crystals

# Supplementary Materials: Spacer-Controlled Supramolecular Assemblies of Cu(II) with Bis(2-hydroxyphenylimine) Ligands. from Monoligand Complexes to Double-stranded Helicates and Metallomacrocycles

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## 1. Molecular Structure of $[Cu_2(L^1)(NO_3)_2(H_2O)]\cdot MeOH$

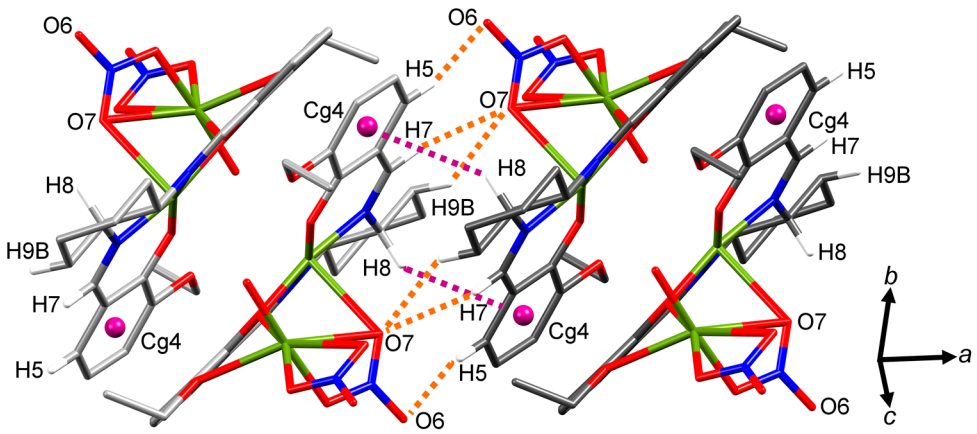



**Figure S1.** CH···O and CH···π interactions between neighboring strands in $[Cu_2(\mathbf{L^1})(NO_3)_2(H_2O)]\cdot MeOH$.

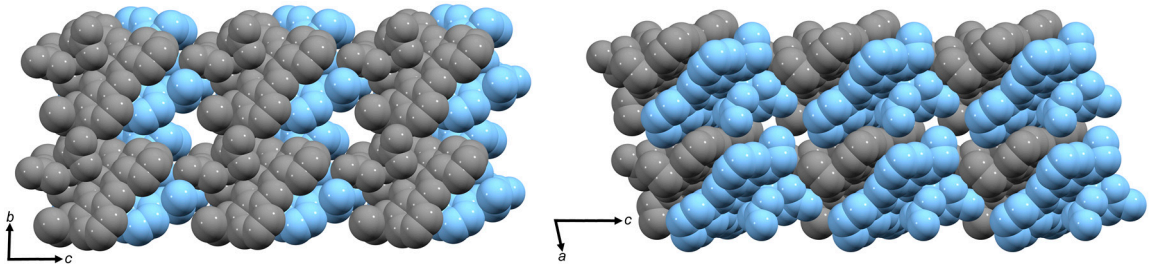



**Figure S2.** The packing motif of $[Cu_2(\mathbf{L^1})(NO_3)_2(H_2O)]\cdot MeOH$. The same enantiomers are represented in the same color.

**Table S1.** Intramolecular hydrogen bonds (Å) in $[Cu_2(\mathbf{L^1})(NO_3)_2(H_2O)]\cdot MeOH$.

| D-H | A | D-H | H···A | D···A | D-H-A |
|---|---|---|---|---|---|
| O1W-H1WB | O1 | 0.80 | 2.15 | 2.736(4) | 130 |
| O1W-H1WB | O2 | 0.80 | 2.05 | 2.785(5) | 153 |

**Table S2.** Intermolecular hydrogen bonds (Å) in $[Cu_2(\mathbf{L}^1)(NO_3)_2(H_2O)]\cdot MeOH$. Symmetry operator (2 − x, 1 − y, −z) generates equivalent atoms that are marked with "#", (1 − x, 1 − y, −z) marked with "#2" and (1 − x, 1 − y, 1 − z) marked with "#3".

