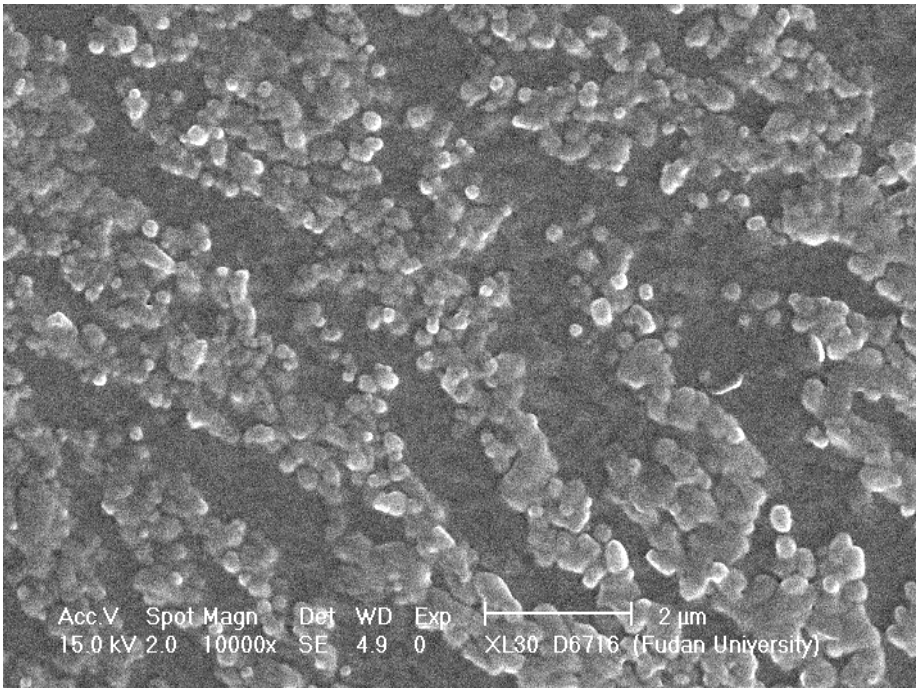



***Figure S7.*** SEM image of hydrogel **2a**/$H_2O$ (0.5 wt%) formed by heating and cooling procedure, scale of bar 2 µm.

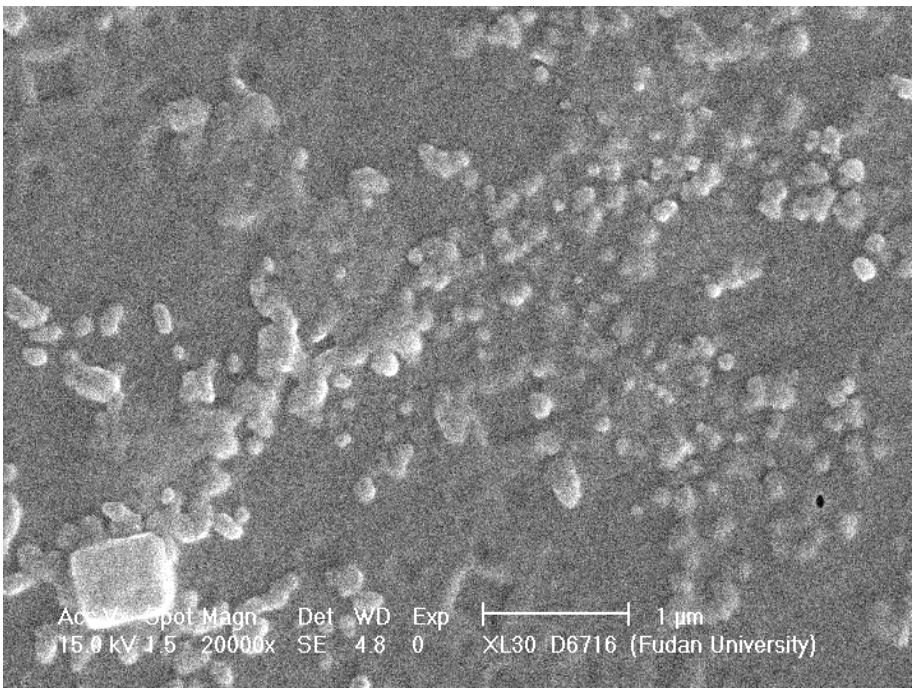



***Figure S8.*** SEM image of hydrogel **2a**/$H_2O$ (1.0 wt%) formed by stirring and resting procedure, scale of bar 1 µm.

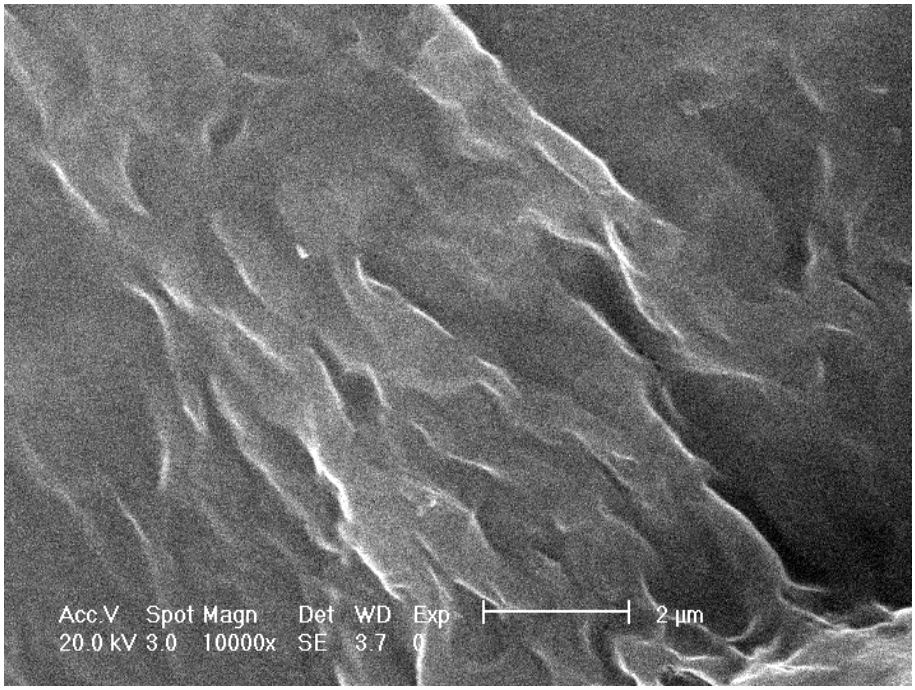



***Figure S9.*** SEM image of gel **2a**/1,2-Ethanediol (1.0 wt%), scale of bar 2 µm.

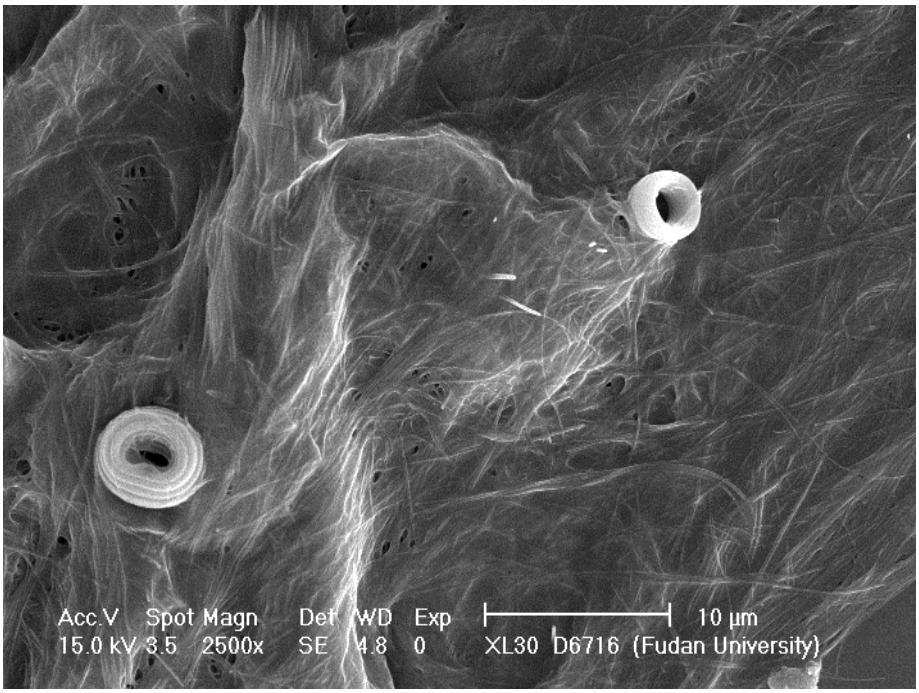



***Figure S10.*** SEM image of gel **2a**/1,3-propanediol (1.0 wt%), scale of bar 10 µm.

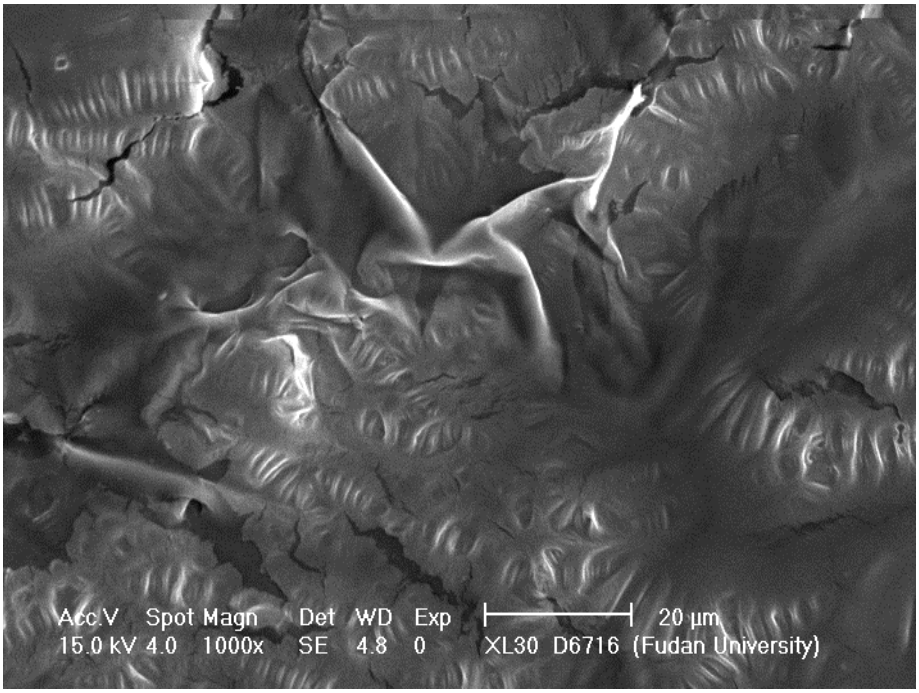



***Figure S11.*** SEM image of gel **2a**/ Glycerin (1.0 wt%), scale of bar 20 µm.

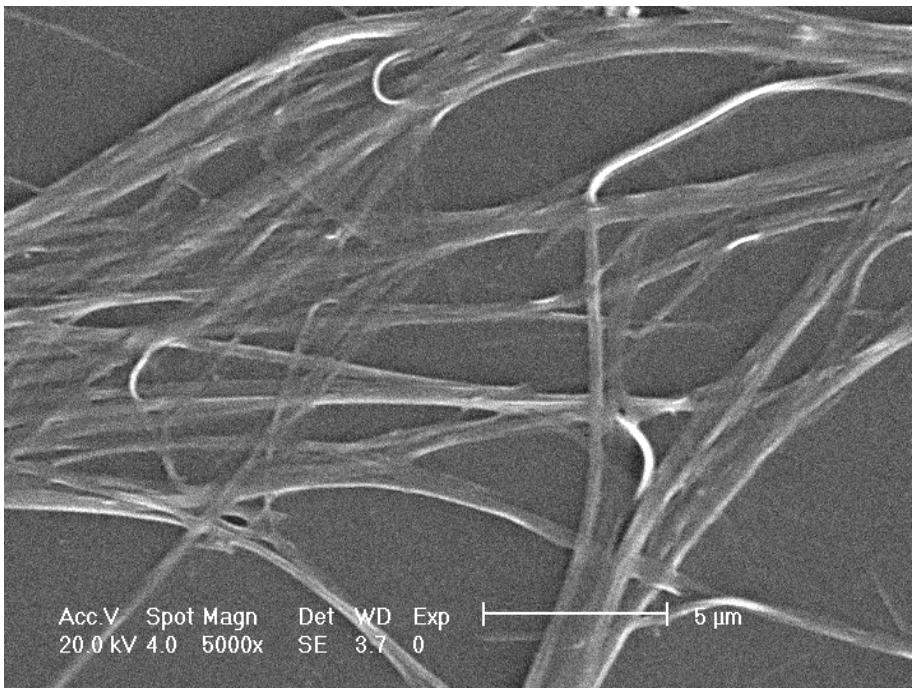



***Figure S12.*** SEM image of partial gel **2a**/ $H_2O$-acetone (1.0 wt%, V/V = 1:1), scale of bar 5 µm.

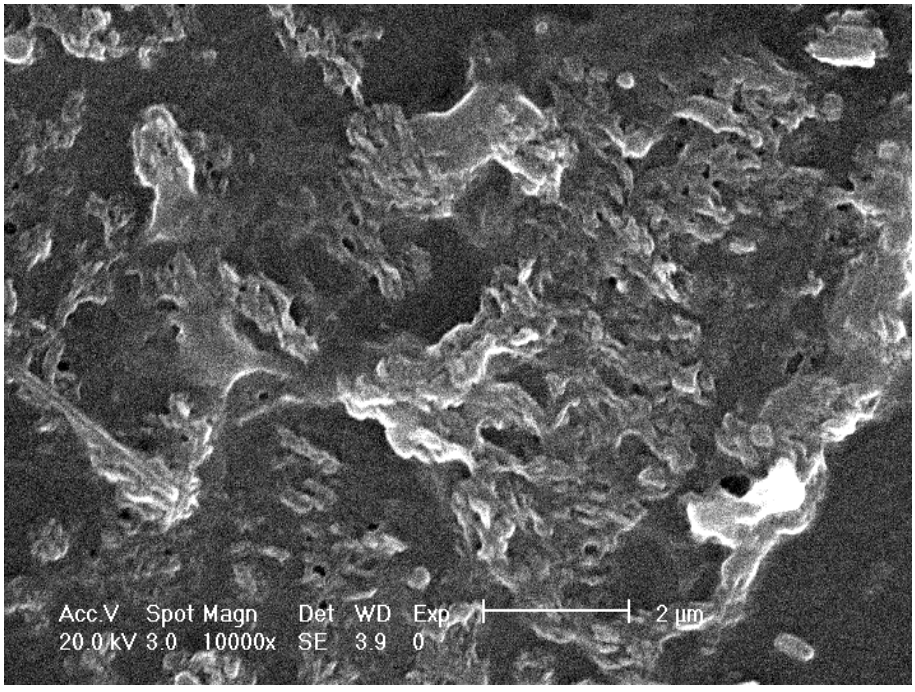



***Figure S13.*** SEM image of gel **2a**/ $H_2O$-AcOH (1.0 wt%, V/V = 1:1), scale of bar 2 µm.

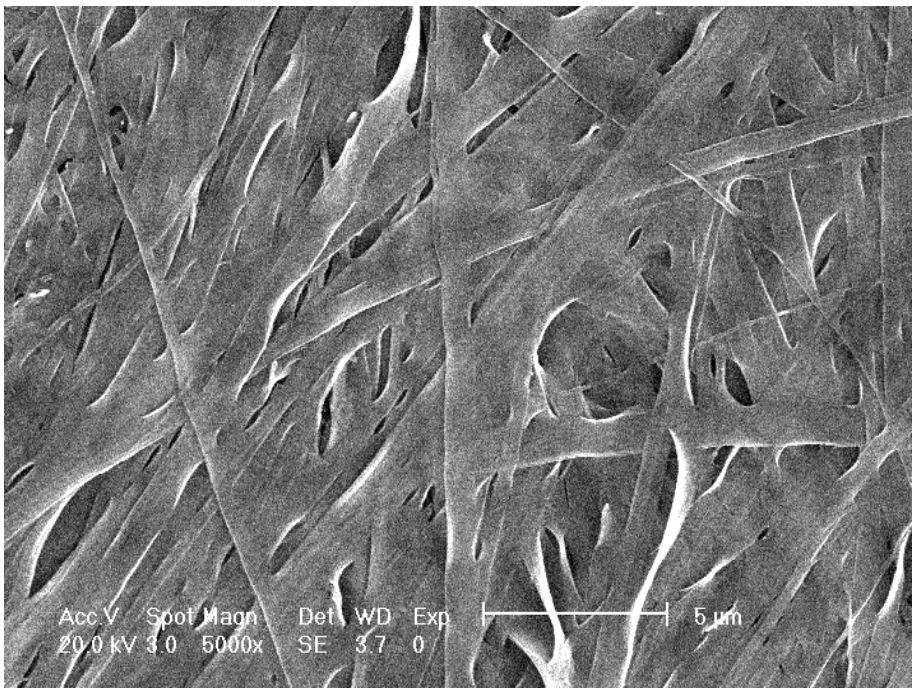



***Figure S14.*** SEM image of gel **2a**/ $H_2O$-DME (1.0 wt%, V/V = 1:1), scale of bar 5 µm.

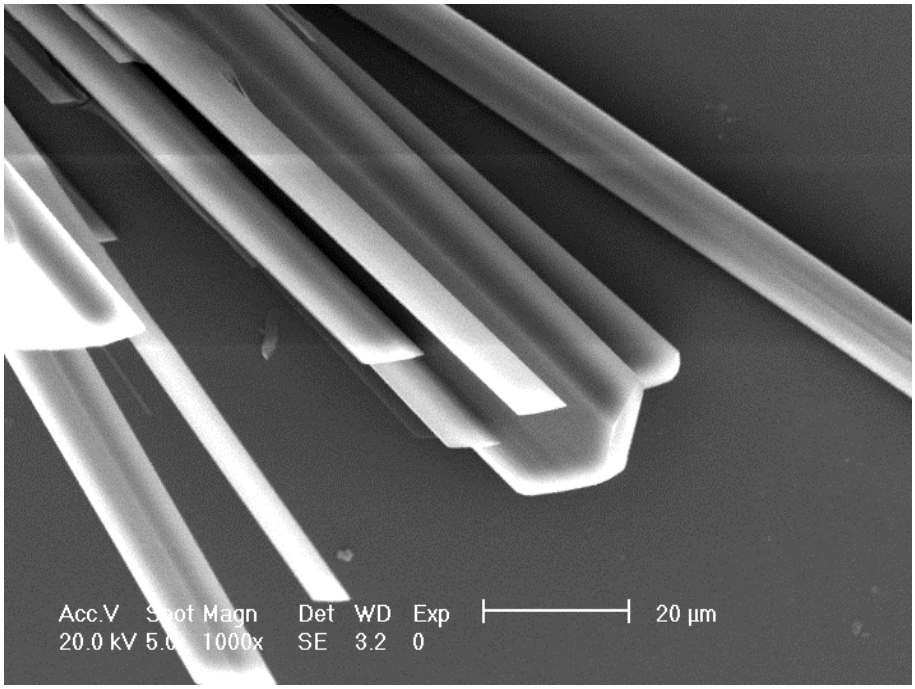



***Figure S15.*** SEM image of gel **2a**/ $H_2O$-DMSO (1.0 wt%, V/V = 1:1), scale of bar 20 µm.

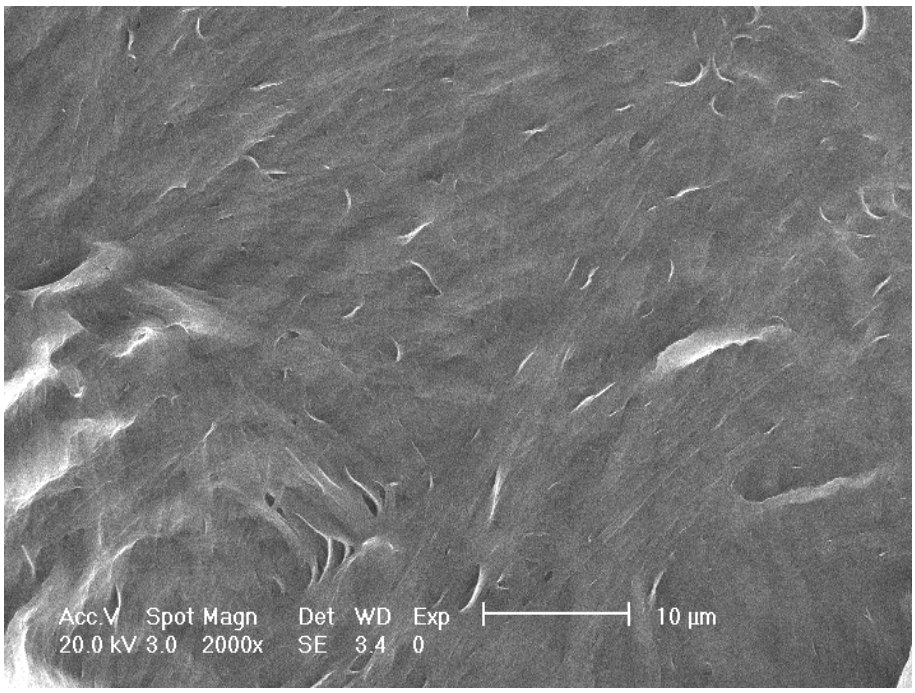



***Figure S16.*** SEM image of gel **2a**/ $H_2O$-EtOH (1.0 wt%, V/V = 1:1), scale of bar 10 µm.

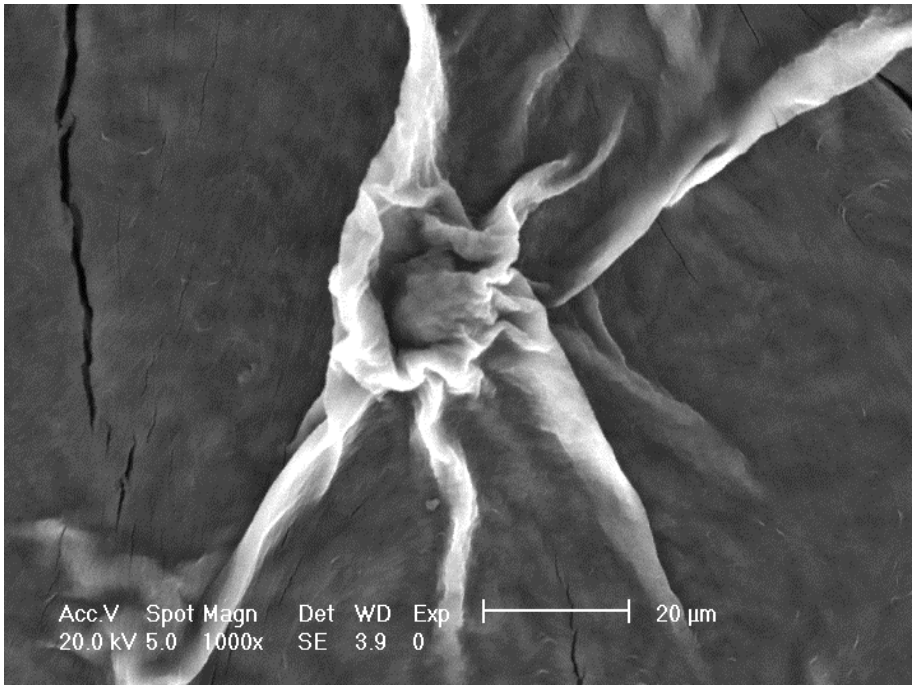



***Figure S17.*** SEM image of gel **2a**/ $H_2O$-MeOH (1.0 wt%, V/V = 1:1), scale of bar 20 µm.

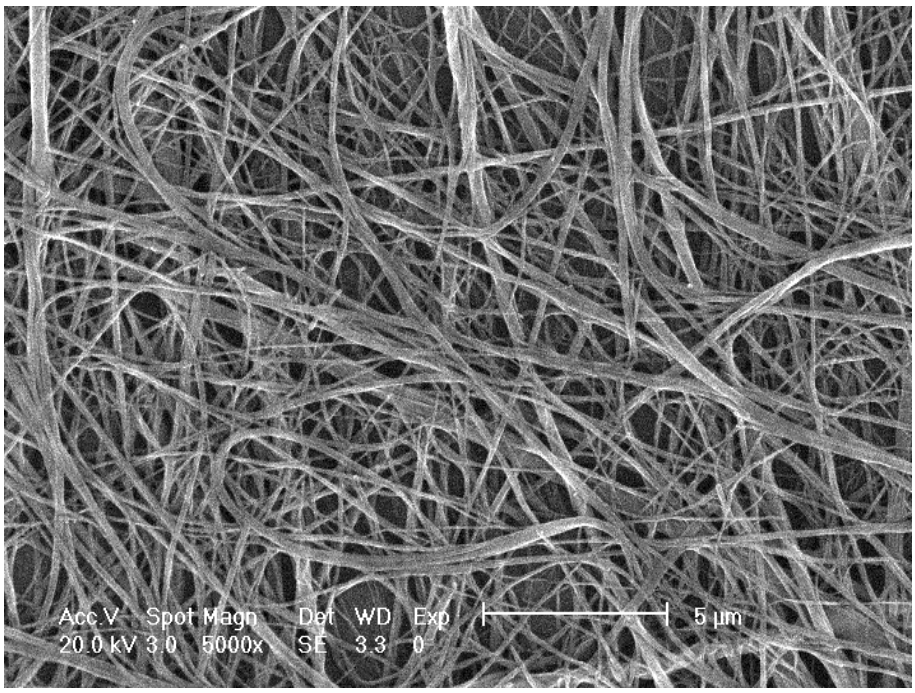



***Figure S18.*** SEM image of gel **2a**/ $H_2O$-NMP (1.0 wt%, V/V = 1:1), scale of bar 5 µm.

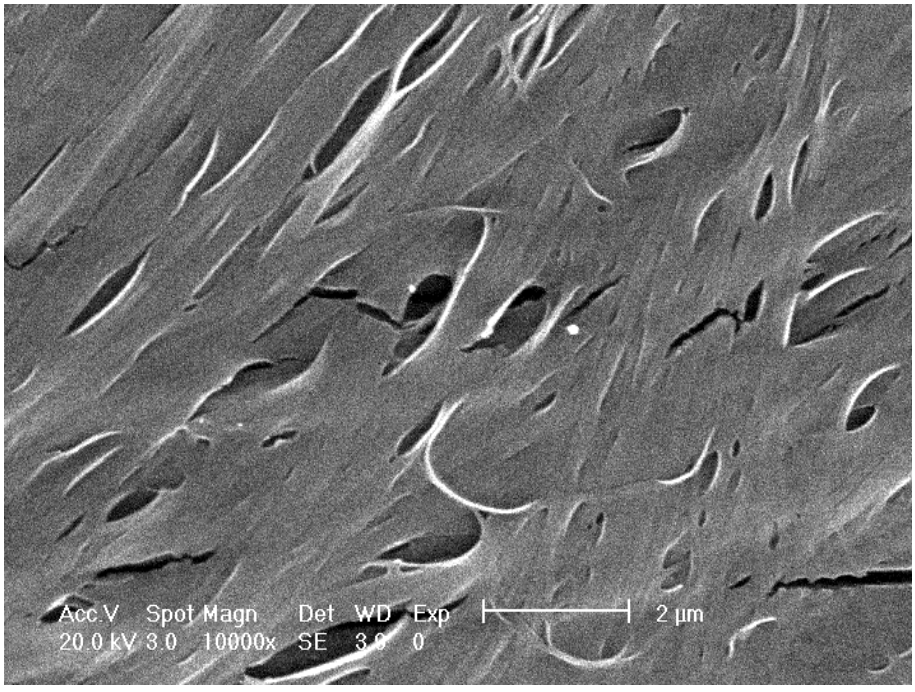



***Figure S19.*** SEM image of gel **2a**/ $H_2O$-*n*-PrOH (1.0 wt%, V/V = 1:1), scale of bar 2 µm.

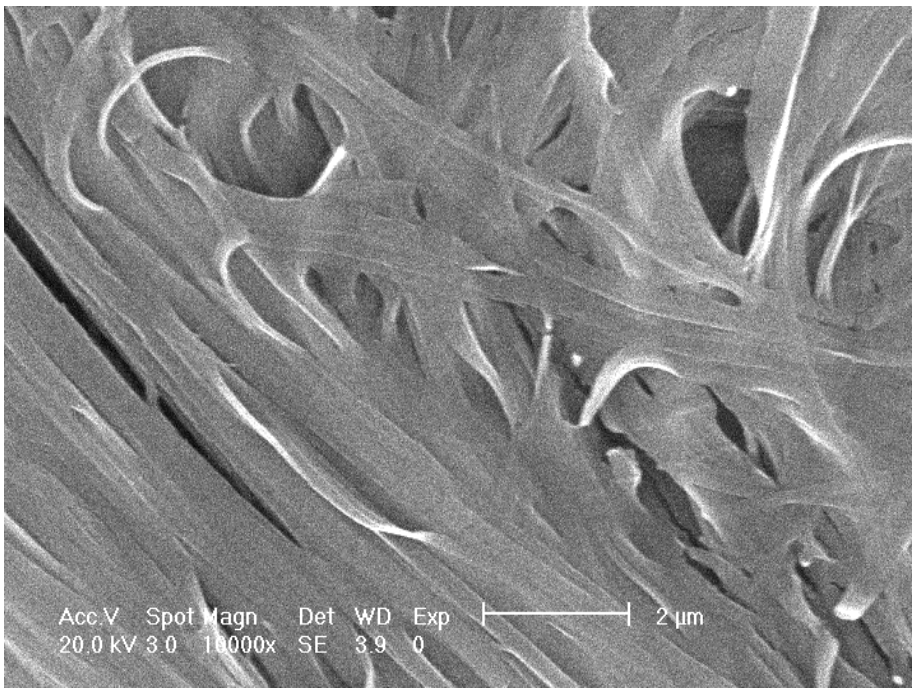



***Figure S20.*** SEM image of gel **2a**/ $H_2O$-*t*-BuOH (1.0 wt%, V/V = 1:1), scale of bar 2 µm.

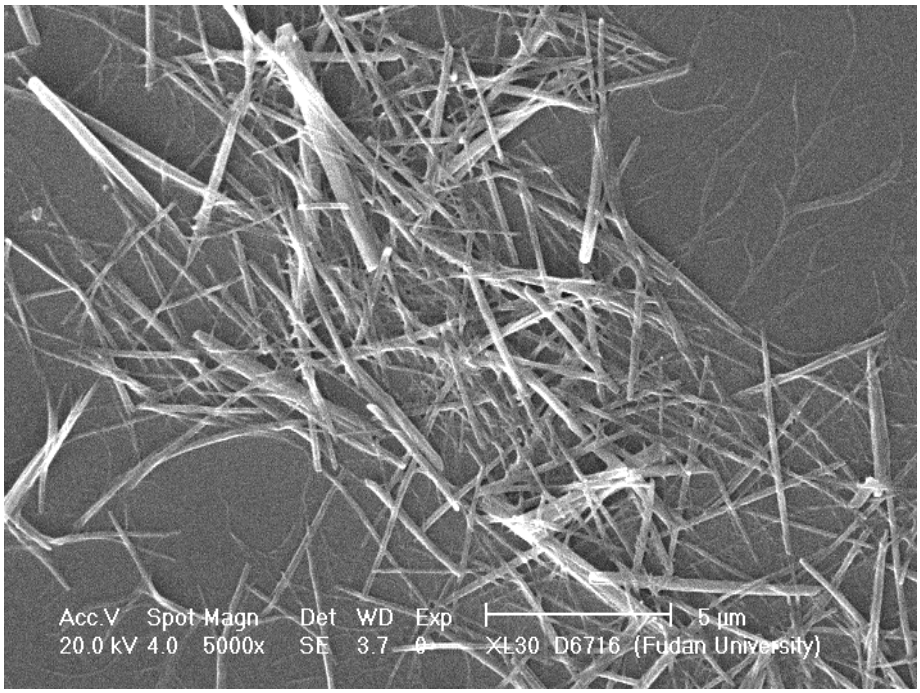



***Figure S21.*** SEM image of gel **2b**/ Glycerin (1.0 wt%), scale of bar 20 µm.

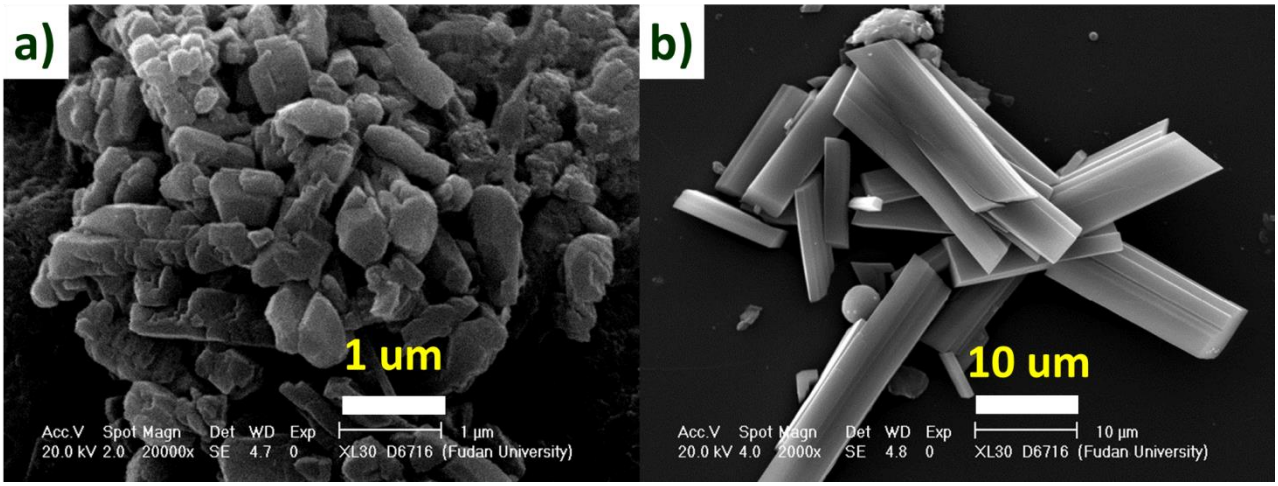



***Figure S22.*** SEM image of a) freshly prepared metallo-hydrogel **2c**/ $H_2O$ (1.0 wt%), scale of bar 1 μm and b) metallo-hydrogel **2c**/ $H_2O$ (1.0 wt%) aged for several hours, scale of bar 10 μm.

## 11. TEM Morphologies of gels formed by Cu(II)-pincer complex 2a with water.

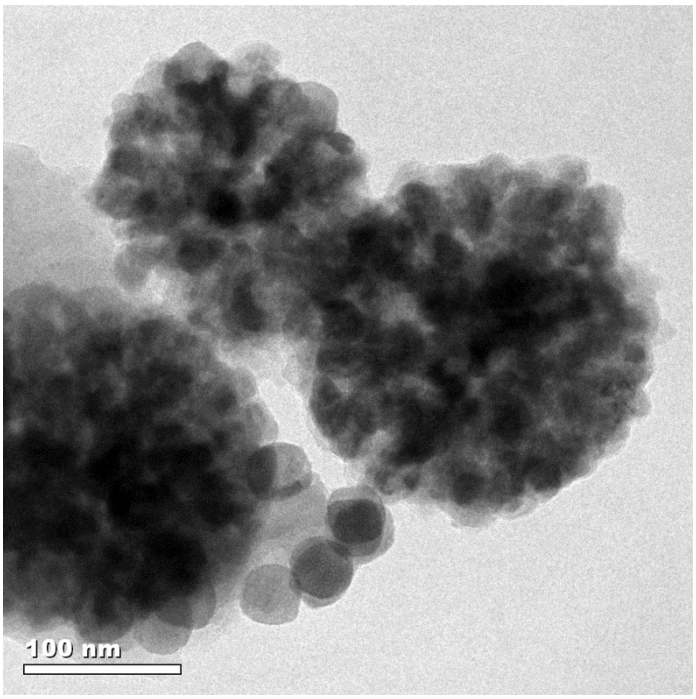



***Figure S23.*** TEM image of gel **2a**/ $H_2O$ (0.5 wt%), scale of bar 200 nm.

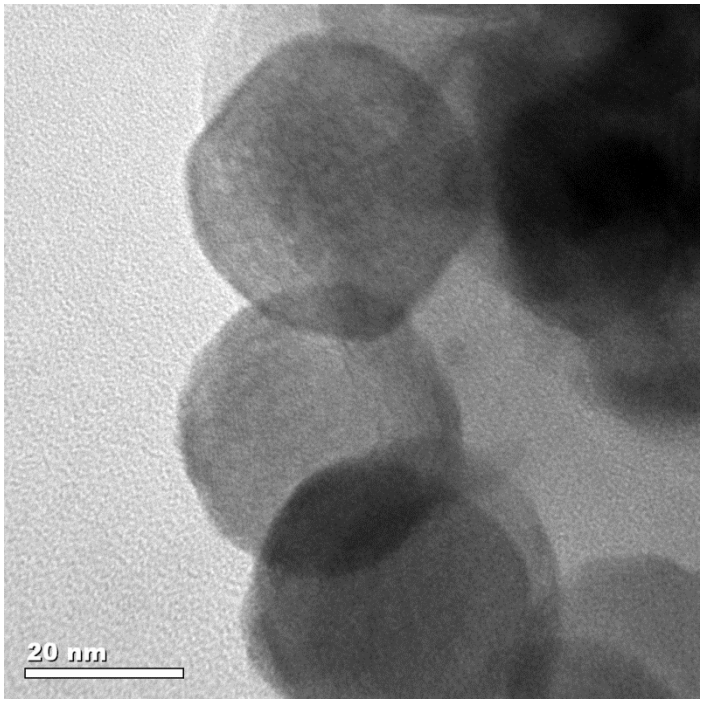



***Figure S24.*** TEM image of gel **2a**/ $H_2O$ (0.5 wt%), scale of bar 20 nm.

## 12. AFM Morphologies of gels formed by Cu(II)-pincer complexes 2a with water.

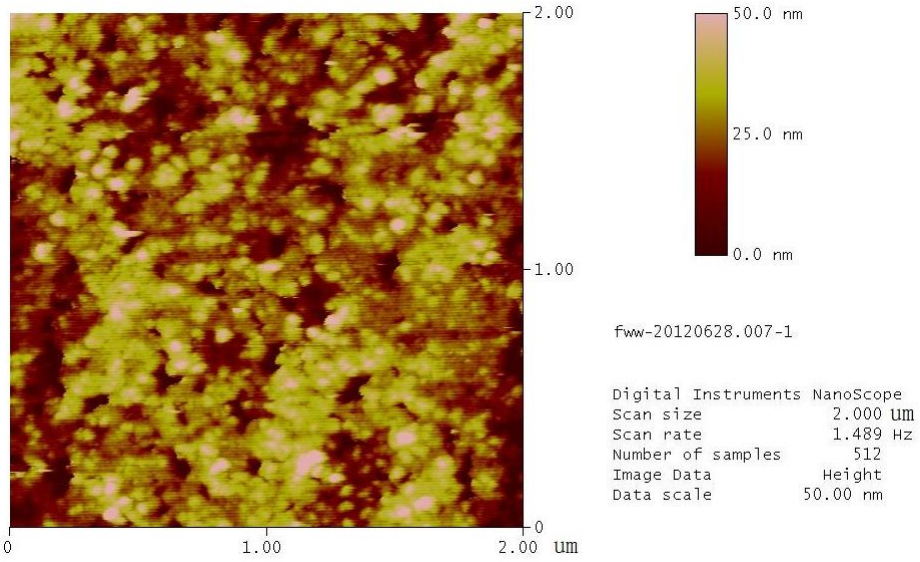



***Figure S25.*** AFM image of hydrogel **2a**/$H_2O$ (1.0 wt%), scale of bar 2 μm.

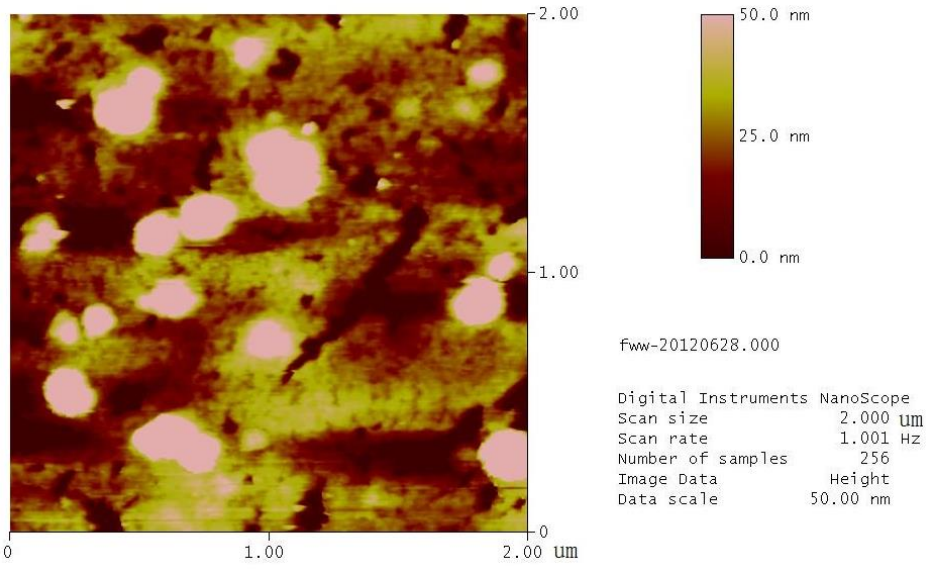



***Figure S26.*** AFM image of sol **2a**/$H_2O$ (1.0 wt%) by shaking, scale of bar 2 μm.

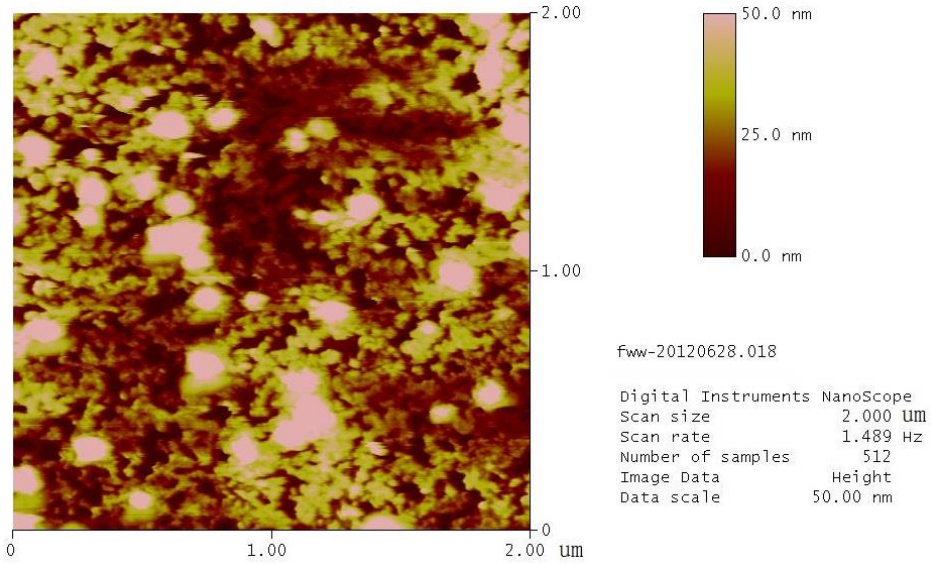



***Figure S27.*** AFM image of self-healing hydrogel **2a**/$H_2O$ (1.0 wt%) after resting for 20 hours, scale of bar 2 μm.

## 13. The direct gel reforming test from xerogel with additional water.

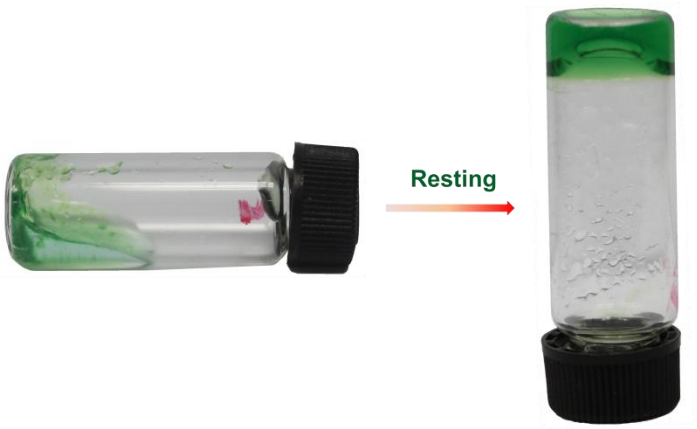



***Figure S28.*** a) 10 mg Xerogel in 0.5 mL $H_2O$ b) Gel directly reformed after resting for several hours.

## 14. Dynamic light scattering (DSL) study of complex 2a.

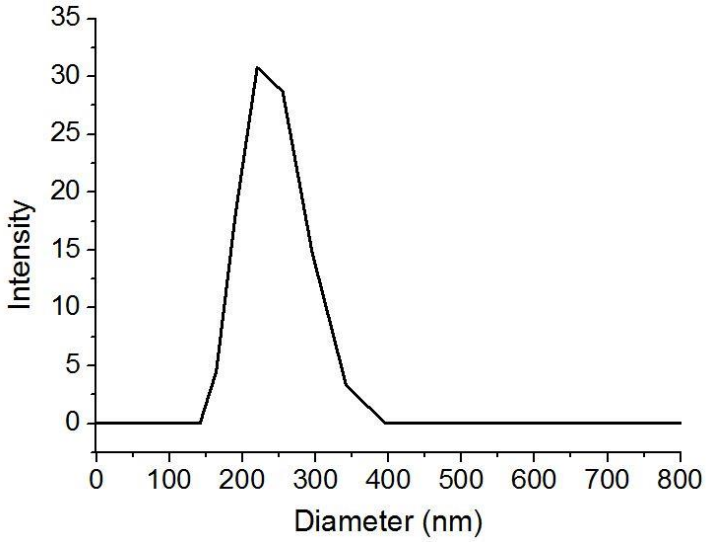



***Figure S29.*** Particle size and particle size distribution of the sol (0.25 wt%) diluted from metallo-hydrogel **2a** (0.5 wt%)

## 15. Viscoelasticity study of gels formed by Cu(II)-pincer complexes 2a with water

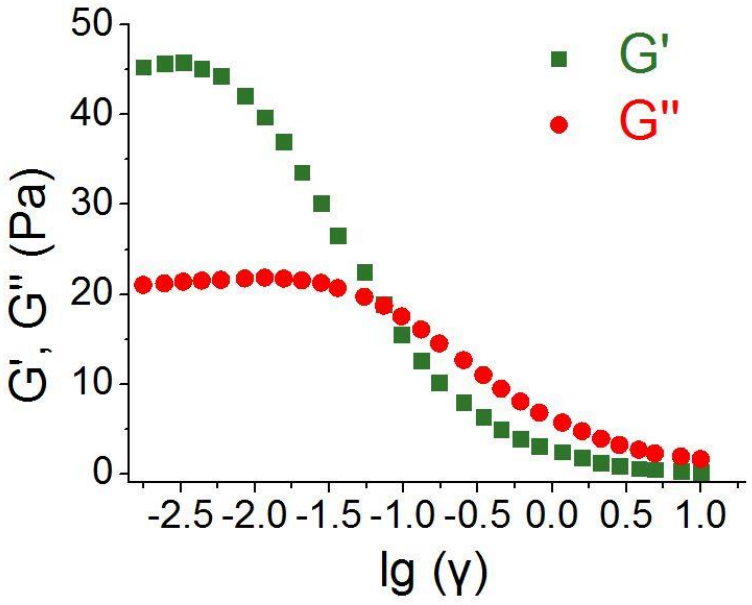



***Figure S30.*** Amplitude sweep rheometry data (storage modulus G' and loss modulus G" *vs.* shear strain γ) for hydrogel **2a** (2 wt%) at 25 °C (angular frequency: 6.283 rad s-1, strain: 0.001–100).

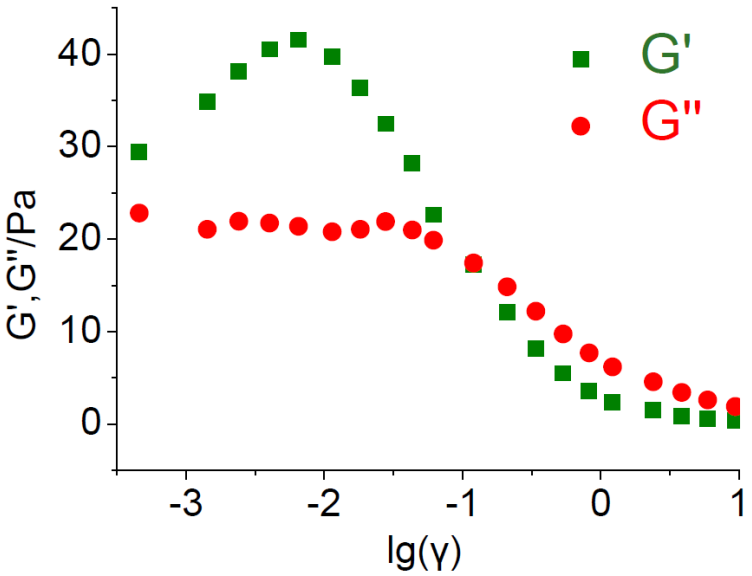



***Figure S31.*** Amplitude sweep rheometry data (storage modulus G' and loss modulus G" *vs.* shear strain γ) for self-healing hydrogel **2a** (2 wt%) after resting for 20 h at 25 °C (angular frequency: 6.283 rad s-1, strain: 0.001–100).

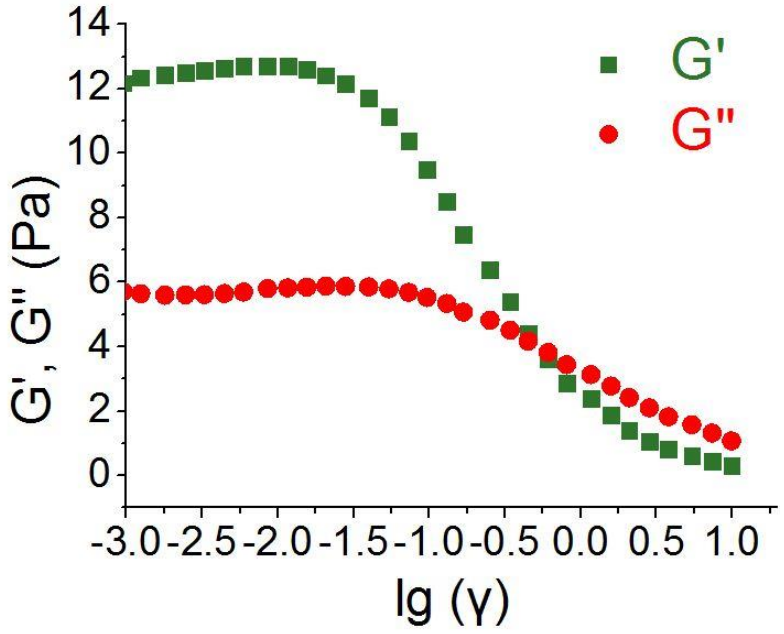



***Figure S32.*** Amplitude sweep rheometry data (storage modulus G' and loss modulus G" *vs.* shear strain γ) for sol **2a** (2 wt%) at 25 °C (angular frequency: 6.283 rad s-1, strain: 0.001–10).

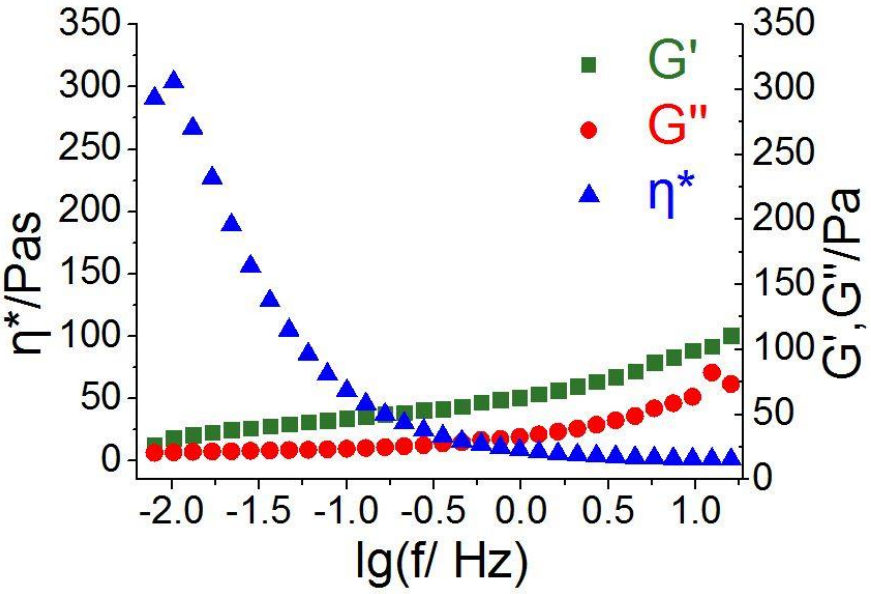



***Figure S33.*** Dynamic frequency sweep rheometry data for hydrogel **2a** (2 wt%) at 25 °C (angular frequency from 0.005–100 rad s-1, strain kept at 0.5 % without deformation, storage modulus (G') > loss modulus (G"), η*: complex viscosity).