| D-H | A | D-H | H···A | D···A | D-H-A |
|---|---|---|---|---|---|
| C5-H5 | O6# | 0.93 | 2.63 | 3.553(6) | 169 |
| C7-H7 | O7# | 0.93 | 2.57 | 3.446(5) | 157 |
| C9-H9B | O7# | 0.97 | 2.72 | 3.561(6) | 146 |
| C13-H13 | O3#2 | 0.98 | 2.59 | 3.544(4) | 163 |
| O1W-O1WA | O9#3 | 0.71 | 2.11 | 2.761(5) | 153 |

**Table S3.** Intermolecular π···π interactions (Å) in $[Cu_2(\mathbf{L}^1)(NO_3)_2(H_2O)]\cdot MeOH$. Symmetry operator (1 − x, 1 − y, −z) generates equivalent atoms that are marked with "#".

| CgX | CgY | CgX···CgY | $\beta$ |
|---|---|---|---|
| Cg4 | Cg6# | 4.62 | 37 |

**Table S4.** Intermolecular CH···π interactions (Å) in $[Cu_2(\mathbf{L}^1)(NO_3)_2(H_2O)]\cdot MeOH$. Symmetry operator (2 − x, 1 − y, −z) generates equivalent atoms that are marked with "#".

| C-H | Cg | C-H | H···Cg | C···Cg | $\gamma$ | C-H-A |
|---|---|---|---|---|---|---|
| C8-H8 | Cg4# | 0.98 | 3.22 | 4.04 | 35 | 142 |

## 2. Molecular Structure of $[Cu_2(L^2)_2]$

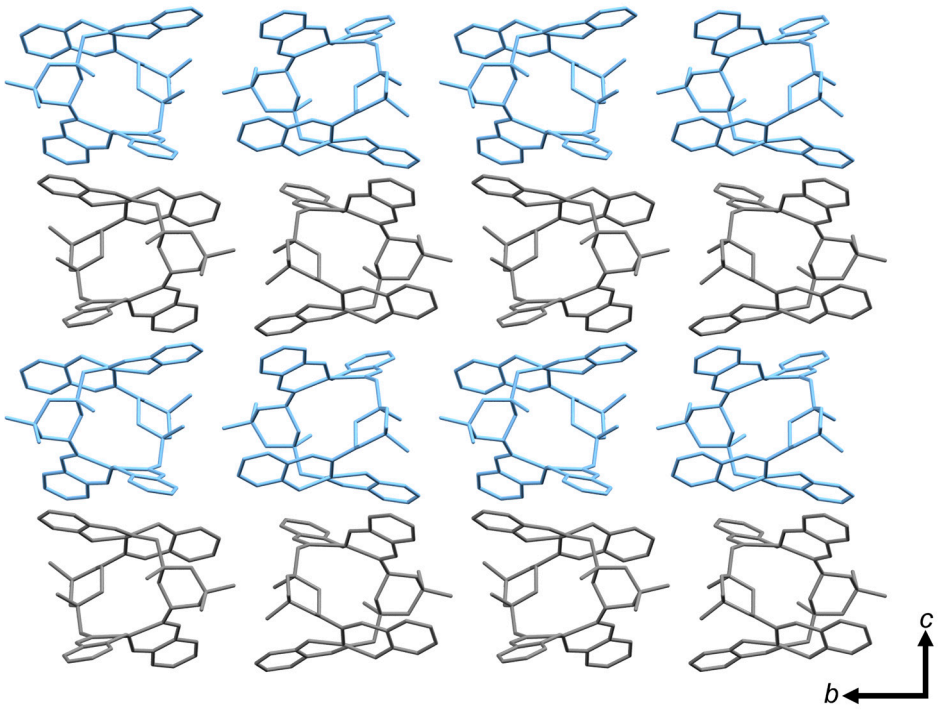



**Figure S3.** The packing motif of $[Cu_2(\mathbf{L}^2)]$. Complex molecules with the same handedness are represented in the same color.