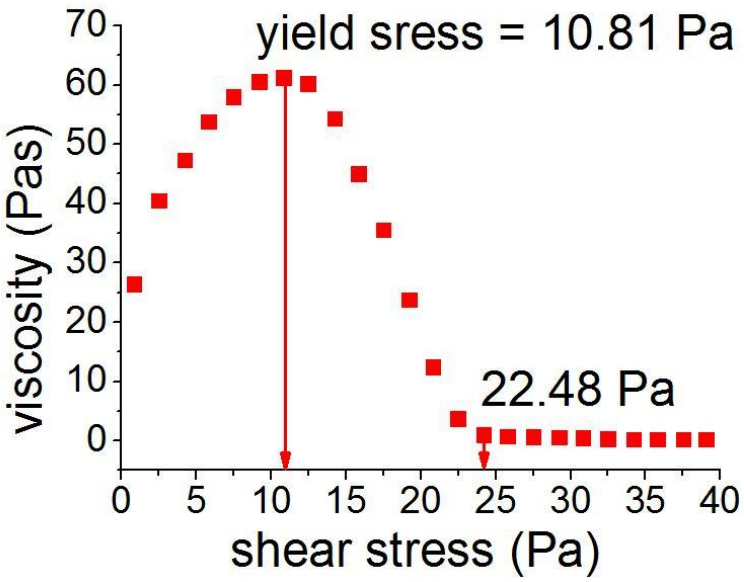



***Figure S34.*** Yield stress test for hydrogel **2a** (2 wt%) at 25 °C (viscosity (Pas) *vs.* shear stress (Pa)).

## 16. Crystal structure information:

### 16.1. Cu(II)-pincer complex 2a·MeOH.

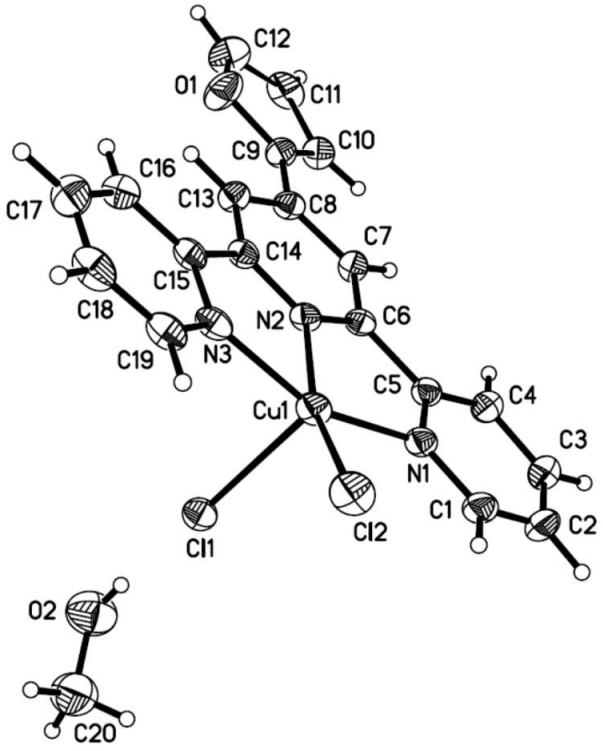



***Figure S35.*** Molecular structure of complex **2a**•MeOH.

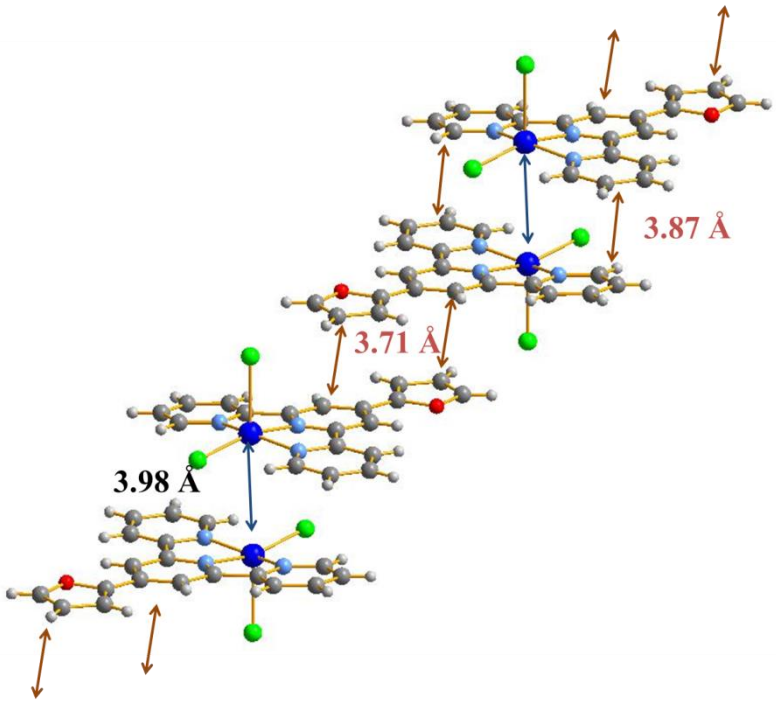



***Figure S36.*** Interactions between the molecules of **2a** (1).

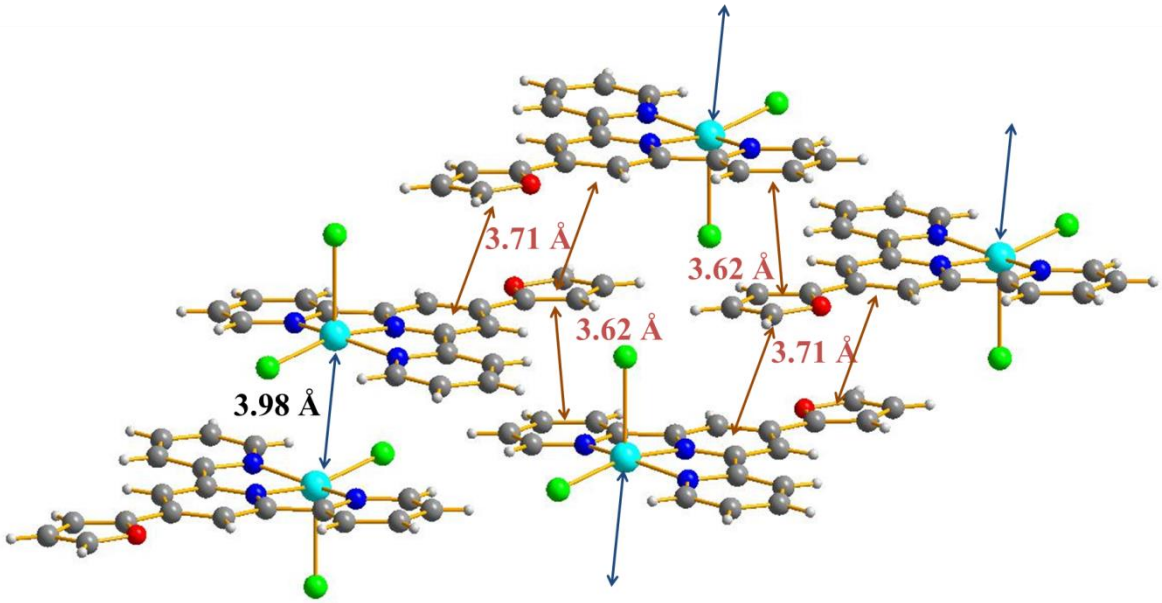



***Figure S37.*** Interactions between the molecules of **2a** (2).

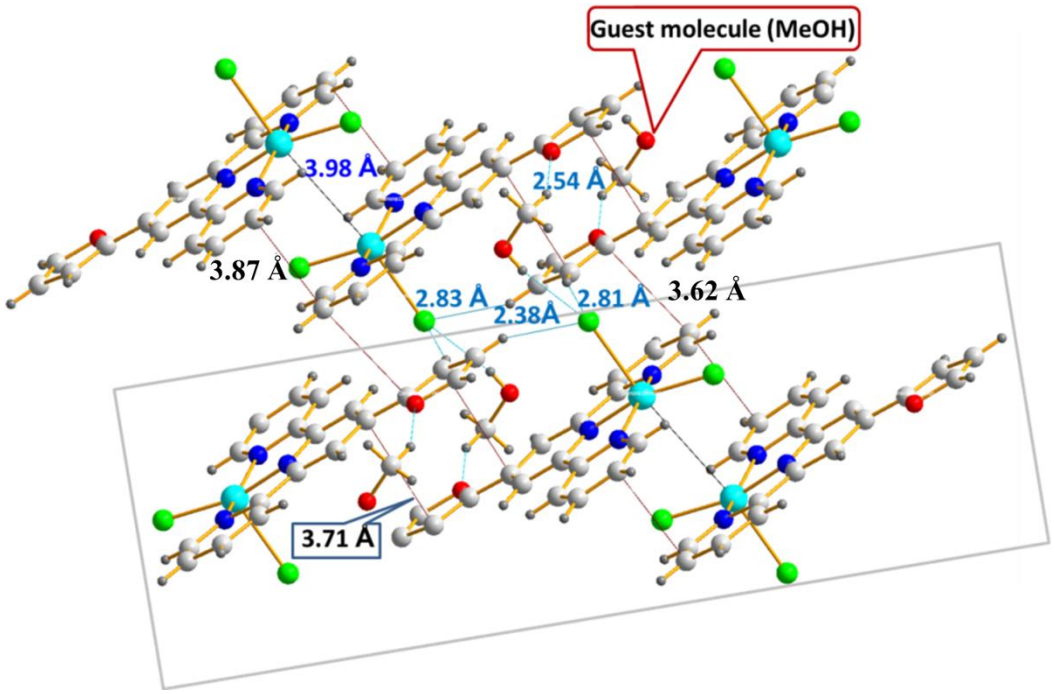



***Figure S38.*** Interactions between the molecules (Complex **2a**) and guest (MeOH).

***Table S3***. Crystal data and structure refinement for Cu(II)-pincer complex **2a**•MeOH.

| | |
|---|---|
| Identification code | Cu(II)-pincer complex **2a**•MeOH |
| Empirical formula | C20 H17 Cl2 Cu N3 O2 |
| Formula weight | 465.81 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 7.923(2) A alpha = 106.831(4) deg.<br>b = 10.679(3) A beta = 97.456(4) deg.<br>c = 12.643(4) A gamma = 102.720(4) deg. |
| Volume | 977.1(5) A^3 |
| Z, Calculated density | 2, 1.583 Mg/m^3 |
| Absorption coefficient | 1.412 mm^-1 |
| F(000) | 474 |
| Crystal size | 0.25 x 0.10 x 0.05 mm |
| Theta range for data collection | 2.07 to 25.02 deg. |
| Limiting indices | -9<=h<=9, -12<=k<=12, -15<=l<=14 |
| Reflections collected / unique | 4827 / 3389 [R(int) = 0.0282] |
| Completeness to theta = 25.02 | 98.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9327 and 0.7191 |
| Refinement method | Full-matrix least-squares on F^2 |

| | |
|---|---|
| Data / restraints / parameters | 3389 / 0 / 255 |
| Goodness-of-fit on F^2 | 0.972 |
| Final R indices [I>2sigma(I)] | R1 = 0.0405, wR2 = 0.0936 |
| R indices (all data) | R1 = 0.0584, wR2 = 0.1049 |
| Largest diff. peak and hole | 0.436 and -0.323 e.A^-3 |

***Table S4.*** Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **2a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cu(1) | 5882(1) | 6126(1) | 9073(1) | 40(1) |
| N(1) | 4558(4) | 7512(3) | 9754(2) | 38(1) |
| N(2) | 3610(3) | 5370(3) | 8015(2) | 33(1) |
| N(3) | 6161(4) | 4291(3) | 8158(2) | 39(1) |
| Cl(1) | 7341(1) | 7434(1) | 7834(1) | 43(1) |
| Cl(2) | 8089(1) | 6668(1) | 10541(1) | 59(1) |
| C(1) | 5140(5) | 8588(4) | 10683(3) | 48(1) |
| C(2) | 4183(6) | 9489(4) | 11036(3) | 54(1) |
| C(3) | 2542(6) | 9258(4) | 10420(3) | 51(1) |
| C(4) | 1875(5) | 8149(4) | 9454(3) | 45(1) |
| C(5) | 2913(5) | 7298(3) | 9141(3) | 37(1) |
| C(6) | 2385(4) | 6059(3) | 8129(3) | 33(1) |
| C(7) | 793(5) | 5596(3) | 7365(3) | 37(1) |
| C(8) | 489(5) | 4402(3) | 6457(3) | 38(1) |
| C(9) | -1137(5) | 3928(4) | 5638(3) | 41(1) |
| C(10) | -2488(5) | 4468(4) | 5488(3) | 45(1) |
| C(11) | -3737(5) | 3549(5) | 4529(3) | 56(1) |
| C(12) | -3049(6) | 2517(5) | 4151(4) | 72(1) |
| C(13) | 1767(5) | 3678(4) | 6382(3) | 38(1) |
| C(14) | 3318(4) | 4190(3) | 7186(3) | 34(1) |
| C(15) | 4781(4) | 3556(4) | 7273(3) | 36(1) |
| C(16) | 4793(5) | 2318(4) | 6551(3) | 46(1) |
| C(17) | 6224(6) | 1810(4) | 6728(4) | 56(1) |
| C(18) | 7617(5) | 2575(4) | 7625(4) | 54(1) |
| C(19) | 7552(5) | 3791(4) | 8313(3) | 44(1) |
| O(2) | 8187(5) | 9108(4) | 6157(3) | 93(1) |
| C(20) | 9920(7) | 9865(5) | 6623(5) | 105(2) |
| O(1) | -1443(4) | 2706(3) | 4813(2) | 65(1) |

***Table S5.*** Bond lengths [A] and angles [deg] for Cu(II)-pincer complex **2a**•MeOH.

| | |
|---|---|
| Cu(1)-N(2) | 1.947(3) |
| Cu(1)-N(3) | 2.043(3) |
| Cu(1)-N(1) | 2.052(3) |
| Cu(1)-Cl(2) | 2.2192(11) |
| Cu(1)-Cl(1) | 2.6006(11) |
| N(1)-C(1) | 1.326(4) |
| N(1)-C(5) | 1.362(4) |
| N(2)-C(14) | 1.336(4) |
| N(2)-C(6) | 1.339(4) |
| N(3)-C(19) | 1.343(4) |
| N(3)-C(15) | 1.363(4) |
| C(1)-C(2) | 1.364(6) |
| C(1)-H(1) | 0.9300 |
| C(2)-C(3) | 1.358(5) |
| C(2)-H(2) | 0.9300 |
| C(3)-C(4) | 1.376(5) |
| C(3)-H(3) | 0.9300 |
| C(4)-C(5) | 1.366(5) |
| C(4)-H(4) | 0.9300 |
| C(5)-C(6) | 1.483(5) |
| C(6)-C(7) | 1.379(4) |
| C(7)-C(8) | 1.395(5) |
| C(7)-H(7) | 0.9300 |
| C(8)-C(13) | 1.400(5) |
| C(8)-C(9) | 1.432(5) |
| C(9)-C(10) | 1.340(5) |
| C(9)-O(1) | 1.362(4) |
| C(10)-C(11) | 1.409(5) |
| C(10)-H(10) | 0.9300 |
| C(11)-C(12) | 1.329(6) |
| C(11)-H(11) | 0.9300 |
| C(12)-O(1) | 1.369(5) |
| C(12)-H(12) | 0.9300 |
| C(13)-C(14) | 1.378(4) |
| C(13)-H(13) | 0.9300 |
| C(14)-C(15) | 1.473(4) |
| C(15)-C(16) | 1.375(5) |
| C(16)-C(17) | 1.381(5) |
| C(16)-H(16) | 0.9300 |
| C(17)-C(18) | 1.383(6) |

| | |
|---|---|
| C(17)-H(17) | 0.9300 |
| C(18)-C(19) | 1.354(5) |
| C(18)-H(18) | 0.9300 |
| C(19)-H(19) | 0.9300 |
| O(2)-C(20) | 1.382(6) |
| O(2)-H(2A) | 0.8200 |
| C(20)-H(20A) | 0.9600 |
| C(20)-H(20B) | 0.9600 |
| C(20)-H(20C) | 0.9600 |
| N(2)-Cu(1)-N(3) | 79.38(11) |
| N(2)-Cu(1)-N(1) | 79.37(12) |
| N(3)-Cu(1)-N(1) | 156.70(11) |
| N(2)-Cu(1)-Cl(2) | 164.37(9) |
| N(3)-Cu(1)-Cl(2) | 99.04(8) |
| N(1)-Cu(1)-Cl(2) | 98.84(9) |
| N(2)-Cu(1)-Cl(1) | 93.90(9) |
| N(3)-Cu(1)-Cl(1) | 94.74(9) |
| N(1)-Cu(1)-Cl(1) | 96.12(9) |
| Cl(2)-Cu(1)-Cl(1) | 101.73(4) |
| C(1)-N(1)-C(5) | 117.7(3) |
| C(1)-N(1)-Cu(1) | 127.6(3) |
| C(5)-N(1)-Cu(1) | 114.6(2) |
| C(14)-N(2)-C(6) | 121.6(3) |
| C(14)-N(2)-Cu(1) | 119.4(2) |
| C(6)-N(2)-Cu(1) | 119.0(2) |
| C(19)-N(3)-C(15) | 118.9(3) |
| C(19)-N(3)-Cu(1) | 127.2(3) |
| C(15)-N(3)-Cu(1) | 113.9(2) |
| N(1)-C(1)-C(2) | 123.1(4) |
| N(1)-C(1)-H(1) | 118.5 |
| C(2)-C(1)-H(1) | 118.5 |
| C(3)-C(2)-C(1) | 118.5(4) |
| C(3)-C(2)-H(2) | 120.8 |
| C(1)-C(2)-H(2) | 120.8 |
| C(2)-C(3)-C(4) | 120.6(4) |
| C(2)-C(3)-H(3) | 119.7 |
| C(4)-C(3)-H(3) | 119.7 |
| C(5)-C(4)-C(3) | 117.9(4) |
| C(5)-C(4)-H(4) | 121.0 |
| C(3)-C(4)-H(4) | 121.0 |
| N(1)-C(5)-C(4) | 122.2(3) |
| N(1)-C(5)-C(6) | 113.3(3) |
| C(4)-C(5)-C(6) | 124.5(3) |
| N(2)-C(6)-C(7) | 120.9(3) |

| | |
|---|---|
| N(2)-C(6)-C(5) | 113.5(3) |
| C(7)-C(6)-C(5) | 125.6(3) |
| C(6)-C(7)-C(8) | 118.7(3) |
| C(6)-C(7)-H(7) | 120.6 |
| C(8)-C(7)-H(7) | 120.6 |
| C(7)-C(8)-C(13) | 119.1(3) |
| C(7)-C(8)-C(9) | 119.4(3) |
| C(13)-C(8)-C(9) | 121.5(3) |
| C(10)-C(9)-O(1) | 109.9(3) |
| C(10)-C(9)-C(8) | 132.5(3) |
| O(1)-C(9)-C(8) | 117.6(3) |
| C(9)-C(10)-C(11) | 107.7(4) |
| C(9)-C(10)-H(10) | 126.2 |
| C(11)-C(10)-H(10) | 126.2 |
| C(12)-C(11)-C(10) | 105.5(4) |
| C(12)-C(11)-H(11) | 127.2 |
| C(10)-C(11)-H(11) | 127.2 |
| C(11)-C(12)-O(1) | 111.6(4) |
| C(11)-C(12)-H(12) | 124.2 |
| O(1)-C(12)-H(12) | 124.2 |
| C(14)-C(13)-C(8) | 119.0(3) |
| C(14)-C(13)-H(13) | 120.5 |
| C(8)-C(13)-H(13) | 120.5 |
| N(2)-C(14)-C(13) | 120.5(3) |
| N(2)-C(14)-C(15) | 112.5(3) |
| C(13)-C(14)-C(15) | 127.0(3) |
| N(3)-C(15)-C(16) | 121.1(3) |
| N(3)-C(15)-C(14) | 114.5(3) |
| C(16)-C(15)-C(14) | 124.4(3) |
| C(15)-C(16)-C(17) | 119.4(4) |
| C(15)-C(16)-H(16) | 120.3 |
| C(17)-C(16)-H(16) | 120.3 |
| C(16)-C(17)-C(18) | 118.7(4) |
| C(16)-C(17)-H(17) | 120.7 |
| C(18)-C(17)-H(17) | 120.7 |
| C(19)-C(18)-C(17) | 120.0(4) |
| C(19)-C(18)-H(18) | 120.0 |
| C(17)-C(18)-H(18) | 120.0 |
| N(3)-C(19)-C(18) | 122.0(4) |
| N(3)-C(19)-H(19) | 119.0 |
| C(18)-C(19)-H(19) | 119.0 |
| C(20)-O(2)-H(2A) | 109.5 |
| O(2)-C(20)-H(20A) | 109.5 |
| O(2)-C(20)-H(20B) | 109.5 |

| | |
|---|---|
| H(20A)-C(20)-H(20B) | 109.5 |
| O(2)-C(20)-H(20C) | 109.5 |
| H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 |
| C(9)-O(1)-C(12) | 105.3(3) |

Symmetry transformations used to generate equivalent atoms:

***Table S6.*** Anisotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **2a•**MeOH**.** The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Cu(1) | 26(1) | 51(1) | 39(1) | 15(1) | -2(1) | 7(1) |
| N(1) | 30(2) | 43(2) | 35(2) | 11(1) | 1(1) | 3(1) |
| N(2) | 18(2) | 41(2) | 36(2) | 11(1) | -1(1) | 5(1) |
| N(3) | 23(2) | 49(2) | 49(2) | 24(2) | 4(1) | 9(1) |
| Cl(1) | 35(1) | 47(1) | 45(1) | 15(1) | 4(1) | 10(1) |
| Cl(2) | 40(1) | 85(1) | 47(1) | 25(1) | -9(1) | 11(1) |
| C(1) | 44(2) | 50(2) | 37(2) | 10(2) | 0(2) | -2(2) |
| C(2) | 62(3) | 45(2) | 38(2) | 2(2) | 4(2) | 1(2) |
| C(3) | 54(3) | 45(2) | 50(2) | 8(2) | 14(2) | 13(2) |
| C(4) | 46(2) | 42(2) | 45(2) | 10(2) | 9(2) | 10(2) |
| C(5) | 33(2) | 39(2) | 35(2) | 12(2) | 5(2) | 5(2) |
| C(6) | 25(2) | 36(2) | 37(2) | 13(2) | 3(2) | 4(2) |
| C(7) | 30(2) | 44(2) | 36(2) | 11(2) | 3(2) | 13(2) |
| C(8) | 33(2) | 39(2) | 36(2) | 14(2) | 1(2) | 4(2) |
| C(9) | 38(2) | 44(2) | 36(2) | 9(2) | 2(2) | 6(2) |
| C(10) | 34(2) | 54(2) | 43(2) | 14(2) | 0(2) | 12(2) |
| C(11) | 21(2) | 86(3) | 57(3) | 28(2) | -6(2) | 10(2) |
| C(12) | 51(3) | 84(3) | 46(3) | -1(2) | -20(2) | -5(3) |
| C(13) | 33(2) | 40(2) | 37(2) | 10(2) | 1(2) | 10(2) |
| C(14) | 26(2) | 37(2) | 41(2) | 15(2) | 7(2) | 9(2) |
| C(15) | 24(2) | 44(2) | 46(2) | 22(2) | 8(2) | 12(2) |
| C(16) | 42(2) | 45(2) | 54(2) | 20(2) | 7(2) | 11(2) |
| C(17) | 60(3) | 50(3) | 69(3) | 25(2) | 20(2) | 27(2) |
| C(18) | 33(2) | 69(3) | 77(3) | 41(3) | 14(2) | 26(2) |
| C(19) | 26(2) | 58(3) | 57(2) | 31(2) | 6(2) | 14(2) |
| O(2) | 92(3) | 93(3) | 94(3) | 44(2) | 11(2) | 14(2) |
| C(20) | 82(4) | 72(4) | 149(6) | 13(4) | 40(4) | 19(3) |
| O(1) | 55(2) | 63(2) | 53(2) | -8(2) | -11(2) | 16(2) |

***Table S7.*** Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **2a**•MeOH.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 6253 | 8735 | 11115 | 57 |
| H(2) | 4645 | 10245 | 11683 | 65 |
| H(3) | 1862 | 9854 | 10654 | 62 |
| H(4) | 752 | 7985 | 9027 | 55 |
| H(7) | -61 | 6070 | 7452 | 44 |
| H(10) | -2583 | 5300 | 5936 | 54 |
| H(11) | -4816 | 3645 | 4224 | 67 |
| H(12) | -3591 | 1761 | 3515 | 86 |
| H(13) | 1572 | 2863 | 5799 | 45 |
| H(16) | 3845 | 1827 | 5949 | 55 |
| H(17) | 6250 | 969 | 6255 | 67 |
| H(18) | 8599 | 2255 | 7754 | 64 |
| H(19) | 8500 | 4295 | 8912 | 53 |
| H(2A) | 7836 | 8672 | 6560 | 140 |
| H(20A) | 10242 | 10530 | 6259 | 158 |
| H(20B) | 10684 | 9275 | 6518 | 158 |
| H(20C) | 10037 | 10316 | 7416 | 158 |

**16.2. Cu(II)-pincer complex 2a Glycol.**

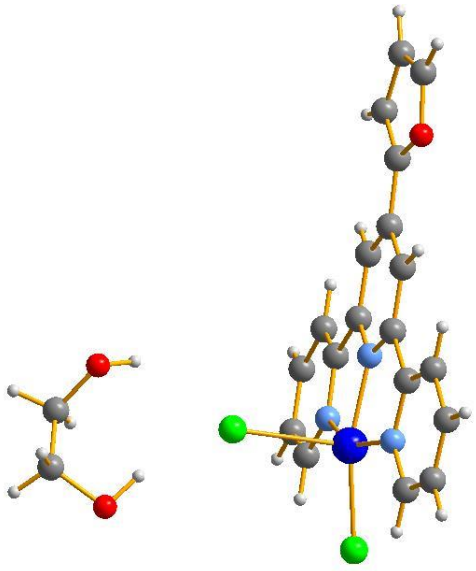


***Figure S39.*** Molecular structure of complex 2a• Glycol.

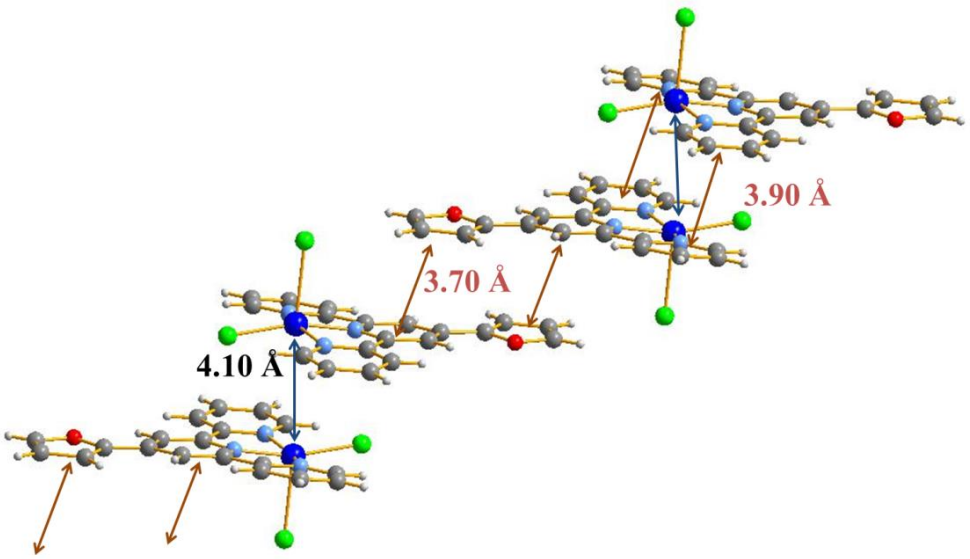



***Figure S40.*** Interactions between the molecules of 2a (1).

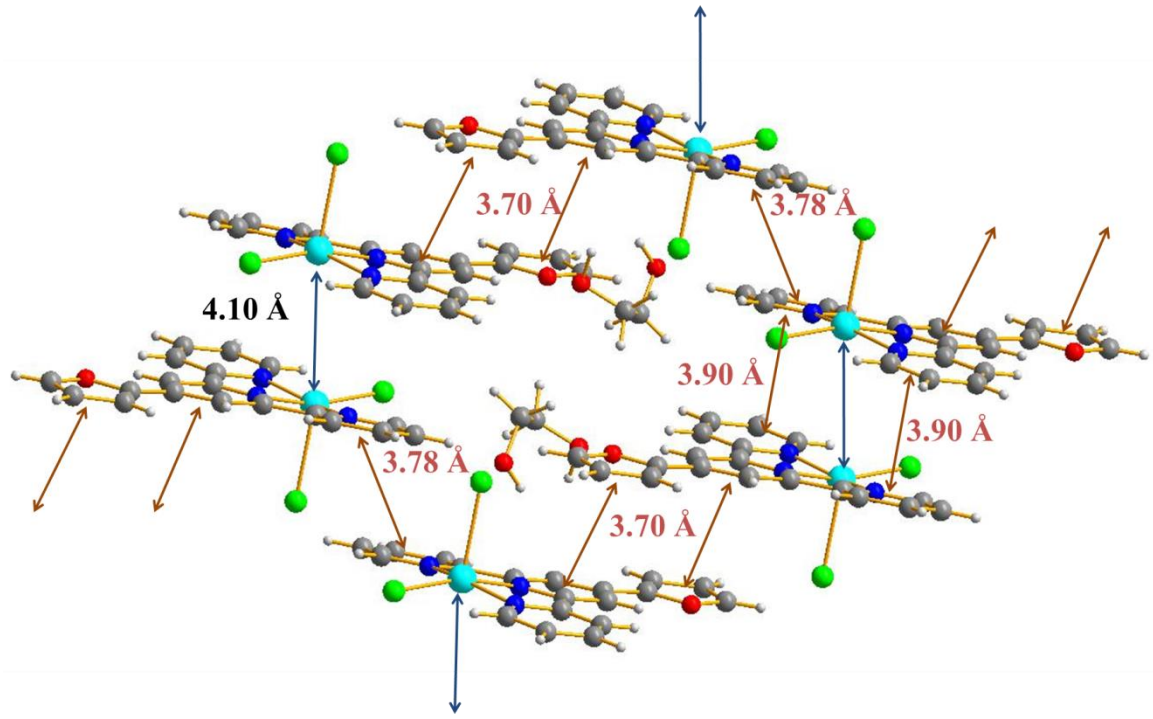



***Figure S41.*** Interactions between the molecules of 2a (2).

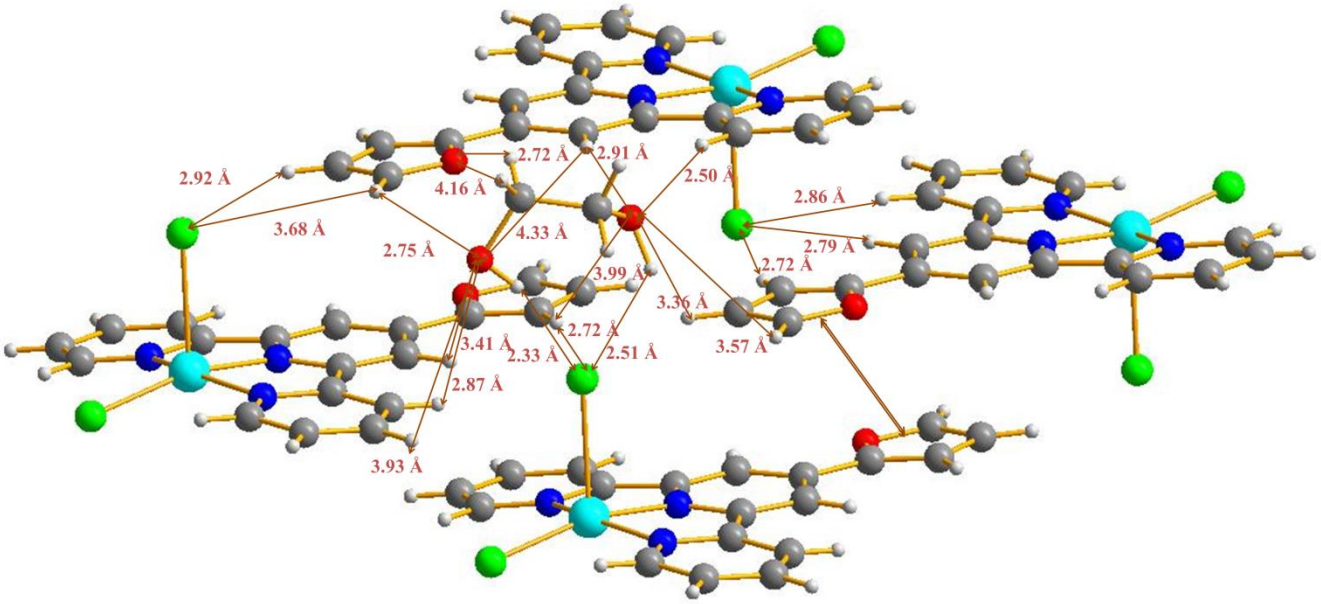



***Figure S42.*** Interactions between the molecules (Complex 2a) and guest (Glycol).

***Table S8.*** Crystal data and structure refinement for Cu(II)-pincer complex **2a•** Glycol.

| | |
|---|---|
| Identification code | Cu(II)-pincer complex **2a•** Glycol. |
| Empirical formula | C21 H19 Cl2 Cu N3 O3 |
| Formula weight | 495.83 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 7.913(3) A alpha = 106.678(5) deg.<br>b = 11.372(5) A beta = 95.448(6) deg.<br>c = 12.349(5) A gamma = 104.176(5) deg. |
| Volume | 1015.7(7) A^3 |
| Z, Calculated density | 2, 1.621 Mg/m^3 |
| Absorption coefficient | 1.368 mm^-1 |
| F(000) | 506 |
| Crystal size | 0.13 x 0.09 x 0.06 mm |
| Theta range for data collection | 1.95 to 26.00 deg. |
| Limiting indices | -9<=h<=9, -14<=k<=13, -15<=l<=12 |
| Reflections collected / unique | 6842 / 3981 [R(int) = 0.1317] |
| Completeness to theta = 26.00 | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9224 and 0.8422 |
| Refinement method | Full-matrix least-squares on F^2 |

| | |
|---|---|
| Data / restraints / parameters | 3981 / 12 / 278 |
| Goodness-of-fit on F^2 | 1.125 |
| Final R indices [I>2sigma(I)] | R1 = 0.0611, wR2 = 0.1700 |
| R indices (all data) | R1 = 0.0766, wR2 = 0.2021 |
| Largest diff. peak and hole | 1.172 and -1.690 e.A^-3 |

***Table S9.*** Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **2a•** Glycol. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cu(1) | 5910(1) | 1313(1) | 4193(1) | 19(1) |
| Cl(1) | 8138(1) | 1869(1) | 5650(1) | 29(1) |
| Cl(2) | 7388(1) | 2511(1) | 2807(1) | 23(1) |
| N(1) | 4658(5) | 2655(4) | 4844(3) | 20(1) |
| N(2) | 3641(4) | 566(3) | 3157(3) | 17(1) |
| N(3) | 6157(5) | -445(4) | 3305(3) | 20(1) |
| O(1) | -1393(5) | -2025(3) | -61(3) | 34(1) |
| C(1) | 5301(6) | 3716(4) | 5739(4) | 26(1) |
| C(2) | 4317(7) | 4570(5) | 6114(4) | 31(1) |
| C(3) | 2634(7) | 4308(4) | 5554(4) | 26(1) |
| C(4) | 1925(6) | 3201(4) | 4600(4) | 22(1) |
| C(5) | 2996(5) | 2407(4) | 4272(3) | 17(1) |
| C(6) | 2416(5) | 1211(4) | 3275(3) | 16(1) |
| C(7) | 829(6) | 747(4) | 2508(3) | 18(1) |
| C(8) | 506(5) | -409(4) | 1591(4) | 18(1) |
| C(9) | 1804(6) | -1073(4) | 1527(4) | 19(1) |
| C(10) | 3328(5) | -554(4) | 2336(4) | 18(1) |
| C(11) | 4780(6) | -1152(4) | 2430(4) | 21(1) |
| C(12) | 4791(6) | -2339(4) | 1718(4) | 22(1) |
| C(13) | 6190(6) | -2816(4) | 1917(4) | 26(1) |
| C(14) | 7548(6) | -2094(5) | 2815(4) | 28(1) |
| C(15) | 7517(6) | -912(5) | 3504(4) | 25(1) |
| C(16) | -1112(6) | -881(4) | 753(4) | 22(1) |
| C(17) | -2462(6) | -380(4) | 604(4) | 23(1) |
| C(18) | -3681(6) | -1272(5) | -371(4) | 28(1) |
| C(19) | -2920(7) | -2260(6) | -751(4) | 37(1) |
| C(20) | 10905(8) | 4915(6) | 1694(5) | 44(2) |
| C(21) | 9142(8) | 5079(6) | 1517(5) | 43(1) |
| O(2) | 11169(5) | 4250(4) | 2477(3) | 43(1) |
| O(3) | 7839(7) | 3931(6) | 905(5) | 83(2) |

***Table S10.*** Bond lengths [A] and angles [deg] for Cu(II)-pincer complex **2a•** Glycol.

| | |
|---|---|
| Cu(1)-N(2) | 1.942(4) |
| Cu(1)-N(1) | 2.037(4) |
| Cu(1)-N(3) | 2.052(4) |
| Cu(1)-Cl(1) | 2.2239(13) |
| Cu(1)-Cl(2) | 2.6628(13) |
| N(1)-C(1) | 1.328(6) |
| N(1)-C(5) | 1.355(6) |
| N(2)-C(10) | 1.330(6) |
| N(2)-C(6) | 1.346(5) |
| N(3)-C(15) | 1.344(6) |
| N(3)-C(11) | 1.360(6) |
| O(1)-C(19) | 1.331(6) |
| O(1)-C(16) | 1.347(6) |
| C(1)-C(2) | 1.394(8) |
| C(1)-H(1) | 0.9500 |
| C(2)-C(3) | 1.362(7) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.402(6) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.388(6) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.484(6) |
| C(6)-C(7) | 1.384(6) |
| C(7)-C(8) | 1.415(6) |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.411(6) |
| C(8)-C(16) | 1.446(6) |
| C(9)-C(10) | 1.373(6) |
| C(9)-H(9) | 0.9500 |
| C(10)-C(11) | 1.482(6) |
| C(11)-C(12) | 1.386(7) |
| C(12)-C(13) | 1.379(6) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.370(7) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(15) | 1.377(7) |
| C(14)-H(14) | 0.9500 |
| C(15)-H(15) | 0.9500 |
| C(16)-C(17) | 1.349(7) |
| C(17)-C(18) | 1.417(6) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.389(8) |
| C(18)-H(18) | 0.9500 |

| | |
|---|---|
| C(19)-H(19) | 0.9500 |
| C(20)-O(2) | 1.418(7) |
| C(20)-C(21) | 1.457(9) |
| C(20)-H(20A) | 0.9900 |
| C(20)-H(20B) | 0.9900 |
| C(21)-O(3) | 1.402(8) |
| C(21)-H(21A) | 0.9900 |
| C(21)-H(21B) | 0.9900 |
| O(2)-H(2A) | 0.98(4) |
| O(3)-H(3A) | 1.02(4) |
| N(2)-Cu(1)-N(1) | 79.94(15) |
| N(2)-Cu(1)-N(3) | 79.22(15) |
| N(1)-Cu(1)-N(3) | 157.57(15) |
| N(2)-Cu(1)-Cl(1) | 164.72(11) |
| N(1)-Cu(1)-Cl(1) | 99.39(11) |
| N(3)-Cu(1)-Cl(1) | 98.52(11) |
| N(2)-Cu(1)-Cl(2) | 93.26(11) |
| N(1)-Cu(1)-Cl(2) | 94.00(10) |
| N(3)-Cu(1)-Cl(2) | 95.38(10) |
| Cl(1)-Cu(1)-Cl(2) | 102.01(5) |
| C(1)-N(1)-C(5) | 118.6(4) |
| C(1)-N(1)-Cu(1) | 127.1(3) |
| C(5)-N(1)-Cu(1) | 114.3(3) |
| C(10)-N(2)-C(6) | 121.0(4) |
| C(10)-N(2)-Cu(1) | 120.1(3) |
| C(6)-N(2)-Cu(1) | 118.9(3) |
| C(15)-N(3)-C(11) | 120.0(4) |
| C(15)-N(3)-Cu(1) | 126.4(3) |
| C(11)-N(3)-Cu(1) | 113.6(3) |
| C(19)-O(1)-C(16) | 107.7(4) |
| N(1)-C(1)-C(2) | 122.2(4) |
| N(1)-C(1)-H(1) | 118.9 |
| C(2)-C(1)-H(1) | 118.9 |
| C(3)-C(2)-C(1) | 119.2(4) |
| C(3)-C(2)-H(2) | 120.4 |
| C(1)-C(2)-H(2) | 120.4 |
| C(2)-C(3)-C(4) | 119.8(5) |
| C(2)-C(3)-H(3) | 120.1 |
| C(4)-C(3)-H(3) | 120.1 |
| C(5)-C(4)-C(3) | 117.4(4) |
| C(5)-C(4)-H(4) | 121.3 |
| C(3)-C(4)-H(4) | 121.3 |
| N(1)-C(5)-C(4) | 122.7(4) |
| N(1)-C(5)-C(6) | 114.3(4) |

| | |
|---|---|
| C(4)-C(5)-C(6) | 123.0(4) |
| N(2)-C(6)-C(7) | 120.4(4) |
| N(2)-C(6)-C(5) | 112.5(3) |
| C(7)-C(6)-C(5) | 127.1(4) |
| C(6)-C(7)-C(8) | 119.5(4) |
| C(6)-C(7)-H(7) | 120.3 |
| C(8)-C(7)-H(7) | 120.3 |
| C(9)-C(8)-C(7) | 117.9(4) |
| C(9)-C(8)-C(16) | 121.8(4) |
| C(7)-C(8)-C(16) | 120.3(4) |
| C(10)-C(9)-C(8) | 118.7(4) |
| C(10)-C(9)-H(9) | 120.6 |
| C(8)-C(9)-H(9) | 120.6 |
| N(2)-C(10)-C(9) | 122.3(4) |
| N(2)-C(10)-C(11) | 112.0(4) |
| C(9)-C(10)-C(11) | 125.7(4) |
| N(3)-C(11)-C(12) | 120.5(4) |
| N(3)-C(11)-C(10) | 114.6(4) |
| C(12)-C(11)-C(10) | 124.9(4) |
| C(13)-C(12)-C(11) | 119.6(4) |
| C(13)-C(12)-H(12) | 120.2 |
| C(11)-C(12)-H(12) | 120.2 |
| C(14)-C(13)-C(12) | 118.8(4) |
| C(14)-C(13)-H(13) | 120.6 |
| C(12)-C(13)-H(13) | 120.6 |
| C(13)-C(14)-C(15) | 120.6(5) |
| C(13)-C(14)-H(14) | 119.7 |
| C(15)-C(14)-H(14) | 119.7 |
| N(3)-C(15)-C(14) | 120.6(4) |
| N(3)-C(15)-H(15) | 119.7 |
| C(14)-C(15)-H(15) | 119.7 |
| O(1)-C(16)-C(17) | 110.6(4) |
| O(1)-C(16)-C(8) | 117.5(4) |
| C(17)-C(16)-C(8) | 131.9(4) |
| C(16)-C(17)-C(18) | 106.6(4) |
| C(16)-C(17)-H(17) | 126.7 |
| C(18)-C(17)-H(17) | 126.7 |
| C(19)-C(18)-C(17) | 105.0(4) |
| C(19)-C(18)-H(18) | 127.5 |
| C(17)-C(18)-H(18) | 127.5 |
| O(1)-C(19)-C(18) | 110.1(4) |
| O(1)-C(19)-H(19) | 124.9 |
| C(18)-C(19)-H(19) | 124.9 |
| O(2)-C(20)-C(21) | 115.2(5) |

| | |
|---|---|
| O(2)-C(20)-H(20A) | 108.5 |
| C(21)-C(20)-H(20A) | 108.5 |
| O(2)-C(20)-H(20B) | 108.5 |
| C(21)-C(20)-H(20B) | 108.5 |
| H(20A)-C(20)-H(20B) | 107.5 |
| O(3)-C(21)-C(20) | 113.0(6) |
| O(3)-C(21)-H(21A) | 109.0 |
| C(20)-C(21)-H(21A) | 109.0 |
| O(3)-C(21)-H(21B) | 109.0 |
| C(20)-C(21)-H(21B) | 109.0 |
| H(21A)-C(21)-H(21B) | 107.8 |
| C(20)-O(2)-H(2A) | 101(3) |
| C(21)-O(3)-H(3A) | 107(4) |

Symmetry transformations used to generate equivalent atoms:

***Table S11.*** Anisotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **2a•** Glycol. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ] ‘

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Cu(1) | 12(1) | 24(1) | 16(1) | 6(1) | -2(1) | 0(1) |
| Cl(1) | 19(1) | 42(1) | 21(1) | 11(1) | -6(1) | 0(1) |
| Cl(2) | 21(1) | 23(1) | 21(1) | 6(1) | 3(1) | 1(1) |
| N(1) | 16(2) | 27(2) | 16(2) | 8(2) | 4(1) | -1(1) |
| N(2) | 13(2) | 18(2) | 18(2) | 6(1) | 4(1) | 2(1) |
| N(3) | 17(2) | 22(2) | 20(2) | 10(2) | -2(1) | -1(1) |
| O(1) | 25(2) | 29(2) | 34(2) | -5(2) | -1(2) | 5(1) |
| C(1) | 22(2) | 26(2) | 20(2) | 5(2) | 2(2) | -7(2) |
| C(2) | 37(3) | 27(2) | 16(2) | 2(2) | 4(2) | -6(2) |
| C(3) | 34(3) | 20(2) | 22(2) | 4(2) | 8(2) | 6(2) |
| C(4) | 22(2) | 26(2) | 16(2) | 7(2) | 1(2) | 1(2) |
| C(5) | 19(2) | 18(2) | 15(2) | 7(2) | 3(2) | 1(2) |
| C(6) | 13(2) | 19(2) | 13(2) | 5(2) | -1(2) | 2(2) |
| C(7) | 16(2) | 21(2) | 14(2) | 4(2) | -2(2) | 4(2) |
| C(8) | 11(2) | 22(2) | 18(2) | 6(2) | 1(2) | 2(2) |
| C(9) | 18(2) | 16(2) | 22(2) | 2(2) | 4(2) | 6(2) |
| C(10) | 16(2) | 18(2) | 21(2) | 7(2) | 7(2) | 1(2) |
| C(11) | 20(2) | 21(2) | 22(2) | 12(2) | 2(2) | 0(2) |
| C(12) | 19(2) | 23(2) | 22(2) | 8(2) | 4(2) | 4(2) |
| C(13) | 22(2) | 23(2) | 37(3) | 13(2) | 10(2) | 10(2) |
| C(14) | 19(2) | 35(3) | 37(3) | 20(2) | 9(2) | 9(2) |
| C(15) | 20(2) | 30(2) | 24(2) | 14(2) | 1(2) | 0(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(16) | 17(2) | 26(2) | 15(2) | 3(2) | -2(2) | -1(2) |
| C(17) | 20(2) | 27(2) | 18(2) | 7(2) | -1(2) | 3(2) |
| C(18) | 16(2) | 37(3) | 23(2) | 11(2) | -4(2) | -1(2) |
| C(19) | 27(3) | 41(3) | 25(2) | -1(2) | -5(2) | -8(2) |
| C(20) | 38(3) | 52(4) | 33(3) | 19(3) | 2(2) | -8(3) |
| C(21) | 54(4) | 47(3) | 34(3) | 23(3) | 13(3) | 10(3) |
| O(2) | 30(2) | 53(2) | 39(2) | 24(2) | -5(2) | -8(2) |
| O(3) | 59(3) | 105(4) | 59(3) | 56(3) | -31(2) | -40(3) |

***Table S12.*** Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **2a•** Glycol.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 6472 | 3900 | 6136 | 31 |
| H(2) | 4815 | 5325 | 6754 | 37 |
| H(3) | 1943 | 4875 | 5809 | 31 |
| H(4) | 756 | 3001 | 4194 | 27 |
| H(7) | -36 | 1201 | 2596 | 22 |
| H(9) | 1627 | -1863 | 936 | 23 |
| H(12) | 3840 | -2820 | 1096 | 26 |
| H(13) | 6211 | -3631 | 1441 | 31 |
| H(14) | 8520 | -2412 | 2963 | 33 |
| H(15) | 8465 | -423 | 4125 | 30 |
| H(17) | -2574 | 415 | 1064 | 27 |
| H(18) | -4779 | -1208 | -695 | 33 |
| H(19) | -3416 | -2997 | -1408 | 45 |
| H(20A) | 11147 | 4448 | 943 | 53 |
| H(20B) | 11781 | 5772 | 1974 | 53 |
| H(21A) | 8826 | 5444 | 2273 | 52 |
| H(21B) | 9160 | 5700 | 1093 | 52 |
| H(3A) | 6990(80) | 3740(70) | 1450(60) | 124 |
| H(2A) | 9950(60) | 3730(50) | 2420(50) | 46(17) |

***Table S13.*** Torsion angles [deg] for Cu(II)-pincer complex **2a•** Glycol.

| | |
|---|---|
| N(2)-Cu(1)-N(1)-C(1) | 179.5(4) |
| N(3)-Cu(1)-N(1)-C(1) | 157.6(4) |
| Cl(1)-Cu(1)-N(1)-C(1) | 15.0(4) |
| Cl(2)-Cu(1)-N(1)-C(1) | -87.9(3) |
| N(2)-Cu(1)-N(1)-C(5) | -1.1(3) |
| N(3)-Cu(1)-N(1)-C(5) | -23.0(5) |

| | |
|---|---|
| Cl(1)-Cu(1)-N(1)-C(5) | -165.6(3) |
| Cl(2)-Cu(1)-N(1)-C(5) | 91.5(3) |
| N(1)-Cu(1)-N(2)-C(10) | -178.4(3) |
| N(3)-Cu(1)-N(2)-C(10) | -6.8(3) |
| Cl(1)-Cu(1)-N(2)-C(10) | -89.6(5) |
| Cl(2)-Cu(1)-N(2)-C(10) | 88.1(3) |
| N(1)-Cu(1)-N(2)-C(6) | 2.7(3) |
| N(3)-Cu(1)-N(2)-C(6) | 174.4(3) |
| Cl(1)-Cu(1)-N(2)-C(6) | 91.6(5) |
| Cl(2)-Cu(1)-N(2)-C(6) | -90.7(3) |
| N(2)-Cu(1)-N(3)-C(15) | -175.7(4) |
| N(1)-Cu(1)-N(3)-C(15) | -153.7(4) |
| Cl(1)-Cu(1)-N(3)-C(15) | -11.0(4) |
| Cl(2)-Cu(1)-N(3)-C(15) | 92.0(3) |
| N(2)-Cu(1)-N(3)-C(11) | 5.5(3) |
| N(1)-Cu(1)-N(3)-C(11) | 27.5(5) |
| Cl(1)-Cu(1)-N(3)-C(11) | 170.1(3) |
| Cl(2)-Cu(1)-N(3)-C(11) | -86.8(3) |
| C(5)-N(1)-C(1)-C(2) | 0.8(6) |
| Cu(1)-N(1)-C(1)-C(2) | -179.8(3) |
| N(1)-C(1)-C(2)-C(3) | 0.5(7) |
| C(1)-C(2)-C(3)-C(4) | -1.0(7) |
| C(2)-C(3)-C(4)-C(5) | 0.3(6) |
| C(1)-N(1)-C(5)-C(4) | -1.6(6) |
| Cu(1)-N(1)-C(5)-C(4) | 178.9(3) |
| C(1)-N(1)-C(5)-C(6) | 178.9(3) |
| Cu(1)-N(1)-C(5)-C(6) | -0.6(4) |
| C(3)-C(4)-C(5)-N(1) | 1.0(6) |
| C(3)-C(4)-C(5)-C(6) | -179.5(4) |
| C(10)-N(2)-C(6)-C(7) | -2.9(6) |
| Cu(1)-N(2)-C(6)-C(7) | 175.9(3) |
| C(10)-N(2)-C(6)-C(5) | 177.4(3) |
| Cu(1)-N(2)-C(6)-C(5) | -3.7(4) |
| N(1)-C(5)-C(6)-N(2) | 2.7(5) |
| C(4)-C(5)-C(6)-N(2) | -176.8(4) |
| N(1)-C(5)-C(6)-C(7) | -176.9(4) |
| C(4)-C(5)-C(6)-C(7) | 3.6(6) |
| N(2)-C(6)-C(7)-C(8) | -0.5(6) |
| C(5)-C(6)-C(7)-C(8) | 179.1(4) |
| C(6)-C(7)-C(8)-C(9) | 2.6(6) |
| C(6)-C(7)-C(8)-C(16) | -177.4(4) |
| C(7)-C(8)-C(9)-C(10) | -1.5(6) |
| C(16)-C(8)-C(9)-C(10) | 178.5(4) |
| C(6)-N(2)-C(10)-C(9) | 4.1(6) |

| | |
|---|---|
| Cu(1)-N(2)-C(10)-C(9) | -174.7(3) |
| C(6)-N(2)-C(10)-C(11) | -174.7(3) |
| Cu(1)-N(2)-C(10)-C(11) | 6.5(4) |
| C(8)-C(9)-C(10)-N(2) | -1.8(6) |
| C(8)-C(9)-C(10)-C(11) | 176.9(4) |
| C(15)-N(3)-C(11)-C(12) | -1.8(6) |
| Cu(1)-N(3)-C(11)-C(12) | 177.1(3) |
| C(15)-N(3)-C(11)-C(10) | 177.3(4) |
| Cu(1)-N(3)-C(11)-C(10) | -3.8(4) |
| N(2)-C(10)-C(11)-N(3) | -1.3(5) |
| C(9)-C(10)-C(11)-N(3) | 179.9(4) |
| N(2)-C(10)-C(11)-C(12) | 177.7(4) |
| C(9)-C(10)-C(11)-C(12) | -1.1(7) |
| N(3)-C(11)-C(12)-C(13) | 1.5(6) |
| C(10)-C(11)-C(12)-C(13) | -177.5(4) |
| C(11)-C(12)-C(13)-C(14) | -0.5(6) |
| C(12)-C(13)-C(14)-C(15) | -0.1(7) |
| C(11)-N(3)-C(15)-C(14) | 1.2(6) |
| Cu(1)-N(3)-C(15)-C(14) | -177.6(3) |
| C(13)-C(14)-C(15)-N(3) | -0.2(7) |
| C(19)-O(1)-C(16)-C(17) | 0.9(5) |
| C(19)-O(1)-C(16)-C(8) | -178.6(4) |
| C(9)-C(8)-C(16)-O(1) | 3.9(6) |
| C(7)-C(8)-C(16)-O(1) | -176.1(4) |
| C(9)-C(8)-C(16)-C(17) | -175.4(4) |
| C(7)-C(8)-C(16)-C(17) | 4.5(7) |
| O(1)-C(16)-C(17)-C(18) | 0.1(5) |
| C(8)-C(16)-C(17)-C(18) | 179.4(5) |
| C(16)-C(17)-C(18)-C(19) | -0.9(5) |
| C(16)-O(1)-C(19)-C(18) | -1.5(5) |
| C(17)-C(18)-C(19)-O(1) | 1.5(6) |
| O(2)-C(20)-C(21)-O(3) | -70.4(7) |