**Table S5.** Intramolecular hydrogen bonds (Å) in $[Cu_2(\mathbf{L}^2)_2]$.

| D-H | A | D-H | H···A | D···A | D-H-A |
|---|---|---|---|---|---|
| C8-H8 | O4 | 0.98 | 2.26 | 2.865(3) | 119 |
| C17-H17B | O3 | 0.97 | 2.34 | 2.950(3) | 120 |
| C32-H32 | O2 | 0.98 | 2.34 | 2.923(3) | 117 |
| C41-H41B | O1 | 0.97 | 2.37 | 2.974(3) | 120 |

**Table S6.** Intermolecular CH···π interactions (Å) in $[Cu_2(\mathbf{L}^2)_2]$. Symmetry operator (1 + x, y, z) generates equivalent atoms that are marked with "#" and (x, 3/2 − y, −1/2 + z) marked with "#2".

| C-H | Cg | C-H | H···Cg | C···Cg | $\gamma$ | C-H-A |
|---|---|---|---|---|---|---|
| C13-H13A | Cg7# | 0.97 | 3.64 | 4.58 | 43 | 143 |
| C41-H41A | Cg7#2 | 0.97 | 3.08 | 3.95 | 27 | 150 |
| C42-H42 | Cg7#2 | 0.93 | 3.19 | 3.88 | 25 | 133 |

**Table S7.** Intermolecular π···π interactions (Å) in $[Cu_2(\mathbf{L}^2)_2]$. Symmetry operator (x, 3/2 − y, −1/2 + z) generates equivalent atoms that are marked with "#".

| CgX | CgY | CgX···CgY | $\beta$ |
|---|---|---|---|
| Cg8 | Cg10# | 4.37 | 35 |

## 3. Molecular Structure of $[Cu_2(L^3)_2]$

**Table S8.** Intramolecular hydrogen bonds (Å) in $[Cu_2(\mathbf{L}^3)_2]$.

| D-H | A | D-H | H···A | D···A | D-H-A |
|---|---|---|---|---|---|
| C10-H10B | O6 | 0.97 | 2.32 | 2.772(3) | 108 |
| C13-H13B | N2 | 0.97 | 2.58 | 2.948(3) | 102 |
| C14-H14A | O7 | 0.97 | 2.50 | 3.089(3) | 119 |
| C15-H15B | O7 | 0.97 | 2.37 | 2.780(3) | 105 |
| C35-H35B | O2 | 0.97 | 2.35 | 2.780(3) | 106 |
| C36-H36A | O2 | 0.97 | 2.59 | 3.149(3) | 117 |
| C40-H40B | O3 | 0.97 | 2.30 | 2.794(3) | 111 |

**Table S9.** Intermolecular cation···π interactions (Å) in $[Cu_2(\mathbf{L}^3)_2]$. Symmetry operator (1 − x, −y, 1 − z) generates equivalent atoms that are marked with "#" and (1 − x, −y, −z) marked with "#2".

| M | Cg | M···Cg | $\beta$ |
|---|---|---|---|
| Cu1 | Cg7# | 3.86 | 31 |
| Cu2 | Cg8#2 | 3.42 | 18 |

**Table S10.** Intermolecular hydrogen bonds (Å) in $[Cu_2(\mathbf{L}^3)_2]$. Symmetry operator (1 − x, −y, 1 − z) generates equivalent atoms that are marked with "#".