Symmetry transformations used to generate equivalent atoms:

***Table S14.*** Hydrogen bonds for Cu(II)-pincer complex **2a•** Glycol [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(2)-H(2A)...Cl(2) | 0.98(4) | 2.33(3) | 3.290(4) | 164(4) |
| O(3)-H(3A)...Cl(2) | 1.02(4) | 2.52(7) | 3.210(5) | 125(6) |

Symmetry transformations used to generate equivalent atoms:

**16.3. Cu(II)-pincer complex 2c ·$H_2O$.**

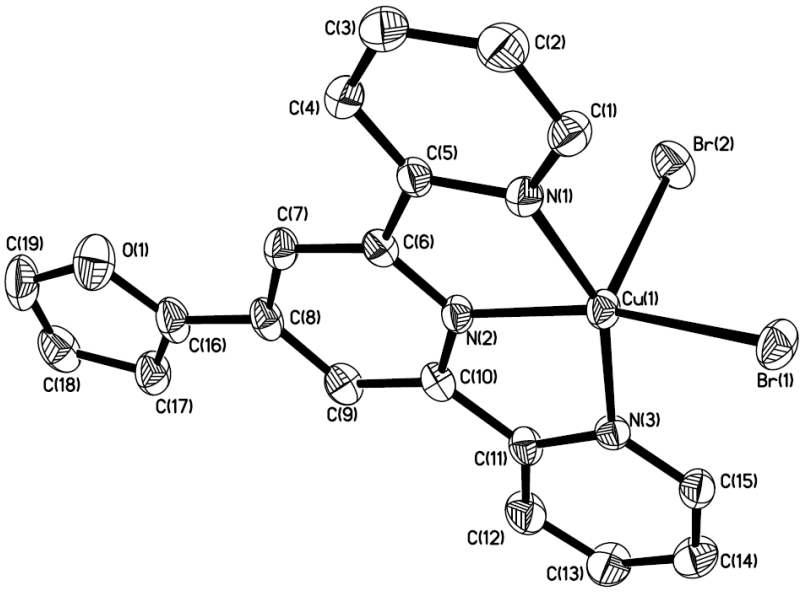



***Figure S43*** Molecular structure of complex **2c ·$H_2O$**.

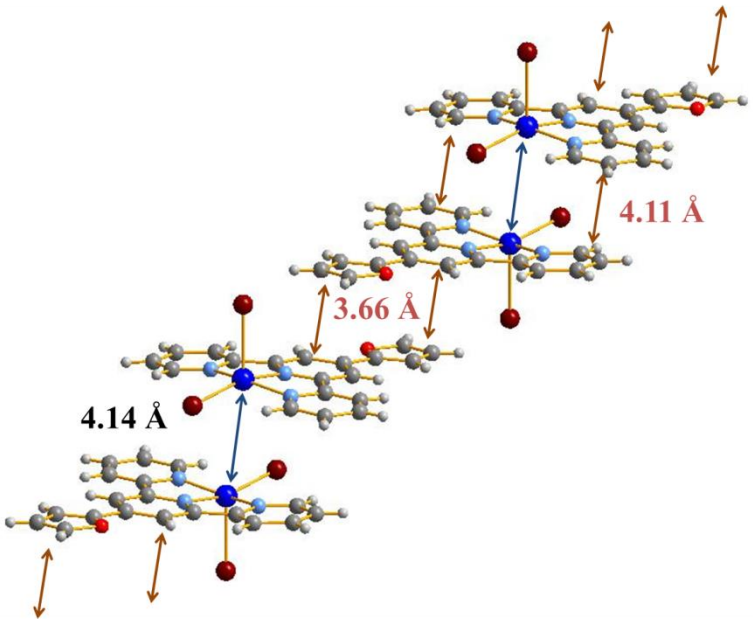



***Figure S44.*** Interactions between the molecules of **2c** (1).

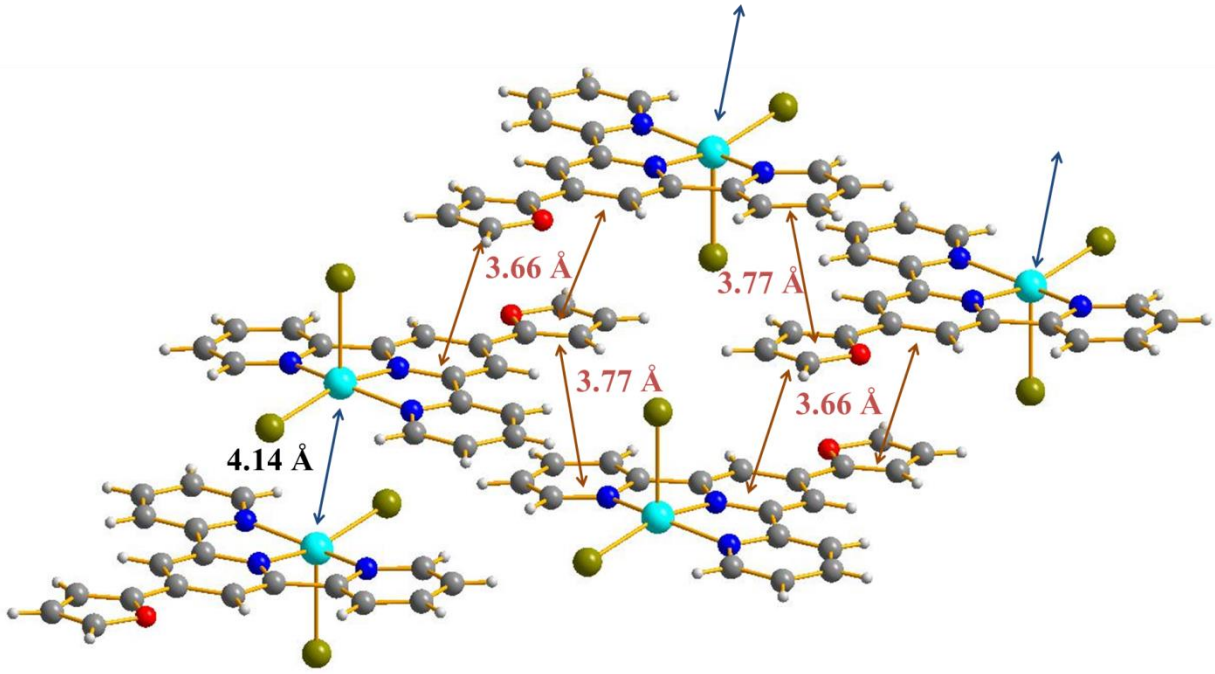



***Figure S45.*** Interactions between the molecules of **2c** (2).

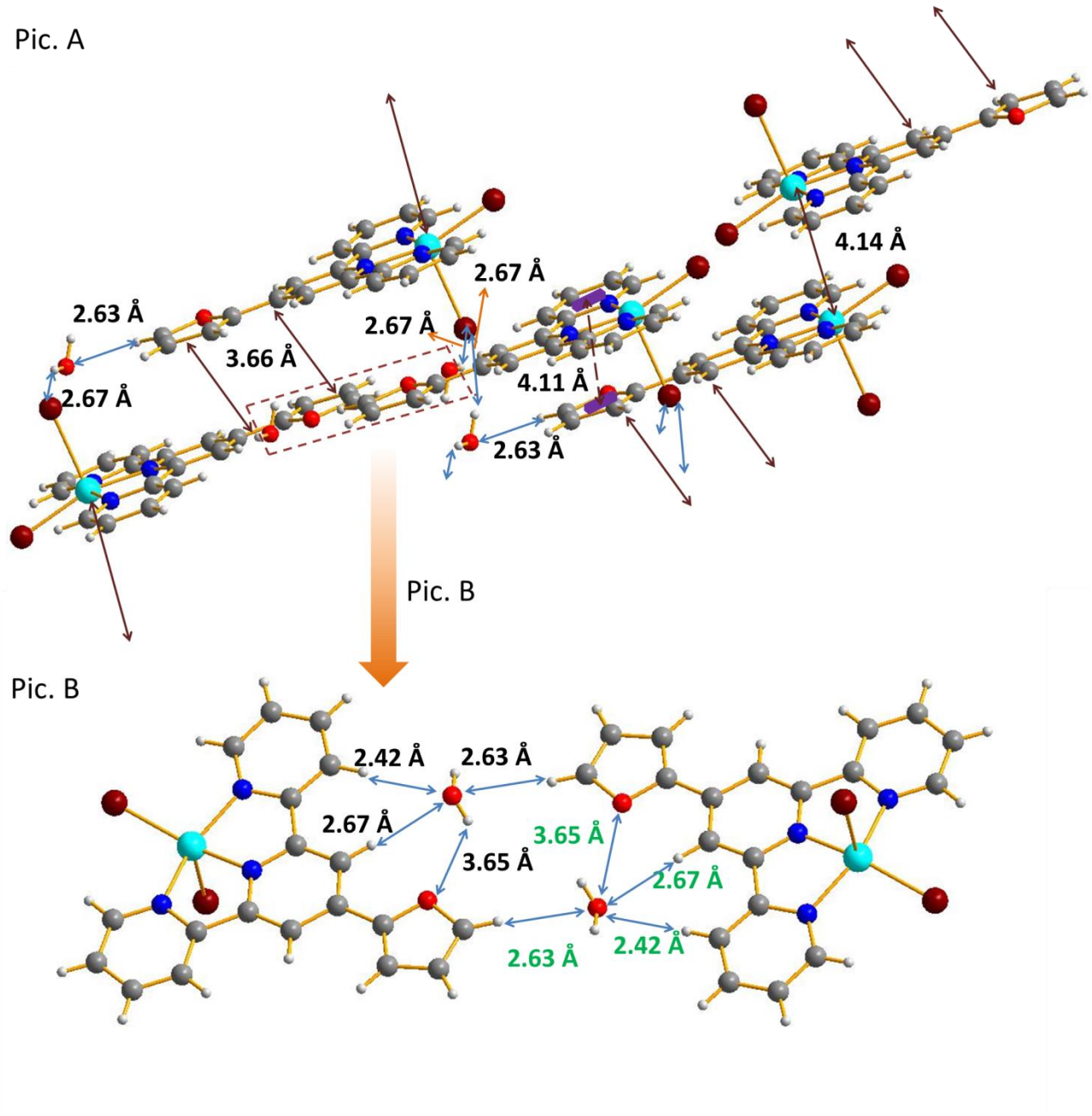



***Figure S46.*** Interactions between the molecules (Complex **2c**) and guest ($H_2O$).

***Table S15.*** Crystal data and structure refinement for Cu(II)-pincer complex **2c** ~~H~~$_2$O.

| | |
|---|---|
| Identification code | Cu(II)-pincer complex **2c** ~~H~~$_2$O. |
| Empirical formula | C19 H15 Br2 Cu N3 O2 |

| | |
|---|---|
| Formula weight | 540.70 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 8.279(3) A alpha = 73.700(5) deg.<br>b = 9.259(4) A beta = 80.076(5) deg.<br>c = 13.038(5) A gamma = 87.051(5) deg. |
| Volume | 944.9(7) A^3 |
| Z, Calculated density | 2, 1.900 Mg/m^3 |
| Absorption coefficient | 5.404 mm^-1 |
| F(000) | 530 |
| Crystal size | 0.12 x 0.10 x 0.08 mm |
| Theta range for data collection | 1.65 to 25.03 deg. |
| Limiting indices | -9<=h<=9, -10<=k<=7, -15<=l<=13 |
| Reflections collected / unique | 3918 / 3258 [R(int) = 0.0445] |
| Completeness to theta = 25.03 | 97.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.6717 and 0.5632 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3258 / 3 / 252 |
| Goodness-of-fit on F^2 | 0.863 |
| Final R indices [I>2sigma(I)] | R1 = 0.0355, wR2 = 0.0810 |
| R indices (all data) | R1 = 0.0526, wR2 = 0.0845 |
| Largest diff. peak and hole | 0.470 and -0.435 e.A^-3 |

***Table S16.*** Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **2c** ·$H_2O$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cu(1) | 4567(1) | 11271(1) | 8490(1) | 36(1) |
| Br(1) | 2502(1) | 11821(1) | 9835(1) | 50(1) |
| Br(2) | 3537(1) | 12991(1) | 6692(1) | 55(1) |
| N(1) | 3650(4) | 9295(4) | 8434(3) | 37(1) |
| N(2) | 6482(4) | 10467(4) | 7763(3) | 35(1) |
| N(3) | 6327(4) | 12722(4) | 8507(3) | 35(1) |
| C(1) | 2155(6) | 8731(5) | 8847(4) | 43(1) |
| C(2) | 1670(6) | 7401(6) | 8741(4) | 54(1) |
| C(3) | 2753(6) | 6618(6) | 8166(5) | 54(1) |
| C(4) | 4285(6) | 7193(5) | 7726(4) | 44(1) |
| C(5) | 4716(5) | 8520(5) | 7869(4) | 36(1) |
| C(6) | 6363(5) | 9206(5) | 7483(4) | 36(1) |
| C(7) | 7699(6) | 8614(5) | 6938(4) | 41(1) |

| | | | | |
|---|---|---|---|---|
| C(8) | 9191(5) | 9355(5) | 6703(4) | 42(1) |
| C(9) | 9307(6) | 10644(5) | 7019(4) | 44(1) |
| C(10) | 7922(5) | 11190(5) | 7553(4) | 38(1) |
| C(11) | 7814(5) | 12495(5) | 7973(4) | 38(1) |
| C(12) | 9096(6) | 13461(6) | 7848(5) | 58(2) |
| C(13) | 8840(6) | 14662(6) | 8260(5) | 62(2) |
| C(14) | 7355(7) | 14888(6) | 8821(5) | 57(2) |
| C(15) | 6113(6) | 13884(5) | 8922(4) | 44(1) |
| C(16) | 10627(6) | 8791(7) | 6117(4) | 52(1) |
| O(1) | 10569(5) | 7506(5) | 5862(4) | 69(2) |
| C(17) | 12096(6) | 9370(5) | 5803(4) | 54(2) |
| C(18) | 13071(7) | 8419(8) | 5278(5) | 65(2) |
| C(19) | 12143(8) | 7289(8) | 5308(5) | 75(2) |
| C(17') | 10569(5) | 7506(5) | 5862(4) | 69(2) |
| C(18') | 12143(8) | 7289(8) | 5308(5) | 75(2) |
| C(19') | 13071(7) | 8419(8) | 5278(5) | 65(2) |
| O(1') | 12096(6) | 9370(5) | 5803(4) | 54(2) |
| O(2) | 6615(6) | 5581(6) | 5997(4) | 77(1) |

***Table S17.*** Bond lengths [A] and angles [deg] for Cu(II)-pincer complex **2c** ·$H_2O$.

| | |
|---|---|
| Cu(1)-N(2) | 1.930(4) |
| Cu(1)-N(3) | 2.039(3) |
| Cu(1)-N(1) | 2.041(4) |
| Cu(1)-Br(1) | 2.3739(10) |
| Cu(1)-Br(2) | 2.6857(11) |
| N(1)-C(1) | 1.332(5) |
| N(1)-C(5) | 1.357(5) |
| N(2)-C(6) | 1.330(5) |
| N(2)-C(10) | 1.346(6) |
| N(3)-C(15) | 1.326(6) |
| N(3)-C(11) | 1.343(5) |
| C(1)-C(2) | 1.365(6) |
| C(1)-H(1) | 0.9300 |
| C(2)-C(3) | 1.378(7) |
| C(2)-H(2) | 0.9300 |
| C(3)-C(4) | 1.367(7) |
| C(3)-H(3) | 0.9300 |
| C(4)-C(5) | 1.367(6) |
| C(4)-H(4) | 0.9300 |
| C(5)-C(6) | 1.479(6) |
| C(6)-C(7) | 1.384(6) |

| | |
|---|---|
| C(7)-C(8) | 1.389(6) |
| C(7)-H(7) | 0.9300 |
| C(8)-C(9) | 1.381(6) |
| C(8)-C(16) | 1.455(6) |
| C(9)-C(10) | 1.385(6) |
| C(9)-H(9) | 0.9300 |
| C(10)-C(11) | 1.453(6) |
| C(11)-C(12) | 1.381(6) |
| C(12)-C(13) | 1.357(7) |
| C(12)-H(12) | 0.9300 |
| C(13)-C(14) | 1.356(7) |
| C(13)-H(13) | 0.9300 |
| C(14)-C(15) | 1.386(7) |
| C(14)-H(14) | 0.9300 |
| C(15)-H(15) | 0.9300 |
| C(16)-C(17) | 1.306(7) |
| C(16)-O(1) | 1.328(6) |
| O(1)-C(19) | 1.411(7) |
| C(17)-C(18) | 1.404(7) |
| C(17)-H(17) | 0.9300 |
| C(18)-C(19) | 1.317(8) |
| C(18)-H(18) | 0.9300 |
| C(19)-H(19) | 0.9300 |
| O(2)-H(2B) | 0.82(2) |
| O(2)-H(2A) | 0.82(2) |
| N(2)-Cu(1)-N(3) | 79.02(15) |
| N(2)-Cu(1)-N(1) | 79.56(15) |
| N(3)-Cu(1)-N(1) | 156.45(14) |
| N(2)-Cu(1)-Br(1) | 163.36(11) |
| N(3)-Cu(1)-Br(1) | 98.93(11) |
| N(1)-Cu(1)-Br(1) | 98.79(11) |
| N(2)-Cu(1)-Br(2) | 96.50(11) |
| N(3)-Cu(1)-Br(2) | 95.84(10) |
| N(1)-Cu(1)-Br(2) | 96.19(11) |
| Br(1)-Cu(1)-Br(2) | 100.14(4) |
| C(1)-N(1)-C(5) | 118.2(4) |
| C(1)-N(1)-Cu(1) | 128.0(3) |
| C(5)-N(1)-Cu(1) | 113.8(3) |
| C(6)-N(2)-C(10) | 121.1(4) |
| C(6)-N(2)-Cu(1) | 119.6(3) |
| C(10)-N(2)-Cu(1) | 119.3(3) |
| C(15)-N(3)-C(11) | 118.7(4) |
| C(15)-N(3)-Cu(1) | 126.7(3) |
| C(11)-N(3)-Cu(1) | 114.4(3) |

| | |
|---|---|
| N(1)-C(1)-C(2) | 122.7(5) |
| N(1)-C(1)-H(1) | 118.7 |
| C(2)-C(1)-H(1) | 118.7 |
| C(1)-C(2)-C(3) | 119.0(5) |
| C(1)-C(2)-H(2) | 120.5 |
| C(3)-C(2)-H(2) | 120.5 |
| C(4)-C(3)-C(2) | 118.9(5) |
| C(4)-C(3)-H(3) | 120.5 |
| C(2)-C(3)-H(3) | 120.5 |
| C(3)-C(4)-C(5) | 119.7(5) |
| C(3)-C(4)-H(4) | 120.2 |
| C(5)-C(4)-H(4) | 120.2 |
| N(1)-C(5)-C(4) | 121.5(4) |
| N(1)-C(5)-C(6) | 114.0(4) |
| C(4)-C(5)-C(6) | 124.4(4) |
| N(2)-C(6)-C(7) | 121.4(4) |
| N(2)-C(6)-C(5) | 112.6(4) |
| C(7)-C(6)-C(5) | 126.0(4) |
| C(6)-C(7)-C(8) | 118.3(4) |
| C(6)-C(7)-H(7) | 120.8 |
| C(8)-C(7)-H(7) | 120.8 |
| C(9)-C(8)-C(7) | 119.7(4) |
| C(9)-C(8)-C(16) | 119.8(5) |
| C(7)-C(8)-C(16) | 120.5(5) |
| C(8)-C(9)-C(10) | 119.2(4) |
| C(8)-C(9)-H(9) | 120.4 |
| C(10)-C(9)-H(9) | 120.4 |
| N(2)-C(10)-C(9) | 120.3(4) |
| N(2)-C(10)-C(11) | 112.6(4) |
| C(9)-C(10)-C(11) | 127.2(4) |
| N(3)-C(11)-C(12) | 120.8(5) |
| N(3)-C(11)-C(10) | 114.5(4) |
| C(12)-C(11)-C(10) | 124.7(4) |
| C(13)-C(12)-C(11) | 119.4(5) |
| C(13)-C(12)-H(12) | 120.3 |
| C(11)-C(12)-H(12) | 120.3 |
| C(14)-C(13)-C(12) | 120.4(5) |
| C(14)-C(13)-H(13) | 119.8 |
| C(12)-C(13)-H(13) | 119.8 |
| C(13)-C(14)-C(15) | 117.7(5) |
| C(13)-C(14)-H(14) | 121.2 |
| C(15)-C(14)-H(14) | 121.2 |
| N(3)-C(15)-C(14) | 122.9(5) |
| N(3)-C(15)-H(15) | 118.6 |

| | |
|---|---|
| C(14)-C(15)-H(15) | 118.6 |
| C(17)-C(16)-O(1) | 110.8(5) |
| C(17)-C(16)-C(8) | 128.4(6) |
| O(1)-C(16)-C(8) | 120.8(5) |
| C(16)-O(1)-C(19) | 106.4(5) |
| C(16)-C(17)-C(18) | 107.6(5) |
| C(16)-C(17)-H(17) | 126.2 |
| C(18)-C(17)-H(17) | 126.2 |
| C(19)-C(18)-C(17) | 107.4(5) |
| C(19)-C(18)-H(18) | 126.3 |
| C(17)-C(18)-H(18) | 126.3 |
| C(18)-C(19)-O(1) | 107.7(5) |
| C(18)-C(19)-H(19) | 126.1 |
| O(1)-C(19)-H(19) | 126.1 |
| H(2B)-O(2)-H(2A) | 104(3) |

Symmetry transformations used to generate equivalent atoms:

***Table S18.*** Anisotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **2c**·$H_2O$. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Cu(1) | 29(1) | 39(1) | 41(1) | -16(1) | 2(1) | 0(1) |
| Br(1) | 44(1) | 59(1) | 48(1) | -26(1) | 11(1) | -5(1) |
| Br(2) | 44(1) | 65(1) | 46(1) | -3(1) | -3(1) | 6(1) |
| N(1) | 35(2) | 39(2) | 39(2) | -14(2) | -5(2) | 2(2) |
| N(2) | 28(2) | 34(2) | 41(2) | -13(2) | -2(2) | 3(2) |
| N(3) | 31(2) | 33(2) | 42(2) | -11(2) | -7(2) | -3(2) |
| C(1) | 37(3) | 49(3) | 47(3) | -21(2) | 3(2) | -6(2) |
| C(2) | 37(3) | 64(4) | 64(4) | -25(3) | 1(3) | -11(3) |
| C(3) | 44(3) | 50(3) | 77(4) | -27(3) | -12(3) | -7(3) |
| C(4) | 43(3) | 46(3) | 50(3) | -23(3) | -7(2) | 5(2) |
| C(5) | 33(2) | 41(3) | 36(3) | -12(2) | -6(2) | 7(2) |
| C(6) | 32(2) | 39(3) | 33(3) | -6(2) | -6(2) | 4(2) |
| C(7) | 41(3) | 42(3) | 39(3) | -13(2) | -1(2) | 7(2) |
| C(8) | 37(3) | 49(3) | 32(3) | -4(2) | 1(2) | 13(2) |
| C(9) | 32(3) | 48(3) | 43(3) | -5(2) | 3(2) | -3(2) |
| C(10) | 32(3) | 38(3) | 41(3) | -5(2) | -5(2) | 3(2) |
| C(11) | 27(2) | 40(3) | 44(3) | -11(2) | 0(2) | -1(2) |
| C(12) | 35(3) | 62(4) | 82(4) | -26(3) | -8(3) | -4(3) |
| C(13) | 40(3) | 69(4) | 86(5) | -37(3) | -3(3) | -18(3) |
| C(14) | 62(4) | 47(3) | 70(4) | -24(3) | -13(3) | -10(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(15) | 40(3) | 42(3) | 54(3) | -20(2) | -7(2) | 2(2) |
| C(16) | 48(3) | 61(4) | 43(3) | -14(3) | -3(3) | 22(3) |
| O(1) | 60(3) | 67(3) | 75(3) | -24(2) | 12(2) | 5(2) |
| C(17) | 45(3) | 61(4) | 55(3) | -21(3) | 1(2) | 11(3) |
| C(18) | 49(3) | 90(5) | 48(4) | -13(3) | -1(3) | 19(3) |
| C(19) | 81(5) | 68(4) | 75(5) | -29(4) | -5(4) | 35(4) |
| C(17') | 60(3) | 67(3) | 75(3) | -24(2) | 12(2) | 5(2) |
| C(18') | 81(5) | 68(4) | 75(5) | -29(4) | -5(4) | 35(4) |
| C(19') | 49(3) | 90(5) | 48(4) | -13(3) | -1(3) | 19(3) |
| O(1') | 45(3) | 61(4) | 55(3) | -21(3) | 1(2) | 11(3) |
| O(2) | 90(3) | 81(3) | 70(3) | -32(3) | -19(3) | -1(3) |

***Table 19.*** Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **2c** ·$H_2O$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 1411 | 9265 | 9223 | 52 |
| H(2) | 624 | 7028 | 9053 | 65 |
| H(3) | 2446 | 5714 | 8078 | 65 |
| H(4) | 5030 | 6684 | 7331 | 53 |
| H(7) | 7601 | 7742 | 6733 | 49 |
| H(9) | 10304 | 11141 | 6875 | 52 |
| H(12) | 10125 | 13290 | 7484 | 70 |
| H(13) | 9688 | 15335 | 8157 | 74 |
| H(14) | 7177 | 15688 | 9128 | 69 |
| H(15) | 5085 | 14033 | 9297 | 53 |
| H(17) | 12435 | 10252 | 5909 | 65 |
| H(18) | 14169 | 8561 | 4966 | 78 |
| H(19) | 12468 | 6491 | 5016 | 90 |
| H(17') | 9669 | 6874 | 6018 | 83 |
| H(18') | 12468 | 6491 | 5016 | 90 |
| H(19') | 14169 | 8561 | 4966 | 78 |
| H(2B) | 6910(110) | 5970(110) | 5340(20) | 180(50) |
| H(2A) | 5710(70) | 5230(130) | 6040(80) | 274 |