| D-H | A | D-H | H···A | D···A | D-H-A |
|---|---|---|---|---|---|
| C27-H27A | O2# | 0.97 | 2.63 | 3.541(3) | 156 |

## 4. Molecular Structure of $[Cu_2(L^4)_2]\cdot 2MeOH$

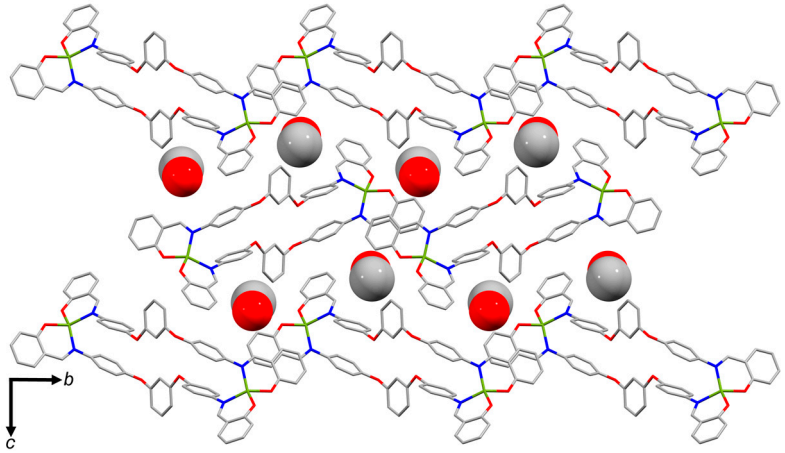



**Figure S4.** Methanol molecules in the void space of $[Cu_2(\mathbf{L}^4)]\cdot 2MeOH$ packing.

**Table S11.** Intramolecular π···π interactions (Å) in $[Cu_2(\mathbf{L}^4)_2]\cdot 2MeOH$. Symmetry operator (x, y, z) generates equivalent atoms that are marked with "#".

| CgX | CgY | CgX···CgY | $\beta$ |
|---|---|---|---|
| Cg4 | Cg6# | 3.60 | 21 |

**Table S12.** Intramolecular CH···π interactions (Å) in $[Cu_2(\mathbf{L}^4)_2]\cdot 2MeOH$. Symmetry operator (−x, 1 − y, 1 − z) generates equivalent atoms that are marked with "#".

| C-H | Cg | C-H | H···Cg | C···Cg | $\gamma$ | C-H-A |
|---|---|---|---|---|---|---|
| C12-H12 | Cg7# | 0.95 | 3.16 | 3.75 | 40 | 123 |
| C28-H28 | Cg6 | 0.95 | 3.17 | 3.76 | 28 | 122 |

**Table S13.** Intermolecular hydrogen bonds (Å) in $[Cu_2(\mathbf{L}^4)_2]\cdot 2MeOH$. Symmetry operator (1 − x, 1 − y, 1 − z) generates equivalent atoms that are marked with "#", (1 + x, y, z) marked with "#2", (−x, −1/2 + y, 1/2 − z) marked with "#3", (−x, 1/2 + y, 1/2 − z) marked with "#4" and (x, −1 + y, z) marked with "#5".

| D-H | A | D-H | H···A | D···A | D-H-A |
|---|---|---|---|---|---|
| C7-H7 | O1A# | 0.95 | 2.55 | 3.431(5) | 155 |
| C10-H10 | O4#2 | 0.95 | 2.55 | 3.381(4) | 146 |
| C23-H23 | O2# | 0.95 | 2.64 | 3.534(4) | 157 |
| C29-H29 | O1#3 | 0.95 | 2.48 | 3.360(4) | 154 |
| C30-H30 | O3#4 | 0.95 | 2.68 | 3.546(4) | 153 |
| O1A-H1A | O1#5 | 0.84 | 2.12 | 2.904(4) | 155 |

**Table S14.** Intermolecular CH···π interactions (Å) in $[Cu_2(\mathbf{L}^4)_2]\cdot 2MeOH$. Symmetry operator (1 − x, 1/2 + y, 1/2 − z) generates equivalent atoms that are marked with "#" and (1 + x, y, z) marked with "#2".

| C-H | Cg | C-H | H···Cg | C···Cg | $\gamma$ | C-H-A |
|---|---|---|---|---|---|---|
| C16-H16 | Cg7# | 0.95 | 2.89 | 3.76 | 14 | 153 |
| C22-H22 | Cg7#2 | 0.95 | 2.71 | 3.56 | 3 | 149 |

**Table S15.** Intermolecular π···π interactions (Å) in $[Cu_2(\mathbf{L}^4)_2]\cdot 2MeOH$. Symmetry operator (−x, 2 − y, 1 − z) generates equivalent atoms that are marked with "#"and (1 − x, 2 − y, 1 − z) marked with "#2".