***Table S20.*** Torsion angles [deg] for Cu(II)-pincer complex **2c** ·$H_2O$.

| | |
|---|---|
| N(2)-Cu(1)-N(1)-C(1) | 177.0(4) |
| N(3)-Cu(1)-N(1)-C(1) | 152.2(4) |

| | |
|---|---|
| Br(1)-Cu(1)-N(1)-C(1) | 13.8(4) |
| Br(2)-Cu(1)-N(1)-C(1) | -87.5(4) |
| N(2)-Cu(1)-N(1)-C(5) | -5.3(3) |
| N(3)-Cu(1)-N(1)-C(5) | -30.1(6) |
| Br(1)-Cu(1)-N(1)-C(5) | -168.5(3) |
| Br(2)-Cu(1)-N(1)-C(5) | 90.2(3) |
| N(3)-Cu(1)-N(2)-C(6) | 175.6(4) |
| N(1)-Cu(1)-N(2)-C(6) | 5.5(3) |
| Br(1)-Cu(1)-N(2)-C(6) | 91.2(5) |
| Br(2)-Cu(1)-N(2)-C(6) | -89.6(3) |
| N(3)-Cu(1)-N(2)-C(10) | -3.9(3) |
| N(1)-Cu(1)-N(2)-C(10) | -174.0(4) |
| Br(1)-Cu(1)-N(2)-C(10) | -88.3(5) |
| Br(2)-Cu(1)-N(2)-C(10) | 90.8(3) |
| N(2)-Cu(1)-N(3)-C(15) | 179.9(4) |
| N(1)-Cu(1)-N(3)-C(15) | -155.2(4) |
| Br(1)-Cu(1)-N(3)-C(15) | -16.9(4) |
| Br(2)-Cu(1)-N(3)-C(15) | 84.4(4) |
| N(2)-Cu(1)-N(3)-C(11) | 4.5(3) |
| N(1)-Cu(1)-N(3)-C(11) | 29.4(6) |
| Br(1)-Cu(1)-N(3)-C(11) | 167.7(3) |
| Br(2)-Cu(1)-N(3)-C(11) | -91.0(3) |
| C(5)-N(1)-C(1)-C(2) | 1.2(7) |
| Cu(1)-N(1)-C(1)-C(2) | 178.8(4) |
| N(1)-C(1)-C(2)-C(3) | -1.4(8) |
| C(1)-C(2)-C(3)-C(4) | 0.5(8) |
| C(2)-C(3)-C(4)-C(5) | 0.4(8) |
| C(1)-N(1)-C(5)-C(4) | -0.3(7) |
| Cu(1)-N(1)-C(5)-C(4) | -178.2(3) |
| C(1)-N(1)-C(5)-C(6) | -177.6(4) |
| Cu(1)-N(1)-C(5)-C(6) | 4.5(5) |
| C(3)-C(4)-C(5)-N(1) | -0.5(7) |
| C(3)-C(4)-C(5)-C(6) | 176.5(4) |
| C(10)-N(2)-C(6)-C(7) | -2.1(7) |
| Cu(1)-N(2)-C(6)-C(7) | 178.4(3) |
| C(10)-N(2)-C(6)-C(5) | 175.0(4) |
| Cu(1)-N(2)-C(6)-C(5) | -4.5(5) |
| N(1)-C(5)-C(6)-N(2) | -0.3(6) |
| C(4)-C(5)-C(6)-N(2) | -177.5(4) |
| N(1)-C(5)-C(6)-C(7) | 176.6(4) |
| C(4)-C(5)-C(6)-C(7) | -0.6(7) |
| N(2)-C(6)-C(7)-C(8) | 1.2(7) |
| C(5)-C(6)-C(7)-C(8) | -175.4(4) |
| C(6)-C(7)-C(8)-C(9) | 0.3(7) |

| | |
|---|---|
| C(6)-C(7)-C(8)-C(16) | -179.1(4) |
| C(7)-C(8)-C(9)-C(10) | -0.9(7) |
| C(16)-C(8)-C(9)-C(10) | 178.4(4) |
| C(6)-N(2)-C(10)-C(9) | 1.4(7) |
| Cu(1)-N(2)-C(10)-C(9) | -179.1(3) |
| C(6)-N(2)-C(10)-C(11) | -176.9(4) |
| Cu(1)-N(2)-C(10)-C(11) | 2.6(5) |
| C(8)-C(9)-C(10)-N(2) | 0.1(7) |
| C(8)-C(9)-C(10)-C(11) | 178.1(4) |
| C(15)-N(3)-C(11)-C(12) | -0.7(7) |
| Cu(1)-N(3)-C(11)-C(12) | 175.2(4) |
| C(15)-N(3)-C(11)-C(10) | 179.8(4) |
| Cu(1)-N(3)-C(11)-C(10) | -4.4(5) |
| N(2)-C(10)-C(11)-N(3) | 1.4(6) |
| C(9)-C(10)-C(11)-N(3) | -176.7(4) |
| N(2)-C(10)-C(11)-C(12) | -178.2(5) |
| C(9)-C(10)-C(11)-C(12) | 3.7(8) |
| N(3)-C(11)-C(12)-C(13) | -0.7(8) |
| C(10)-C(11)-C(12)-C(13) | 178.8(5) |
| C(11)-C(12)-C(13)-C(14) | 2.2(9) |
| C(12)-C(13)-C(14)-C(15) | -2.2(9) |
| C(11)-N(3)-C(15)-C(14) | 0.6(7) |
| Cu(1)-N(3)-C(15)-C(14) | -174.6(4) |
| C(13)-C(14)-C(15)-N(3) | 0.8(8) |
| C(9)-C(8)-C(16)-C(17) | -1.7(8) |
| C(7)-C(8)-C(16)-C(17) | 177.7(5) |
| C(9)-C(8)-C(16)-O(1) | 175.9(5) |
| C(7)-C(8)-C(16)-O(1) | -4.7(7) |
| C(17)-C(16)-O(1)-C(19) | -1.9(6) |
| C(8)-C(16)-O(1)-C(19) | -179.9(5) |
| O(1)-C(16)-C(17)-C(18) | 1.6(6) |
| C(8)-C(16)-C(17)-C(18) | 179.4(5) |
| C(16)-C(17)-C(18)-C(19) | -0.7(7) |
| C(17)-C(18)-C(19)-O(1) | -0.5(7) |
| C(16)-O(1)-C(19)-C(18) | 1.4(7) |

Symmetry transformations used to generate equivalent atoms:

***Table S21.*** Hydrogen bonds for Cu(II)-pincer complex **2c** ·$H_2O$ [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(2)-H(2B)...Br(2)#1 | 0.82(2) | 2.64(5) | 3.405(5) | 154(8) |

| | | | | |
|---|---|---|---|---|
| O(2)-H(2A)...Br(2)#2 | 0.82(2) | 2.67(6) | 3.417(5) | 152(11) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1 #2 x,y-1,z

**16.4. Cu(II)-pincer complex 3.**

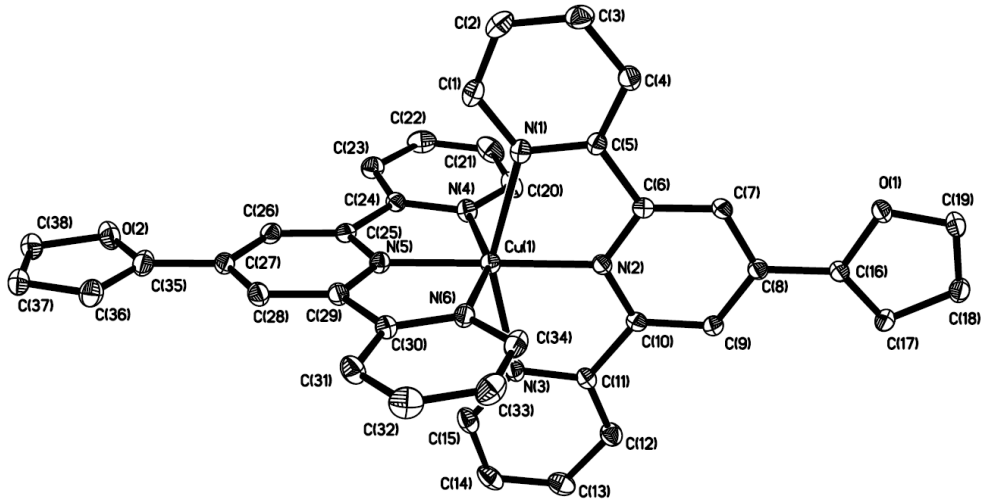



***Figure S47.*** Molecular Structure of Complex **3**, $NO_3^-$ was omitted for clarity.

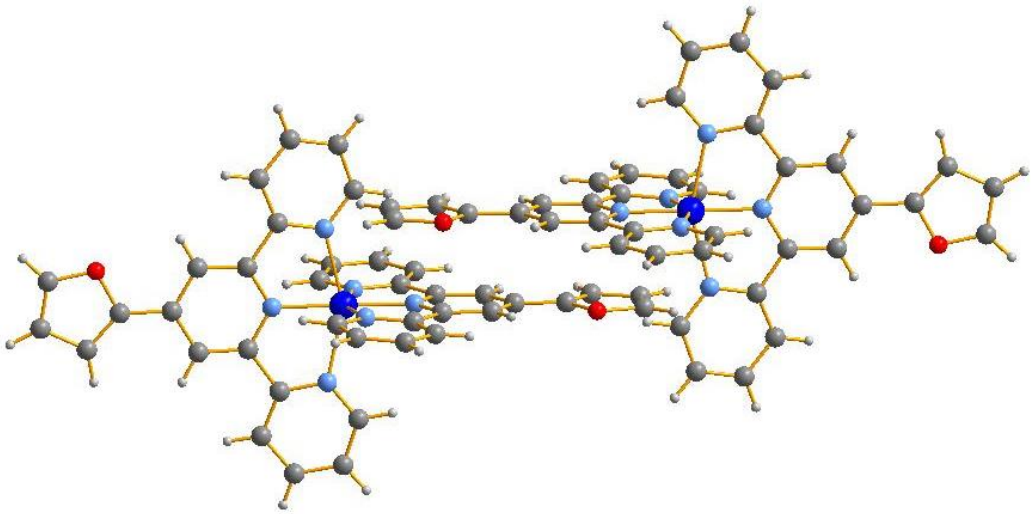


***Figure S48.*** Interactions between the molecules of complex **3**.

***Table S27.*** Crystal data and structure refinement for Cu(II)-pincer complex **3**.

| | |
|---|---|
| Identification code | Cu(II)-pincer complex **3** |
| Empirical formula | C39 H34 Cu N8 O11 |
| Formula weight | 854.28 |
| Temperature | 193(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 10.1291(9) A alpha = 93.3160(10) deg.<br>b = 10.9396(9) A beta = 104.6870(10) deg.<br>c = 17.7746(16) A gamma = 92.3080(10) deg. |
| Volume | 1898.9(3) A^3 |
| Z, Calculated density | 2, 1.494 Mg/m^3 |
| Absorption coefficient | 0.649 mm^-1 |
| F(000) | 882 |
| Crystal size | 0.33 x 0.15 x 0.13 mm |
| Theta range for data collection | 1.19 to 27.00 deg. |
| Limiting indices | -12<=h<=10, -13<=k<=13, -22<=l<=22 |
| Reflections collected / unique | 13525 / 8171 [R(int) = 0.0200] |
| Completeness to theta = 27.00 | 98.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9204 and 0.8143 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 8171 / 4 / 499 |
| Goodness-of-fit on F^2 | 1.111 |
| Final R indices [I>2sigma(I)] | R1 = 0.0532, wR2 = 0.1740 |
| R indices (all data) | R1 = 0.0629, wR2 = 0.1891 |
| Largest diff. peak and hole | 0.502 and -0.656 e.A^-3 |

***Table S28.*** Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(39) | 693(6) | 6821(5) | 1104(3) | 72(1) |
| O(10) | 2723(4) | 3523(3) | 9306(3) | 76(1) |
| O(9) | -244(3) | 7773(3) | 980(2) | 48(1) |
| Cu(1) | 8758(1) | 1399(1) | 2624(1) | 24(1) |
| N(1) | 10235(2) | 80(2) | 3166(1) | 26(1) |
| N(2) | 9275(2) | 2003(2) | 3740(1) | 22(1) |
| N(3) | 7520(3) | 3002(2) | 2632(1) | 26(1) |
| N(4) | 7094(3) | 87(2) | 2588(1) | 27(1) |
| N(5) | 8239(2) | 816(2) | 1517(1) | 23(1) |
| N(6) | 10246(2) | 2392(2) | 2179(1) | 26(1) |
| N(7) | 3591(3) | 6424(3) | 89(2) | 42(1) |
| O(1) | 11399(2) | 2761(2) | 6601(1) | 28(1) |
| O(3) | 4354(4) | 7195(4) | -77(2) | 80(1) |
| O(4) | 2480(3) | 6067(3) | -377(2) | 53(1) |
| O(5) | 3916(5) | 6008(4) | 738(3) | 101(2) |
| C(1) | 10662(3) | -914(3) | 2828(2) | 30(1) |
| C(2) | 11698(4) | -1589(3) | 3218(2) | 34(1) |
| C(3) | 12344(4) | -1227(3) | 3978(2) | 35(1) |
| C(4) | 11911(3) | -219(3) | 4339(2) | 31(1) |
| C(5) | 10845(3) | 410(2) | 3914(2) | 22(1) |
| C(6) | 10271(3) | 1479(2) | 4253(2) | 22(1) |
| C(7) | 10678(3) | 1903(2) | 5024(2) | 23(1) |
| C(8) | 10038(3) | 2894(2) | 5287(2) | 23(1) |
| C(9) | 9012(3) | 3428(2) | 4749(2) | 24(1) |
| C(10) | 8651(3) | 2959(2) | 3981(2) | 23(1) |
| C(11) | 7589(3) | 3480(3) | 3356(2) | 23(1) |
| C(12) | 6780(3) | 4400(3) | 3504(2) | 31(1) |
| C(13) | 5882(3) | 4866(3) | 2868(2) | 36(1) |
| C(14) | 5835(3) | 4405(3) | 2124(2) | 37(1) |
| C(15) | 6659(3) | 3473(3) | 2029(2) | 32(1) |
| C(16) | 10417(3) | 3352(3) | 6097(2) | 24(1) |
| C(17) | 9948(3) | 4264(3) | 6499(2) | 27(1) |
| C(18) | 10676(3) | 4231(3) | 7292(2) | 30(1) |
| C(19) | 11530(3) | 3312(3) | 7322(2) | 31(1) |
| C(20) | 6595(3) | -273(3) | 3169(2) | 35(1) |
| C(21) | 5605(4) | -1217(4) | 3081(2) | 42(1) |
| C(22) | 5095(3) | -1790(3) | 2357(2) | 38(1) |
| C(23) | 5568(3) | -1424(3) | 1730(2) | 30(1) |

| | | | | |
|---|---|---|---|---|
| C(24) | 6578(3) | -487(2) | 1868(2) | 23(1) |
| C(25) | 7198(3) | -39(2) | 1254(2) | 23(1) |
| C(26) | 6789(3) | -442(3) | 484(2) | 26(1) |
| C(27) | 7479(3) | 15(3) | -40(2) | 26(1) |
| C(28) | 8568(3) | 883(3) | 244(2) | 28(1) |
| C(29) | 8909(3) | 1283(3) | 1026(2) | 25(1) |
| C(30) | 10031(3) | 2207(3) | 1402(2) | 25(1) |
| C(31) | 10796(3) | 2841(3) | 988(2) | 33(1) |
| C(32) | 11804(4) | 3695(3) | 1395(2) | 42(1) |
| C(33) | 12036(4) | 3880(3) | 2193(2) | 40(1) |
| C(34) | 11249(3) | 3205(3) | 2568(2) | 33(1) |
| C(35) | 7069(4) | -418(3) | -854(2) | 38(1) |
| C(36) | 7646(3) | -15(2) | -1392(2) | 36(1) |
| C(37) | 6971(3) | -640(3) | -2105(2) | 32(1) |
| C(38) | 6019(3) | -1400(3) | -1973(2) | 33(1) |
| O(2) | 6077(3) | -1252(3) | -1177(2) | 37(1) |
| O(2') | 7646(3) | -15(2) | -1392(2) | 36(1) |
| C(38') | 6971(3) | -640(3) | -2105(2) | 32(1) |
| C(37') | 6019(3) | -1400(3) | -1973(2) | 33(1) |
| C(36') | 6077(3) | -1252(3) | -1177(2) | 37(1) |

***Table S29.*** Bond lengths [A] and angles [deg] for Cu(II)-pincer complex **3**.

| | |
|---|---|
| C(39)-O(9) | 1.425(6) |
| C(39)-H(39A) | 0.9800 |
| C(39)-H(39B) | 0.9800 |
| C(39)-H(39C) | 0.9800 |
| O(10)-H(10A) | 0.862(17) |
| O(10)-H(10B) | 0.85(2) |
| O(9)-H(9) | 0.98(7) |
| Cu(1)-N(5) | 1.965(2) |
| Cu(1)-N(2) | 1.985(2) |
| Cu(1)-N(4) | 2.155(3) |
| Cu(1)-N(6) | 2.157(3) |
| Cu(1)-N(3) | 2.198(3) |
| Cu(1)-N(1) | 2.203(2) |
| N(1)-C(5) | 1.337(4) |
| N(1)-C(1) | 1.351(4) |
| N(2)-C(10) | 1.346(3) |
| N(2)-C(6) | 1.348(3) |
| N(3)-C(15) | 1.343(4) |
| N(3)-C(11) | 1.345(4) |
| N(4)-C(20) | 1.333(4) |

| | |
|---|---|
| N(4)-C(24) | 1.359(4) |
| N(5)-C(29) | 1.344(4) |
| N(5)-C(25) | 1.351(4) |
| N(6)-C(34) | 1.342(4) |
| N(6)-C(30) | 1.344(4) |
| N(7)-O(3) | 1.220(4) |
| N(7)-O(5) | 1.235(5) |
| N(7)-O(4) | 1.248(4) |
| O(1)-C(19) | 1.357(4) |
| O(1)-C(16) | 1.369(3) |
| C(1)-C(2) | 1.371(5) |
| C(1)-H(1) | 0.9500 |
| C(2)-C(3) | 1.372(5) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.386(4) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.384(4) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.491(4) |
| C(6)-C(7) | 1.375(4) |
| C(7)-C(8) | 1.402(4) |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.395(4) |
| C(8)-C(16) | 1.447(4) |
| C(9)-C(10) | 1.382(4) |
| C(9)-H(9A) | 0.9500 |
| C(10)-C(11) | 1.494(4) |
| C(11)-C(12) | 1.378(4) |
| C(12)-C(13) | 1.396(4) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.376(5) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(15) | 1.372(5) |
| C(14)-H(14) | 0.9500 |
| C(15)-H(15) | 0.9500 |
| C(16)-C(17) | 1.363(4) |
| C(17)-C(18) | 1.420(4) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.348(5) |
| C(18)-H(18) | 0.9500 |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.384(5) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.364(5) |

| | |
|---|---|
| C(21)-H(21) | 0.9500 |
| C(22)-C(23) | 1.393(5) |
| C(22)-H(22) | 0.9500 |
| C(23)-C(24) | 1.384(4) |
| C(23)-H(23) | 0.9500 |
| C(24)-C(25) | 1.486(4) |
| C(25)-C(26) | 1.367(4) |
| C(26)-C(27) | 1.401(4) |
| C(26)-H(26) | 0.9500 |
| C(27)-C(28) | 1.397(4) |
| C(27)-C(35) | 1.445(4) |
| C(28)-C(29) | 1.384(4) |
| C(28)-H(28) | 0.9500 |
| C(29)-C(30) | 1.485(4) |
| C(30)-C(31) | 1.388(4) |
| C(31)-C(32) | 1.382(5) |
| C(31)-H(31) | 0.9500 |
| C(32)-C(33) | 1.378(5) |
| C(32)-H(32) | 0.9500 |
| C(33)-C(34) | 1.379(5) |
| C(33)-H(33) | 0.9500 |
| C(34)-H(34) | 0.9500 |
| C(35)-O(2) | 1.321(5) |
| C(35)-C(36) | 1.328(5) |
| C(36)-C(37) | 1.401(4) |
| C(36)-H(36) | 0.9500 |
| C(37)-C(38) | 1.322(5) |
| C(37)-H(37) | 0.9500 |
| C(38)-O(2) | 1.401(4) |
| C(38)-H(38) | 0.9500 |
| O(9)-C(39)-H(39A) | 109.5 |
| O(9)-C(39)-H(39B) | 109.5 |
| H(39A)-C(39)-H(39B) | 109.5 |
| O(9)-C(39)-H(39C) | 109.5 |
| H(39A)-C(39)-H(39C) | 109.5 |
| H(39B)-C(39)-H(39C) | 109.5 |
| H(10A)-O(10)-H(10B) | 105(3) |
| C(39)-O(9)-H(9) | 90(4) |
| N(5)-Cu(1)-N(2) | 179.49(9) |
| N(5)-Cu(1)-N(4) | 78.54(9) |
| N(2)-Cu(1)-N(4) | 101.64(9) |
| N(5)-Cu(1)-N(6) | 78.07(9) |
| N(2)-Cu(1)-N(6) | 101.78(9) |
| N(4)-Cu(1)-N(6) | 156.48(10) |

| | |
|---|---|
| N(5)-Cu(1)-N(3) | 102.14(9) |
| N(2)-Cu(1)-N(3) | 77.38(9) |
| N(4)-Cu(1)-N(3) | 94.44(9) |
| N(6)-Cu(1)-N(3) | 92.72(9) |
| N(5)-Cu(1)-N(1) | 103.43(9) |
| N(2)-Cu(1)-N(1) | 77.06(9) |
| N(4)-Cu(1)-N(1) | 90.14(9) |
| N(6)-Cu(1)-N(1) | 92.99(9) |
| N(3)-Cu(1)-N(1) | 154.43(9) |
| C(5)-N(1)-C(1) | 118.4(3) |
| C(5)-N(1)-Cu(1) | 112.63(18) |
| C(1)-N(1)-Cu(1) | 128.7(2) |
| C(10)-N(2)-C(6) | 120.1(2) |
| C(10)-N(2)-Cu(1) | 119.76(18) |
| C(6)-N(2)-Cu(1) | 120.15(18) |
| C(15)-N(3)-C(11) | 118.4(3) |
| C(15)-N(3)-Cu(1) | 128.6(2) |
| C(11)-N(3)-Cu(1) | 112.84(18) |
| C(20)-N(4)-C(24) | 118.1(3) |
| C(20)-N(4)-Cu(1) | 129.1(2) |
| C(24)-N(4)-Cu(1) | 112.66(18) |
| C(29)-N(5)-C(25) | 120.6(2) |
| C(29)-N(5)-Cu(1) | 119.78(19) |
| C(25)-N(5)-Cu(1) | 119.62(18) |
| C(34)-N(6)-C(30) | 118.7(3) |
| C(34)-N(6)-Cu(1) | 128.2(2) |
| C(30)-N(6)-Cu(1) | 112.90(19) |
| O(3)-N(7)-O(5) | 119.0(4) |
| O(3)-N(7)-O(4) | 121.4(3) |
| O(5)-N(7)-O(4) | 119.6(4) |
| C(19)-O(1)-C(16) | 106.6(2) |
| N(1)-C(1)-C(2) | 122.7(3) |
| N(1)-C(1)-H(1) | 118.7 |
| C(2)-C(1)-H(1) | 118.7 |
| C(1)-C(2)-C(3) | 118.6(3) |
| C(1)-C(2)-H(2) | 120.7 |
| C(3)-C(2)-H(2) | 120.7 |
| C(2)-C(3)-C(4) | 119.6(3) |
| C(2)-C(3)-H(3) | 120.2 |
| C(4)-C(3)-H(3) | 120.2 |
| C(5)-C(4)-C(3) | 118.7(3) |
| C(5)-C(4)-H(4) | 120.7 |
| C(3)-C(4)-H(4) | 120.7 |
| N(1)-C(5)-C(4) | 122.0(3) |

| | |
|---|---|
| N(1)-C(5)-C(6) | 115.0(2) |
| C(4)-C(5)-C(6) | 123.0(3) |
| N(2)-C(6)-C(7) | 121.3(2) |
| N(2)-C(6)-C(5) | 114.4(2) |
| C(7)-C(6)-C(5) | 124.2(2) |
| C(6)-C(7)-C(8) | 119.5(2) |
| C(6)-C(7)-H(7) | 120.3 |
| C(8)-C(7)-H(7) | 120.3 |
| C(9)-C(8)-C(7) | 118.4(2) |
| C(9)-C(8)-C(16) | 120.4(2) |
| C(7)-C(8)-C(16) | 121.2(2) |
| C(10)-C(9)-C(8) | 119.3(2) |
| C(10)-C(9)-H(9A) | 120.3 |
| C(8)-C(9)-H(9A) | 120.3 |
| N(2)-C(10)-C(9) | 121.4(2) |
| N(2)-C(10)-C(11) | 115.1(2) |
| C(9)-C(10)-C(11) | 123.5(2) |
| N(3)-C(11)-C(12) | 122.7(3) |
| N(3)-C(11)-C(10) | 114.2(2) |
| C(12)-C(11)-C(10) | 123.1(3) |
| C(11)-C(12)-C(13) | 117.9(3) |
| C(11)-C(12)-H(12) | 121.1 |
| C(13)-C(12)-H(12) | 121.1 |
| C(14)-C(13)-C(12) | 119.6(3) |
| C(14)-C(13)-H(13) | 120.2 |
| C(12)-C(13)-H(13) | 120.2 |
| C(15)-C(14)-C(13) | 118.8(3) |
| C(15)-C(14)-H(14) | 120.6 |
| C(13)-C(14)-H(14) | 120.6 |
| N(3)-C(15)-C(14) | 122.6(3) |
| N(3)-C(15)-H(15) | 118.7 |
| C(14)-C(15)-H(15) | 118.7 |
| C(17)-C(16)-O(1) | 109.7(2) |
| C(17)-C(16)-C(8) | 132.8(3) |
| O(1)-C(16)-C(8) | 117.4(2) |
| C(16)-C(17)-C(18) | 106.4(3) |
| C(16)-C(17)-H(17) | 126.8 |
| C(18)-C(17)-H(17) | 126.8 |
| C(19)-C(18)-C(17) | 106.5(3) |
| C(19)-C(18)-H(18) | 126.8 |
| C(17)-C(18)-H(18) | 126.8 |
| C(18)-C(19)-O(1) | 110.8(3) |
| C(18)-C(19)-H(19) | 124.6 |
| O(1)-C(19)-H(19) | 124.6 |

| | |
|---|---|
| N(4)-C(20)-C(21) | 123.4(3) |
| N(4)-C(20)-H(20) | 118.3 |
| C(21)-C(20)-H(20) | 118.3 |
| C(22)-C(21)-C(20) | 118.2(3) |
| C(22)-C(21)-H(21) | 120.9 |
| C(20)-C(21)-H(21) | 120.9 |
| C(21)-C(22)-C(23) | 120.2(3) |
| C(21)-C(22)-H(22) | 119.9 |
| C(23)-C(22)-H(22) | 119.9 |
| C(24)-C(23)-C(22) | 118.3(3) |
| C(24)-C(23)-H(23) | 120.9 |
| C(22)-C(23)-H(23) | 120.9 |
| N(4)-C(24)-C(23) | 121.9(3) |
| N(4)-C(24)-C(25) | 114.7(2) |
| C(23)-C(24)-C(25) | 123.5(3) |
| N(5)-C(25)-C(26) | 121.1(3) |
| N(5)-C(25)-C(24) | 114.4(2) |
| C(26)-C(25)-C(24) | 124.5(3) |
| C(25)-C(26)-C(27) | 119.6(3) |
| C(25)-C(26)-H(26) | 120.2 |
| C(27)-C(26)-H(26) | 120.2 |
| C(28)-C(27)-C(26) | 118.5(3) |
| C(28)-C(27)-C(35) | 121.3(3) |
| C(26)-C(27)-C(35) | 120.2(3) |
| C(29)-C(28)-C(27) | 119.3(3) |
| C(29)-C(28)-H(28) | 120.4 |
| C(27)-C(28)-H(28) | 120.4 |
| N(5)-C(29)-C(28) | 120.9(3) |
| N(5)-C(29)-C(30) | 114.3(2) |
| C(28)-C(29)-C(30) | 124.8(3) |
| N(6)-C(30)-C(31) | 122.3(3) |
| N(6)-C(30)-C(29) | 114.7(2) |
| C(31)-C(30)-C(29) | 123.0(3) |
| C(32)-C(31)-C(30) | 118.2(3) |
| C(32)-C(31)-H(31) | 120.9 |
| C(30)-C(31)-H(31) | 120.9 |
| C(33)-C(32)-C(31) | 119.7(3) |
| C(33)-C(32)-H(32) | 120.2 |
| C(31)-C(32)-H(32) | 120.2 |
| C(32)-C(33)-C(34) | 119.0(3) |
| C(32)-C(33)-H(33) | 120.5 |
| C(34)-C(33)-H(33) | 120.5 |
| N(6)-C(34)-C(33) | 122.1(3) |
| N(6)-C(34)-H(34) | 119.0 |

| | |
|---|---|
| C(33)-C(34)-H(34) | 119.0 |
| O(2)-C(35)-C(36) | 109.8(3) |
| O(2)-C(35)-C(27) | 126.1(3) |
| C(36)-C(35)-C(27) | 124.1(3) |
| C(35)-C(36)-C(37) | 107.4(3) |
| C(35)-C(36)-H(36) | 126.3 |
| C(37)-C(36)-H(36) | 126.3 |
| C(38)-C(37)-C(36) | 107.7(3) |
| C(38)-C(37)-H(37) | 126.2 |
| C(36)-C(37)-H(37) | 126.2 |
| C(37)-C(38)-O(2) | 107.4(3) |
| C(37)-C(38)-H(38) | 126.3 |
| O(2)-C(38)-H(38) | 126.3 |
| C(35)-O(2)-C(38) | 107.7(3) |