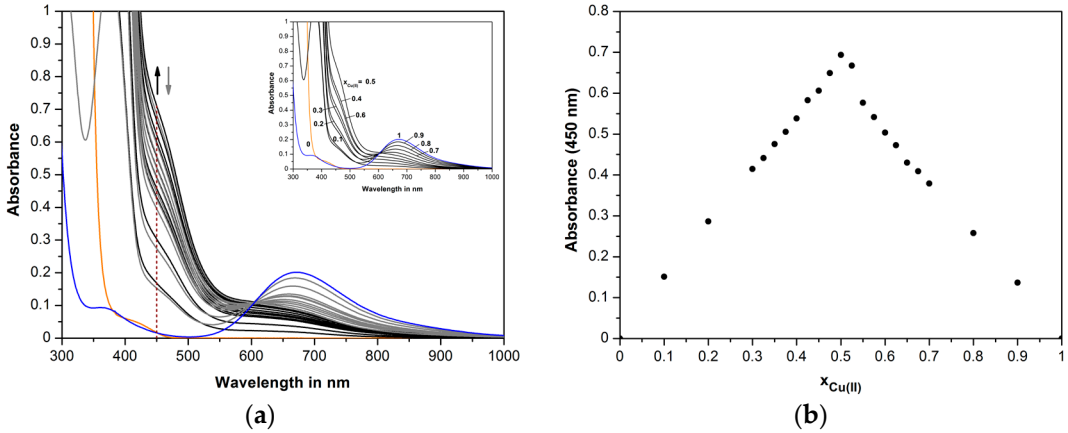
| CgX | CgY | CgX···CgY | $\beta$ |
|---|---|---|---|
| Cg3 | Cg3# | 4.06 | 37 |
| Cg3 | Cg4#2 | 4.80 | 37 |

## 5. Crystallographic Data

**Table S16.** Crystal and structure refinement data for $[Cu_2(\mathbf{L}^1)(NO_3)_2(H_2O)]\cdot MeOH$, $[Cu_2(\mathbf{L}^2)_2]$, $[Cu_2(\mathbf{L}^3)_2]$ and $[Cu_2(\mathbf{L}^4)_2]\cdot 2MeOH$.

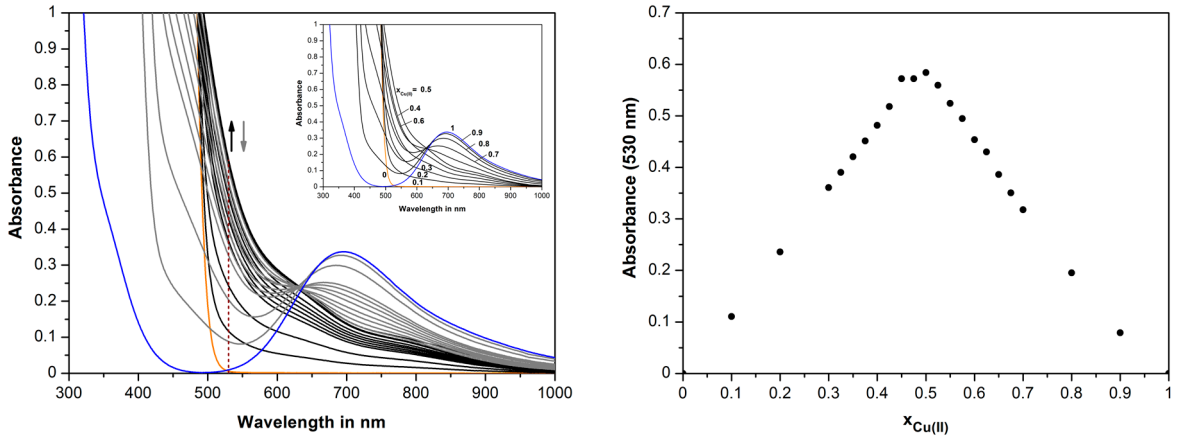
| | $[Cu_2(L^1)(NO_3)_2(H_2O)]$ MeOH | $[Cu_2(L^2)_2]$ | $[Cu_2(L^3)_2]$ | $[Cu_2(L^4)_2]\cdot 2MeOH$ |
|---|---|---|---|---|
| Formula | $C_{25}H_{34}Cu_2N_4O_{12}$ | $C_{48}H_{56}Cu_2N_4O_4$ | $C_{48}H_{60}Cu_2N_4O_8$ | $C_{66}H_{52}Cu_2N_4O_{10}$ |
| Crystal System | Triclinic | Monoclinic | Triclinic | Monoclinic |
| Space Group | *P*-1 | $P2_1/c$ | *P*-1 | $P2_1/c$ |
| *a*/Å | 10.007(5) | 10.3999(2) | 10.5604(2) | 7.6338(2) |
| *b*/Å | 10.439(5) | 23.3578(5) | 10.6979(2) | 17.6710(6) |
| *c*/Å | 15.017(5) | 18.2923(4) | 23.3837(5) | 20.0160(7) |
| *α*/° | 83.678(5) | 90 | 87.011(1) | 90 |
| *β*/° | 75.384(5) | 99.419(1) | 86.293(1) | 92.407(1) |
| *γ*/° | 77.738(5) | 90 | 64.747(1) | 90 |
| *V*/Å$^3$ | 1480.7(11) | 4383.6(2) | 2383.41(8) | 2697.71(15) |
| *d* (calcd.)/g/cm$^{-3}$ | 1.559 | 1.333 | 1.321 | 1.463 |
| *Z* | 2 | 4 | 2 | 2 |
| Diffractometer | Bruker APEX-II | Bruker APEX-II | Bruker APEX-II | Bruker APEX-II |
| Radiation (*λ*/Å) | Mo-K*α*, 0.71069 | Mo-K*α*, 0.71073 | Mo-K*α*, 0.71073 | Mo-K*α*, 0.71073 |
| Size/mm$^3$ | 0.39 × 0.15 × 0.10 | 0.24 × 0.20 × 0.04 | 0.17 × 0.11 × 0.07 | 0.60 × 0.23 × 0.03 |
| Temperature/K | 296(2) | 296(2) | 296(2) | 143(2) |
| *θ* range/° | 1.40–30.12 | 2.42–29.18 | 2.27–31.12 | 2.52–27.25 |
| Indices | $-13 \le h \le 14$ | $-14 \le h \le 13$ | $-15 \le h \le 15$ | $-9 \le h \le 6$ |
| | $-14 \le k \le 14$ | $-31 \le k \le 31$ | $-15 \le k \le 15$ | $-20 \le k \le 22$ |
| | $-21 \le l \le 21$ | $-22 \le l \le 25$ | $-33 \le l \le 34$ | $-25 \le l \le 25$ |
| Reflections | 31967 | 52153 | 62441 | 22683 |
| Indipendent reflections; $R_{int}$ | 8701 (0.0352) | 11769 (0.0295) | 15304 (0.0224) | 5973 (0.0479) |
| Reflections ($I > 2\sigma(I)$) | 5214 | 7584 | 9778 | 3947 |
| data/restraints/parameters | 8701/0/402 | 11769/0/529 | 15304/0/563 | 5973/0/372 |
| *μ*/mm$^{-1}$ | 1.503 | 1.018 | 0.947 | 0.857 |
| Absorption correction | multi-scan | multi-scan | multi-scan | multi-scan |
| *R* indices ($I_{obs}$ with $I > 2\sigma(I)$) | $R_1 = 0.0517$ | $R_1 = 0.0396$ | $R_1 = 0.0460$ | $R_1 = 0.0487$ |
| | $wR_2 = 0.1496$ | $wR_2 = 0.0871$ | $wR_2 = 0.1105$ | $wR_2 = 0.1145$ |
| *R* indices (all data) | $R_1 = 0.0953$ | $R_1 = 0.0805$ | $R_1 = 0.0826$ | $R_1 = 0.0924$ |
| | $wR_2 = 0.1776$ | $wR_2 = 0.1009$ | $wR_2 = 0.1228$ | $wR_2 = 0.1375$ |
| Largest diff. peak and hole/e/Å$^3$ | 1.264 and −0.378 | 0.472 and −0.434 | 0.672 and −0.441 | 0.882 and −0.545 |
| Goodness-of-fit on $F^2$ | 1.016 | 1.050 | 1.159 | 1.027 |
| F(000) | 709 | 1848 | 996 | 1228 |
| Data collection mode | $\phi$ and $\omega$ scans | | | |
| Absorption correction | SADABS, Bruker 2008; SADABS | | | |
| Structure solution | direct, SHELXS-97 (Sheldrick, 2008) | | | |
| Structure refinement | Full-matrix least-squares on $F^2$, SHELXL-97 (Sheldrick, 2008); SHELXL-2013 (Sheldrick, 2013) | | | |