Symmetry transformations used to generate equivalent atoms:

***Table S30.*** Anisotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **3**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(39) | 81(4) | 92(4) | 52(3) | 22(3) | 27(2) | 27(3) |
| O(10) | 59(2) | 50(2) | 105(3) | -15(2) | -2(2) | -11(2) |
| O(9) | 52(2) | 52(2) | 41(1) | 1(1) | 14(1) | -5(1) |
| Cu(1) | 24(1) | 25(1) | 21(1) | 1(1) | 5(1) | 0(1) |
| N(1) | 26(1) | 27(1) | 23(1) | -1(1) | 7(1) | -2(1) |
| N(2) | 22(1) | 23(1) | 20(1) | 3(1) | 5(1) | 2(1) |
| N(3) | 26(1) | 29(1) | 20(1) | 2(1) | 2(1) | -3(1) |
| N(4) | 26(1) | 31(1) | 24(1) | 2(1) | 5(1) | 0(1) |
| N(5) | 23(1) | 23(1) | 23(1) | 0(1) | 6(1) | -2(1) |
| N(6) | 28(1) | 26(1) | 22(1) | -2(1) | 5(1) | 2(1) |
| N(7) | 45(2) | 34(2) | 43(2) | 0(1) | 4(1) | -2(1) |
| O(1) | 30(1) | 31(1) | 21(1) | 2(1) | 2(1) | 7(1) |
| O(3) | 100(3) | 92(3) | 42(2) | -11(2) | 21(2) | -61(2) |
| O(4) | 42(2) | 57(2) | 52(2) | 1(1) | -1(1) | -2(1) |
| O(5) | 103(3) | 81(3) | 88(3) | 49(2) | -38(2) | -29(2) |
| C(1) | 35(2) | 29(2) | 28(1) | -6(1) | 12(1) | -4(1) |
| C(2) | 39(2) | 25(1) | 43(2) | -6(1) | 20(1) | -3(1) |
| C(3) | 37(2) | 33(2) | 41(2) | 5(1) | 14(1) | 12(1) |
| C(4) | 33(2) | 35(2) | 25(1) | 1(1) | 5(1) | 9(1) |
| C(5) | 23(1) | 23(1) | 21(1) | 0(1) | 8(1) | -2(1) |
| C(6) | 20(1) | 22(1) | 24(1) | 3(1) | 6(1) | 1(1) |
| C(7) | 23(1) | 24(1) | 22(1) | 4(1) | 2(1) | 3(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(8) | 23(1) | 22(1) | 22(1) | 2(1) | 4(1) | 0(1) |
| C(9) | 25(1) | 22(1) | 23(1) | 1(1) | 5(1) | 3(1) |
| C(10) | 22(1) | 23(1) | 23(1) | 4(1) | 5(1) | 4(1) |
| C(11) | 22(1) | 27(1) | 21(1) | 4(1) | 4(1) | 0(1) |
| C(12) | 29(2) | 36(2) | 27(1) | 3(1) | 6(1) | 7(1) |
| C(13) | 30(2) | 38(2) | 41(2) | 12(1) | 7(1) | 8(1) |
| C(14) | 30(2) | 45(2) | 33(2) | 16(1) | -3(1) | -1(1) |
| C(15) | 29(2) | 39(2) | 23(1) | 6(1) | 0(1) | -6(1) |
| C(16) | 25(1) | 24(1) | 21(1) | 3(1) | 3(1) | 1(1) |
| C(17) | 32(2) | 24(1) | 24(1) | -2(1) | 6(1) | 0(1) |
| C(18) | 35(2) | 30(2) | 25(1) | -2(1) | 7(1) | -1(1) |
| C(19) | 34(2) | 35(2) | 21(1) | 1(1) | 1(1) | 1(1) |
| C(20) | 35(2) | 48(2) | 24(1) | 8(1) | 6(1) | 6(1) |
| C(21) | 35(2) | 56(2) | 40(2) | 19(2) | 16(2) | 7(2) |
| C(22) | 32(2) | 30(2) | 54(2) | 9(1) | 15(2) | -4(1) |
| C(23) | 28(2) | 28(1) | 33(2) | 1(1) | 5(1) | -1(1) |
| C(24) | 23(1) | 23(1) | 22(1) | 3(1) | 4(1) | 2(1) |
| C(25) | 23(1) | 20(1) | 26(1) | 2(1) | 5(1) | 2(1) |
| C(26) | 27(1) | 23(1) | 26(1) | -1(1) | 2(1) | 2(1) |
| C(27) | 28(1) | 27(1) | 22(1) | 0(1) | 3(1) | 8(1) |
| C(28) | 31(2) | 31(2) | 23(1) | 3(1) | 8(1) | 4(1) |
| C(29) | 26(1) | 26(1) | 22(1) | 2(1) | 6(1) | 2(1) |
| C(30) | 25(1) | 26(1) | 23(1) | 2(1) | 7(1) | 1(1) |
| C(31) | 35(2) | 39(2) | 26(1) | 8(1) | 8(1) | -3(1) |
| C(32) | 32(2) | 41(2) | 53(2) | 6(2) | 14(2) | -9(1) |
| C(33) | 30(2) | 37(2) | 49(2) | -8(2) | 6(1) | -6(1) |
| C(34) | 31(2) | 32(2) | 32(2) | -8(1) | 5(1) | 3(1) |
| C(35) | 41(2) | 42(2) | 26(2) | -6(1) | -1(1) | 19(2) |
| C(36) | 37(2) | 34(1) | 31(1) | -5(1) | 0(1) | -4(1) |
| C(37) | 35(2) | 35(2) | 25(1) | -2(1) | 7(1) | 1(1) |
| C(38) | 33(2) | 37(2) | 26(1) | 0(1) | 5(1) | 1(1) |
| O(2) | 37(2) | 52(2) | 26(1) | 5(1) | 11(1) | 9(1) |
| O(2') | 37(2) | 34(1) | 31(1) | -5(1) | 0(1) | -4(1) |
| C(38') | 35(2) | 35(2) | 25(1) | -2(1) | 7(1) | 1(1) |
| C(37') | 33(2) | 37(2) | 26(1) | 0(1) | 5(1) | 1(1) |
| C(36') | 37(2) | 52(2) | 26(1) | 5(1) | 11(1) | 9(1) |

***Table S31.*** Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Cu(II)-pincer complex **3**.

| x | y | z | U(eq) | | |
|---|---|---|---|---|---|
| H(39A) | 1543 | 7098 | 983 | 108 | |

| | | | | |
|---|---|---|---|---|
| H(39B) | 290 | 6092 | 765 | 108 |
| H(39C) | 889 | 6620 | 1650 | 108 |
| H(1) | 10226 | -1155 | 2298 | 36 |
| H(2) | 11963 | -2293 | 2966 | 41 |
| H(3) | 13084 | -1665 | 4256 | 43 |
| H(4) | 12337 | 35 | 4869 | 37 |
| H(7) | 11387 | 1528 | 5377 | 28 |
| H(9A) | 8566 | 4106 | 4908 | 28 |
| H(12) | 6831 | 4707 | 4023 | 37 |
| H(13) | 5306 | 5498 | 2948 | 43 |
| H(14) | 5244 | 4725 | 1685 | 45 |
| H(15) | 6619 | 3149 | 1515 | 38 |
| H(17) | 9268 | 4813 | 6289 | 33 |
| H(18) | 10580 | 4755 | 7718 | 36 |
| H(19) | 12141 | 3081 | 7785 | 37 |
| H(20) | 6936 | 141 | 3671 | 43 |
| H(21) | 5290 | -1459 | 3513 | 50 |
| H(22) | 4414 | -2441 | 2280 | 45 |
| H(23) | 5208 | -1807 | 1222 | 36 |
| H(26) | 6041 | -1029 | 305 | 32 |
| H(28) | 9069 | 1195 | -95 | 33 |
| H(31) | 10630 | 2692 | 439 | 40 |
| H(32) | 12336 | 4151 | 1127 | 50 |
| H(33) | 12726 | 4464 | 2480 | 48 |
| H(34) | 11423 | 3320 | 3119 | 39 |
| H(36) | 8382 | 586 | -1310 | 43 |
| H(37) | 7162 | -537 | -2594 | 39 |
| H(38) | 5407 | -1946 | -2350 | 39 |
| H(38') | 7162 | -537 | -2594 | 39 |
| H(37') | 5407 | -1946 | -2350 | 39 |
| H(36') | 5507 | -1676 | -916 | 45 |
| H(10A) | 2610(30) | 4301(17) | 9320(20) | 56 |
| H(9) | -1010(70) | 7150(60) | 900(40) | 100(20) |
| H(10B) | 3410(60) | 3430(50) | 9680(40) | 148 |

***Table S32.*** Torsion angles [deg] for Cu(II)-pincer complex **3**.

| | |
|---|---|
| N(5)-Cu(1)-N(1)-C(5) | 172.09(19) |
| N(2)-Cu(1)-N(1)-C(5) | -7.76(19) |
| N(4)-Cu(1)-N(1)-C(5) | -109.67(19) |
| N(6)-Cu(1)-N(1)-C(5) | 93.65(19) |
| N(3)-Cu(1)-N(1)-C(5) | -9.0(3) |
| N(5)-Cu(1)-N(1)-C(1) | -1.6(3) |

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|---|---|
| N(2)-Cu(1)-N(1)-C(1) | 178.6(3) |
| N(4)-Cu(1)-N(1)-C(1) | 76.7(3) |
| N(6)-Cu(1)-N(1)-C(1) | -80.0(2) |
| N(3)-Cu(1)-N(1)-C(1) | 177.3(2) |
| N(5)-Cu(1)-N(2)-C(10) | 21(11) |
| N(4)-Cu(1)-N(2)-C(10) | -88.3(2) |
| N(6)-Cu(1)-N(2)-C(10) | 93.9(2) |
| N(3)-Cu(1)-N(2)-C(10) | 3.7(2) |
| N(1)-Cu(1)-N(2)-C(10) | -175.8(2) |
| N(5)-Cu(1)-N(2)-C(6) | -157(11) |
| N(4)-Cu(1)-N(2)-C(6) | 93.3(2) |
| N(6)-Cu(1)-N(2)-C(6) | -84.5(2) |
| N(3)-Cu(1)-N(2)-C(6) | -174.7(2) |
| N(1)-Cu(1)-N(2)-C(6) | 5.9(2) |
| N(5)-Cu(1)-N(3)-C(15) | -1.5(3) |
| N(2)-Cu(1)-N(3)-C(15) | 178.3(3) |
| N(4)-Cu(1)-N(3)-C(15) | -80.7(3) |
| N(6)-Cu(1)-N(3)-C(15) | 76.9(3) |
| N(1)-Cu(1)-N(3)-C(15) | 179.6(2) |
| N(5)-Cu(1)-N(3)-C(11) | 172.77(19) |
| N(2)-Cu(1)-N(3)-C(11) | -7.39(19) |
| N(4)-Cu(1)-N(3)-C(11) | 93.6(2) |
| N(6)-Cu(1)-N(3)-C(11) | -108.9(2) |
| N(1)-Cu(1)-N(3)-C(11) | -6.1(3) |
| N(5)-Cu(1)-N(4)-C(20) | 177.2(3) |
| N(2)-Cu(1)-N(4)-C(20) | -3.3(3) |
| N(6)-Cu(1)-N(4)-C(20) | 171.4(3) |
| N(3)-Cu(1)-N(4)-C(20) | -81.3(3) |
| N(1)-Cu(1)-N(4)-C(20) | 73.6(3) |
| N(5)-Cu(1)-N(4)-C(24) | 2.04(19) |
| N(2)-Cu(1)-N(4)-C(24) | -178.46(19) |
| N(6)-Cu(1)-N(4)-C(24) | -3.8(4) |
| N(3)-Cu(1)-N(4)-C(24) | 103.54(19) |
| N(1)-Cu(1)-N(4)-C(24) | -101.65(19) |
| N(2)-Cu(1)-N(5)-C(29) | 69(11) |
| N(4)-Cu(1)-N(5)-C(29) | 179.2(2) |
| N(6)-Cu(1)-N(5)-C(29) | -3.2(2) |
| N(3)-Cu(1)-N(5)-C(29) | 87.1(2) |
| N(1)-Cu(1)-N(5)-C(29) | -93.4(2) |
| N(2)-Cu(1)-N(5)-C(25) | -110(11) |
| N(4)-Cu(1)-N(5)-C(25) | 0.2(2) |
| N(6)-Cu(1)-N(5)-C(25) | 177.9(2) |
| N(3)-Cu(1)-N(5)-C(25) | -91.9(2) |
| N(1)-Cu(1)-N(5)-C(25) | 87.6(2) |

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|---|---|
| N(5)-Cu(1)-N(6)-C(34) | 179.4(3) |
| N(2)-Cu(1)-N(6)-C(34) | -0.1(3) |
| N(4)-Cu(1)-N(6)-C(34) | -174.8(2) |
| N(3)-Cu(1)-N(6)-C(34) | 77.5(3) |
| N(1)-Cu(1)-N(6)-C(34) | -77.5(3) |
| N(5)-Cu(1)-N(6)-C(30) | 4.65(19) |
| N(2)-Cu(1)-N(6)-C(30) | -174.85(19) |
| N(4)-Cu(1)-N(6)-C(30) | 10.5(4) |
| N(3)-Cu(1)-N(6)-C(30) | -97.2(2) |
| N(1)-Cu(1)-N(6)-C(30) | 107.8(2) |
| C(5)-N(1)-C(1)-C(2) | -0.4(4) |
| Cu(1)-N(1)-C(1)-C(2) | 172.9(2) |
| N(1)-C(1)-C(2)-C(3) | -1.2(5) |
| C(1)-C(2)-C(3)-C(4) | 2.0(5) |
| C(2)-C(3)-C(4)-C(5) | -1.1(5) |
| C(1)-N(1)-C(5)-C(4) | 1.4(4) |
| Cu(1)-N(1)-C(5)-C(4) | -173.0(2) |
| C(1)-N(1)-C(5)-C(6) | -177.3(2) |
| Cu(1)-N(1)-C(5)-C(6) | 8.4(3) |
| C(3)-C(4)-C(5)-N(1) | -0.6(5) |
| C(3)-C(4)-C(5)-C(6) | 177.9(3) |
| C(10)-N(2)-C(6)-C(7) | -0.3(4) |
| Cu(1)-N(2)-C(6)-C(7) | 178.0(2) |
| C(10)-N(2)-C(6)-C(5) | 178.3(2) |
| Cu(1)-N(2)-C(6)-C(5) | -3.3(3) |
| N(1)-C(5)-C(6)-N(2) | -4.0(3) |
| C(4)-C(5)-C(6)-N(2) | 177.4(3) |
| N(1)-C(5)-C(6)-C(7) | 174.6(3) |
| C(4)-C(5)-C(6)-C(7) | -4.0(4) |
| N(2)-C(6)-C(7)-C(8) | 0.5(4) |
| C(5)-C(6)-C(7)-C(8) | -178.0(3) |
| C(6)-C(7)-C(8)-C(9) | -0.7(4) |
| C(6)-C(7)-C(8)-C(16) | 178.8(3) |
| C(7)-C(8)-C(9)-C(10) | 0.7(4) |
| C(16)-C(8)-C(9)-C(10) | -178.8(3) |
| C(6)-N(2)-C(10)-C(9) | 0.2(4) |
| Cu(1)-N(2)-C(10)-C(9) | -178.1(2) |
| C(6)-N(2)-C(10)-C(11) | 178.6(2) |
| Cu(1)-N(2)-C(10)-C(11) | 0.3(3) |
| C(8)-C(9)-C(10)-N(2) | -0.4(4) |
| C(8)-C(9)-C(10)-C(11) | -178.6(3) |
| C(15)-N(3)-C(11)-C(12) | 2.3(4) |
| Cu(1)-N(3)-C(11)-C(12) | -172.6(2) |
| C(15)-N(3)-C(11)-C(10) | -175.5(2) |

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|---|---|
| Cu(1)-N(3)-C(11)-C(10) | 9.5(3) |
| N(2)-C(10)-C(11)-N(3) | -6.9(4) |
| C(9)-C(10)-C(11)-N(3) | 171.4(3) |
| N(2)-C(10)-C(11)-C(12) | 175.2(3) |
| C(9)-C(10)-C(11)-C(12) | -6.5(4) |
| N(3)-C(11)-C(12)-C(13) | -1.7(5) |
| C(10)-C(11)-C(12)-C(13) | 176.0(3) |
| C(11)-C(12)-C(13)-C(14) | -0.2(5) |
| C(12)-C(13)-C(14)-C(15) | 1.4(5) |
| C(11)-N(3)-C(15)-C(14) | -1.1(5) |
| Cu(1)-N(3)-C(15)-C(14) | 172.9(2) |
| C(13)-C(14)-C(15)-N(3) | -0.7(5) |
| C(19)-O(1)-C(16)-C(17) | 0.3(3) |
| C(19)-O(1)-C(16)-C(8) | -177.2(3) |
| C(9)-C(8)-C(16)-C(17) | 1.0(5) |
| C(7)-C(8)-C(16)-C(17) | -178.4(3) |
| C(9)-C(8)-C(16)-O(1) | 177.8(3) |
| C(7)-C(8)-C(16)-O(1) | -1.7(4) |
| O(1)-C(16)-C(17)-C(18) | -0.2(3) |
| C(8)-C(16)-C(17)-C(18) | 176.8(3) |
| C(16)-C(17)-C(18)-C(19) | -0.1(4) |
| C(17)-C(18)-C(19)-O(1) | 0.3(4) |
| C(16)-O(1)-C(19)-C(18) | -0.4(3) |
| C(24)-N(4)-C(20)-C(21) | 1.6(5) |
| Cu(1)-N(4)-C(20)-C(21) | -173.3(2) |
| N(4)-C(20)-C(21)-C(22) | -1.5(5) |
| C(20)-C(21)-C(22)-C(23) | 0.0(5) |
| C(21)-C(22)-C(23)-C(24) | 1.1(5) |
| C(20)-N(4)-C(24)-C(23) | -0.4(4) |
| Cu(1)-N(4)-C(24)-C(23) | 175.4(2) |
| C(20)-N(4)-C(24)-C(25) | -179.5(3) |
| Cu(1)-N(4)-C(24)-C(25) | -3.7(3) |
| C(22)-C(23)-C(24)-N(4) | -1.0(4) |
| C(22)-C(23)-C(24)-C(25) | 178.1(3) |
| C(29)-N(5)-C(25)-C(26) | -0.6(4) |
| Cu(1)-N(5)-C(25)-C(26) | 178.3(2) |
| C(29)-N(5)-C(25)-C(24) | 178.7(2) |
| Cu(1)-N(5)-C(25)-C(24) | -2.3(3) |
| N(4)-C(24)-C(25)-N(5) | 4.0(3) |
| C(23)-C(24)-C(25)-N(5) | -175.1(3) |
| N(4)-C(24)-C(25)-C(26) | -176.6(3) |
| C(23)-C(24)-C(25)-C(26) | 4.2(4) |
| N(5)-C(25)-C(26)-C(27) | 1.5(4) |
| C(24)-C(25)-C(26)-C(27) | -177.8(3) |

| | |
|---|---|
| C(25)-C(26)-C(27)-C(28) | -0.4(4) |
| C(25)-C(26)-C(27)-C(35) | 179.1(3) |
| C(26)-C(27)-C(28)-C(29) | -1.5(4) |
| C(35)-C(27)-C(28)-C(29) | 179.0(3) |
| C(25)-N(5)-C(29)-C(28) | -1.4(4) |
| Cu(1)-N(5)-C(29)-C(28) | 179.7(2) |
| C(25)-N(5)-C(29)-C(30) | -179.7(2) |
| Cu(1)-N(5)-C(29)-C(30) | 1.3(3) |
| C(27)-C(28)-C(29)-N(5) | 2.4(4) |
| C(27)-C(28)-C(29)-C(30) | -179.4(3) |
| C(34)-N(6)-C(30)-C(31) | -1.1(4) |
| Cu(1)-N(6)-C(30)-C(31) | 174.2(2) |
| C(34)-N(6)-C(30)-C(29) | 179.4(2) |
| Cu(1)-N(6)-C(30)-C(29) | -5.3(3) |
| N(5)-C(29)-C(30)-N(6) | 2.9(4) |
| C(28)-C(29)-C(30)-N(6) | -175.3(3) |
| N(5)-C(29)-C(30)-C(31) | -176.6(3) |
| C(28)-C(29)-C(30)-C(31) | 5.1(5) |
| N(6)-C(30)-C(31)-C(32) | -0.4(5) |
| C(29)-C(30)-C(31)-C(32) | 179.1(3) |
| C(30)-C(31)-C(32)-C(33) | 0.9(5) |
| C(31)-C(32)-C(33)-C(34) | 0.0(5) |
| C(30)-N(6)-C(34)-C(33) | 2.0(4) |
| Cu(1)-N(6)-C(34)-C(33) | -172.5(2) |
| C(32)-C(33)-C(34)-N(6) | -1.5(5) |
| C(28)-C(27)-C(35)-O(2) | 178.4(3) |
| C(26)-C(27)-C(35)-O(2) | -1.0(5) |
| C(28)-C(27)-C(35)-C(36) | -2.0(5) |
| C(26)-C(27)-C(35)-C(36) | 178.5(3) |
| O(2)-C(35)-C(36)-C(37) | 0.0(4) |
| C(27)-C(35)-C(36)-C(37) | -179.6(3) |
| C(35)-C(36)-C(37)-C(38) | -0.4(4) |
| C(36)-C(37)-C(38)-O(2) | 0.6(4) |
| C(36)-C(35)-O(2)-C(38) | 0.3(4) |
| C(27)-C(35)-O(2)-C(38) | 179.9(3) |
| C(37)-C(38)-O(2)-C(35) | -0.6(4) |

Symmetry transformations used to generate equivalent atoms:

***Table S33.*** Hydrogen bonds for Cu(II)-pincer complex **3** [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(9)-H(9)...O(10)#1 | 0.98(7) | 1.80(7) | 2.749(5) | 161(6) |

| | | | | |
|---|---|---|---|---|
| O(10)-H(10B)...O(3)#2 | 0.85(2) | 2.33(5) | 3.085(6) | 147(8) |
| O(10)-H(10A)...O(4)#3 | 0.862(17) | 1.994(19) | 2.840(5) | 167(3) |

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1 #2 -x+1,-y+1,-z+1 #3 x,y,z+1

**17. X-Ray diffraction (XRD) study.**

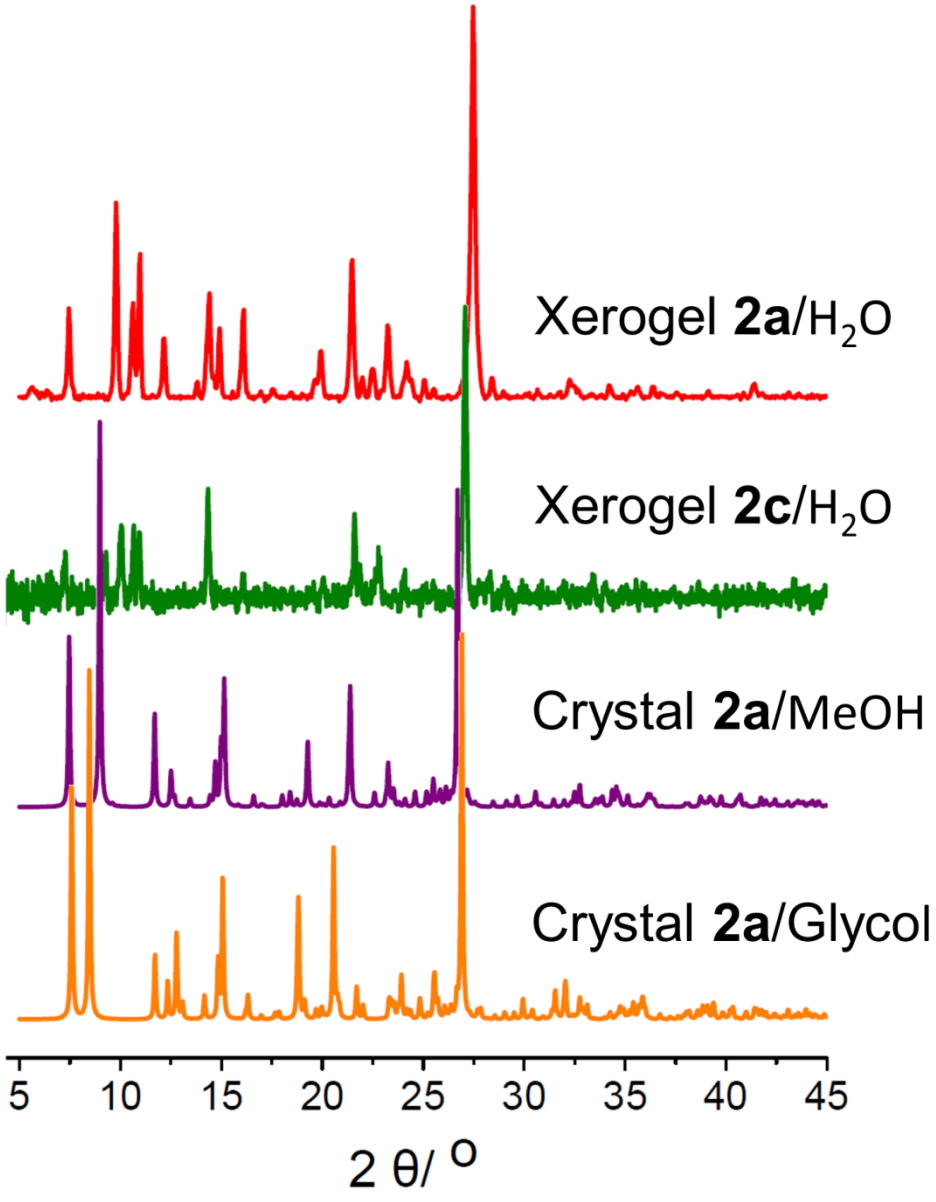


***Figure S49.*** X-Ray diffraction pattern of: Xerogel **2**a/$H_2O$ (5 wt%), xerogel **2c**/$H_2O$ (1 wt%), crystal **2**a•MeOH and crystal **2**a•Glycol.

## 18. SEM Morphologies of sols prepared from metallogels 2a with additional complex 1a after heating and cooling procedure.

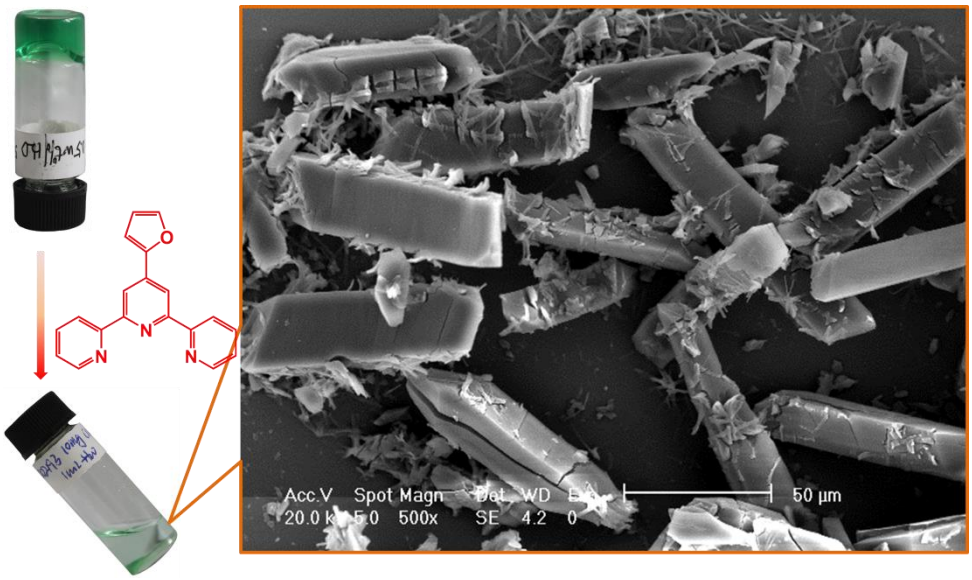


***Figure S50.*** SEM image of the sol prepared from hydrogel **2a**/$H_2O$ (1.0 wt%) with additional 1 equiv. complex **1a** after heating and cooling procedure, scale of bar 50 μm.

## 19. $^{1}$H NMR, $^{13}$C NMR and ESI-MS spectra for important compounds.

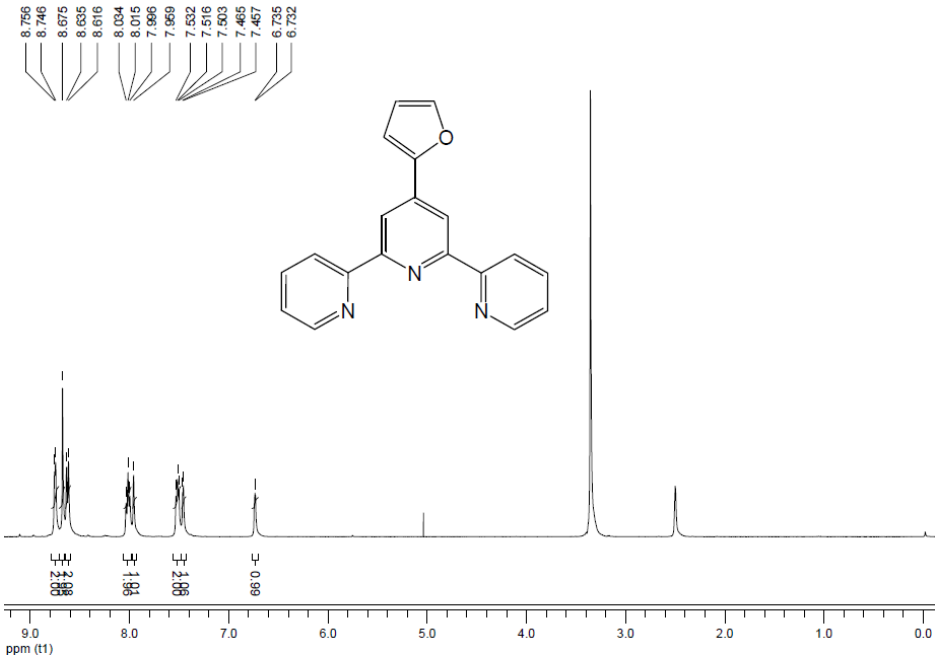


***Figure S51.*** $^{1}$H NMR (DMSO-$D_6$, 400 MHz, 298 K) spectrum of **1a**.

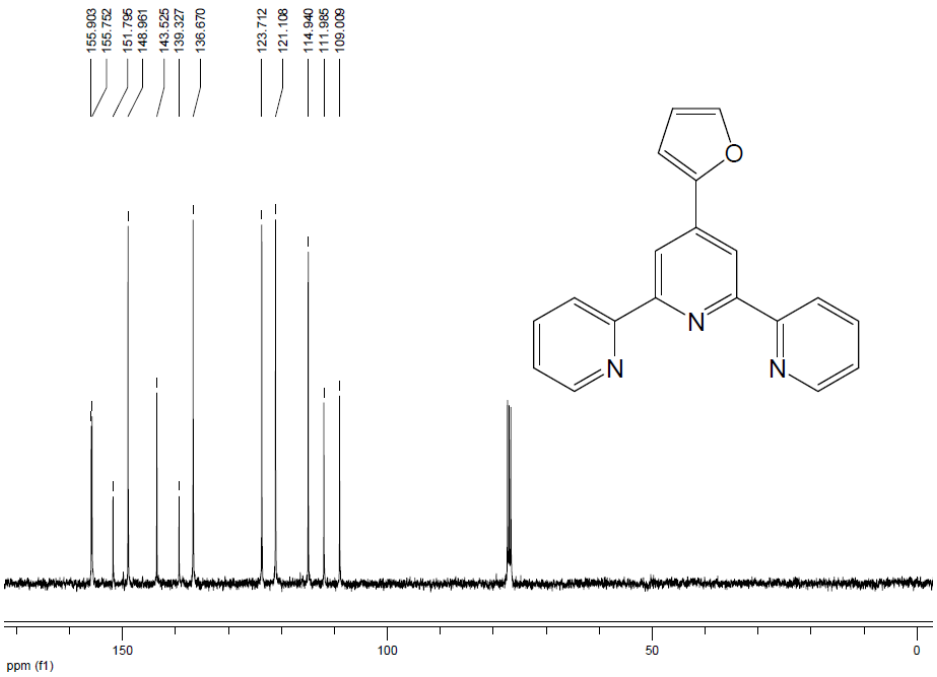


***Figure S52.*** $^{13}C$ NMR ($CDCl_3$, 100 MHz, 298 K) spectrum of **1a**.

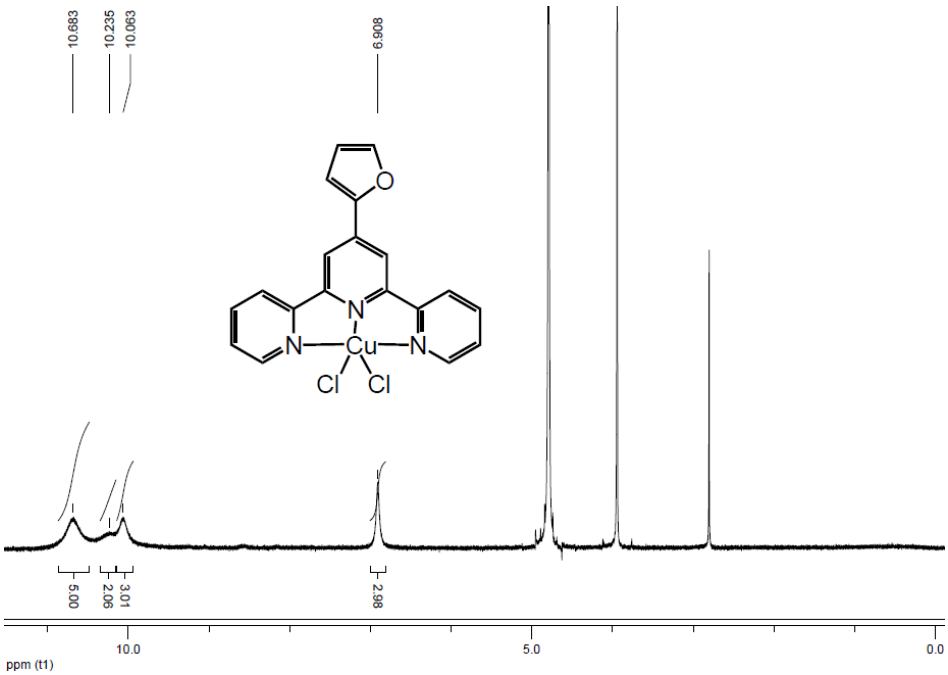


***Figure S53.*** $^{1}H$ NMR ($D_2O$, 400 MHz, 353 K) spectrum of **2a**.

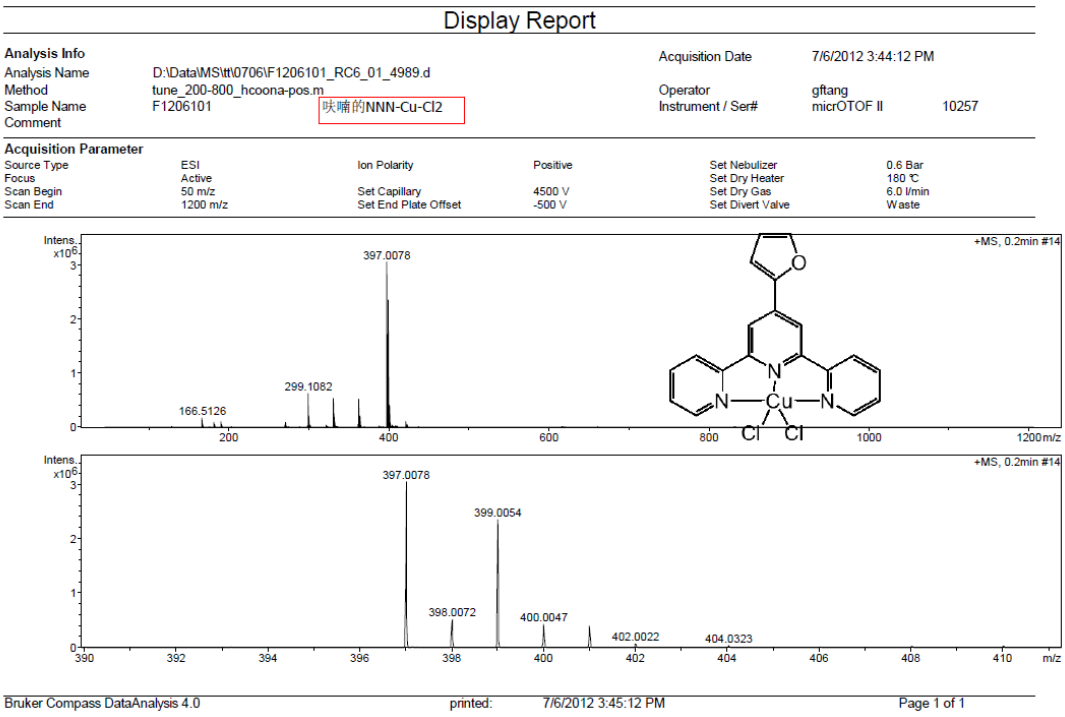


***Figure S54.*** ESI-MS spectrum of **2a**.

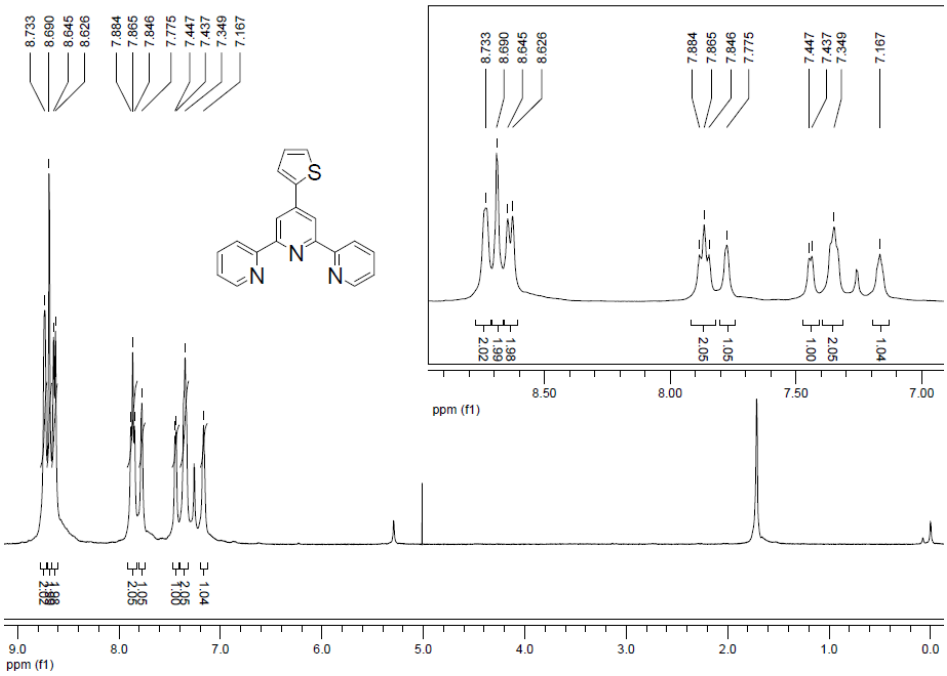


***Figure S55.*** $^{1}$H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of **1b**.

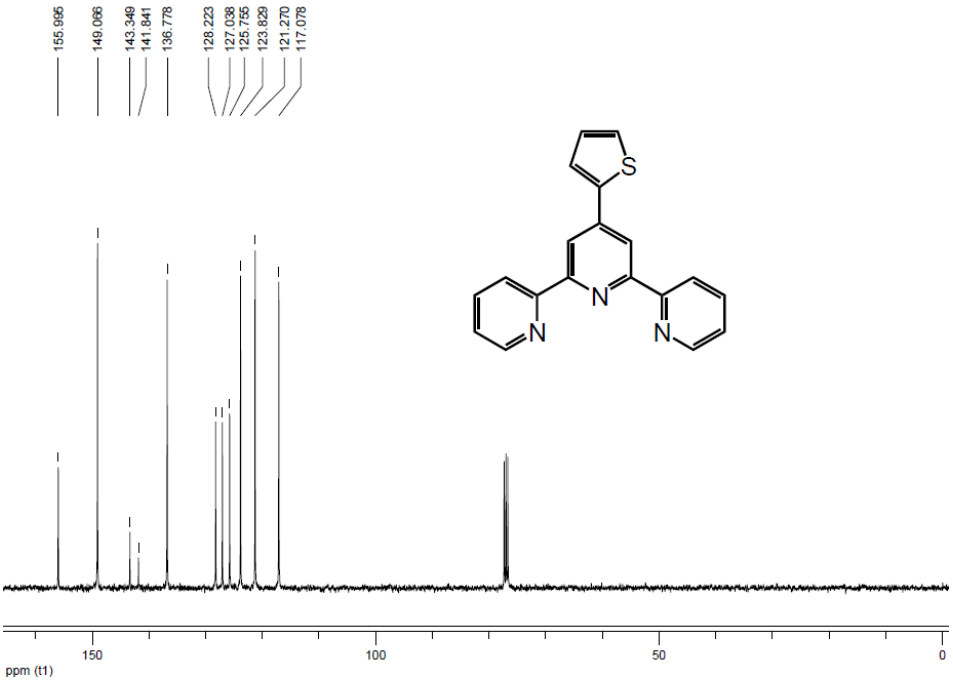


***Figure S56.*** $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K) spectrum of **1b**.

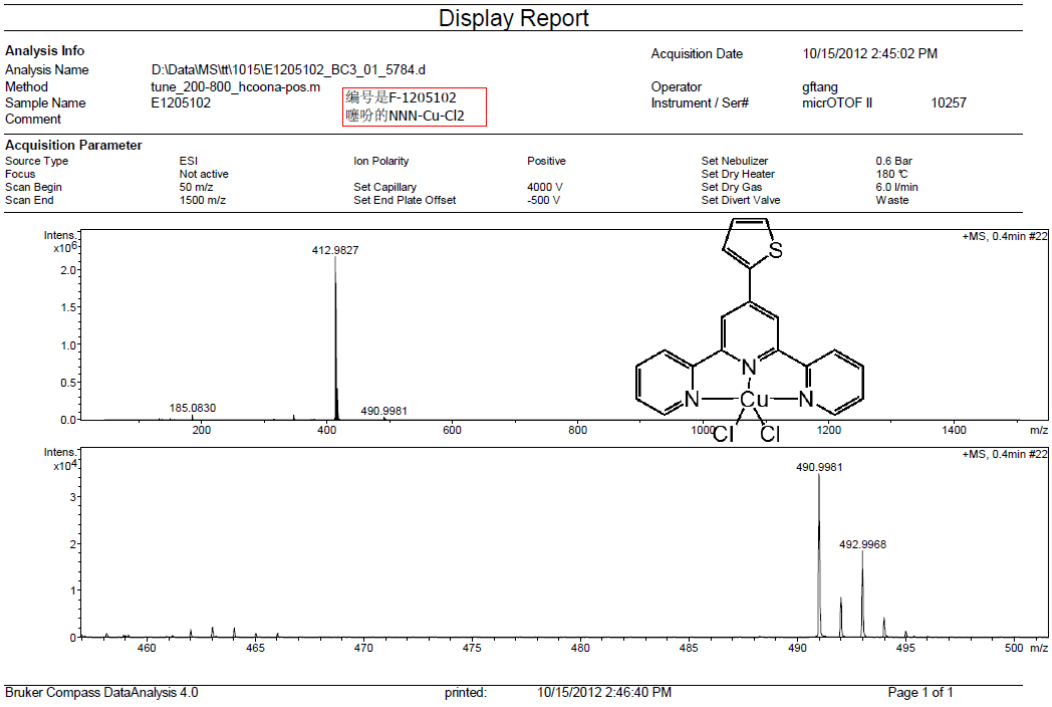


***Figure S57.*** ESI-MS spectrum of **2b**.

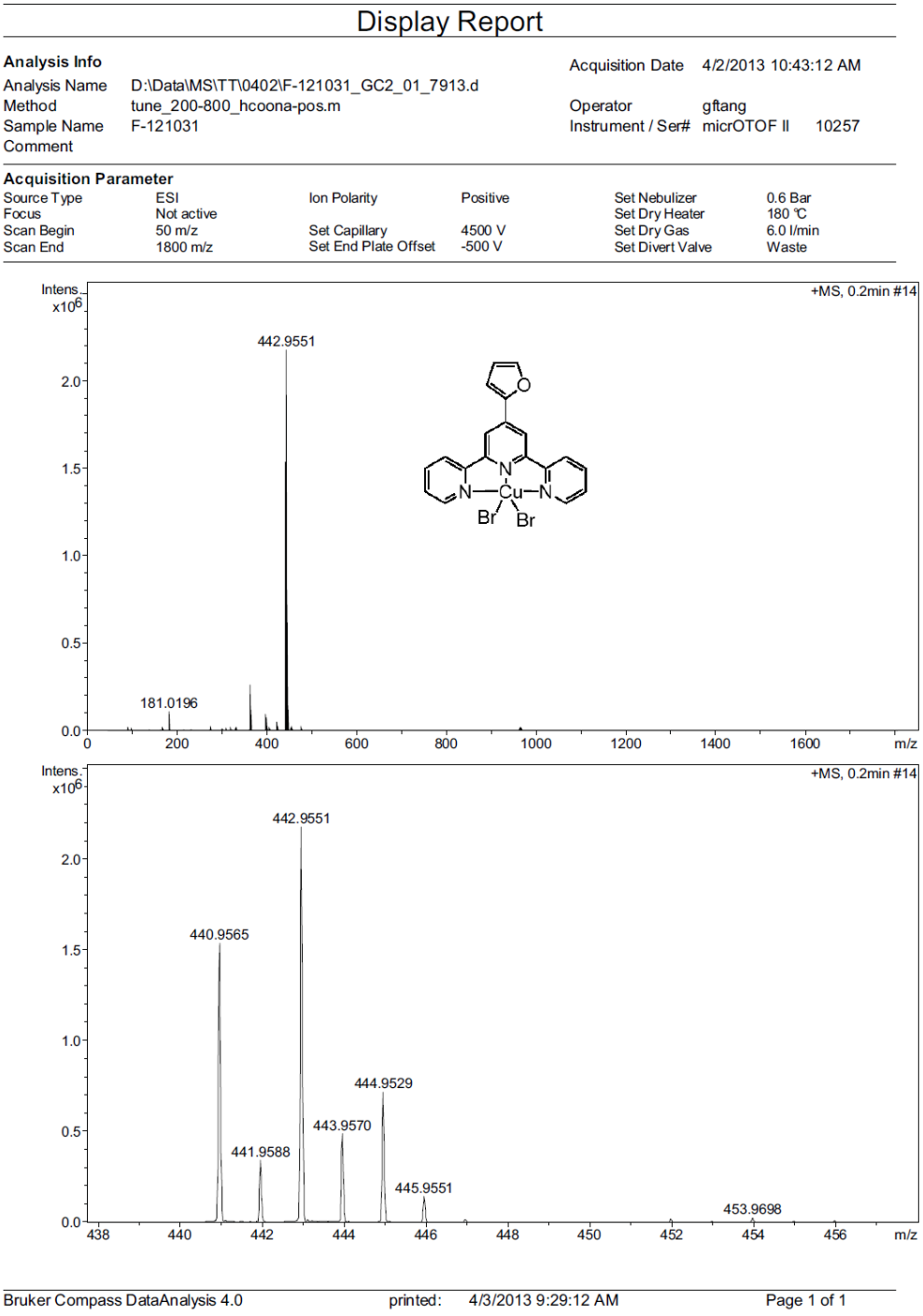


***Figure S58.*** ESI-MS spectrum of **2c**.

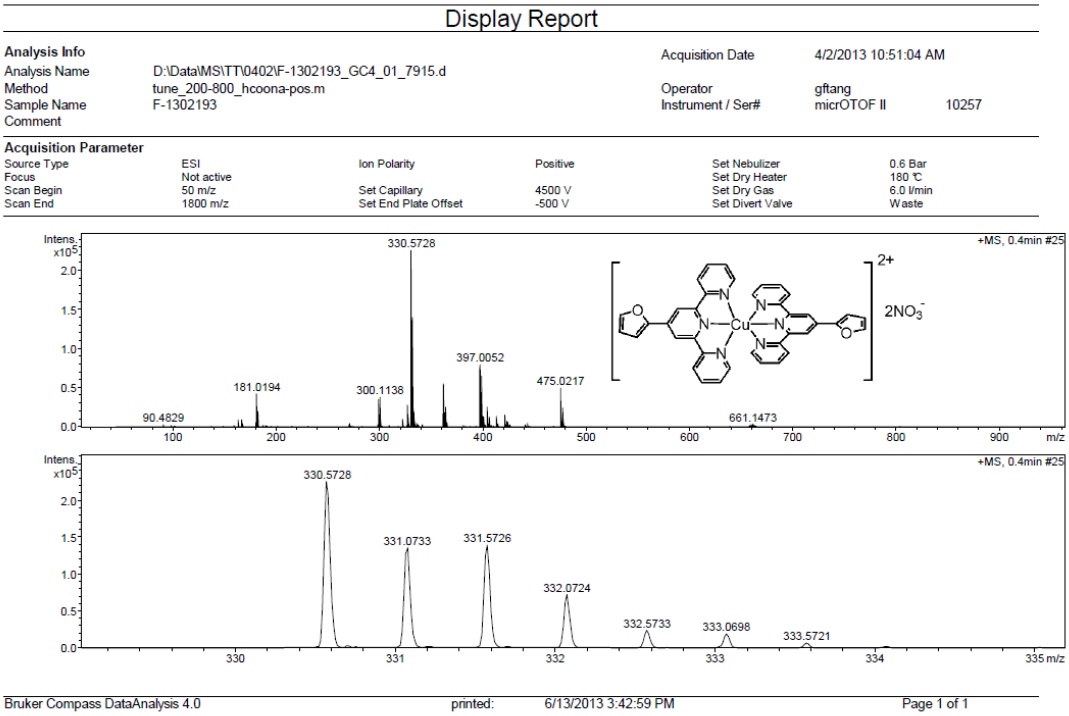


***Figure S59.*** ESI-MS spectrum of complex **3**.

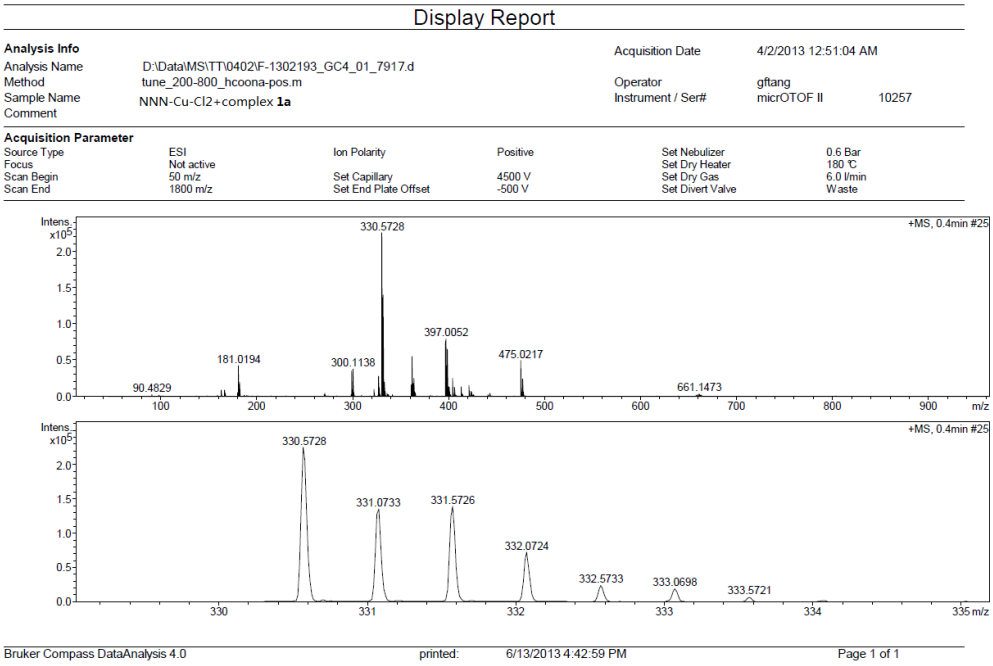


***Figure S60.*** ESI-MS spectrum of the sol prepared from hydrogel **2a**/$H_2O$ (1.0 wt%) with additional 1 equiv. complex **1a** after heating and cooling procedure.

## 20. References


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