## 6. Solution Studies of Complex Formation of Cu(Ii) with Diimine Ligands



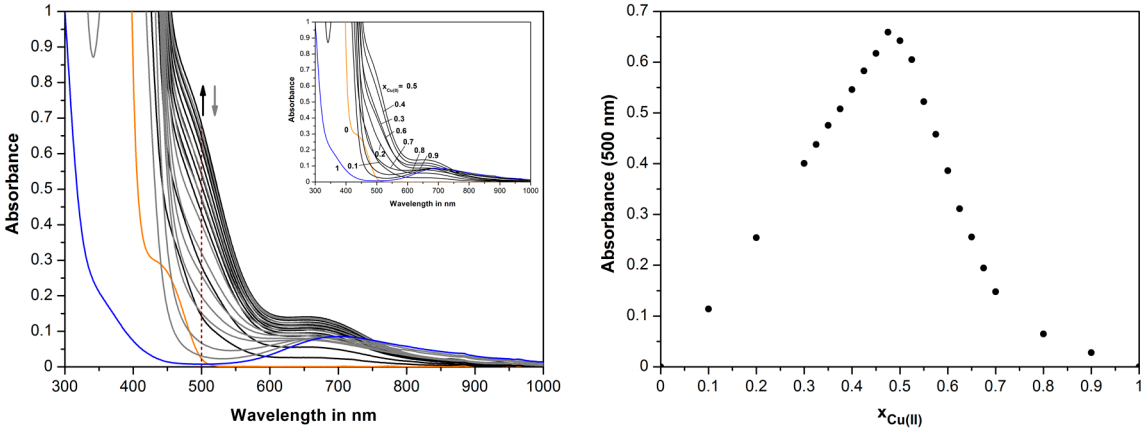

(**a**) (**b**)

**Figure S5.** UV/Vis spectra (**a**) and *Job* plot at 450 nm (**b**) for complexation of copper(II) acetate (blue) with $\mathbf{H_2L^2}$ (orange) in THF. $[\mathbf{H_2L^2}]$ + [Cu(II)] = 1·10$^{-3}$ M ($x_{Cu(II)}$ = 0–1), *t* = 30 min.




(**a**) (**b**)

**Figure S6.** UV/Vis spectra (**a**) and *Job* plot at 530 nm (**b**) for complexation of copper(II) acetate (blue) with **H₂L³** (orange) in dichloromethane/methanol (v/v = 1:1). [**H₂L³**] + [Cu(II)] = 3·10⁻³ M ($x_{Cu(II)}$ = 0–1), $t$ = 30 min.




(**a**) (**b**)

**Figure S7.** UV/Vis spectra (**a**) and *Job* plot at 500 nm (**b**) for complexation of copper(II) acetate (blue) with **H₂L⁴** (orange) in dichloromethane/methanol (v/v = 1:1). [**H₂L⁴**] + [Cu(II)] = 1·10⁻³ M ($x_{Cu(II)}$ = 0–1), $t$ = 30 min.