Modulating $p$-hydroxycinnamate behavior as a ditopic linker or photoacid in copper(II) complexes by auxiliary pyridine ligand

Electronic Supplementary Information

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**Table S1. Crystallographic Data for compounds 1-3**

<table>
<thead>
<tr>
<th></th>
<th>C$<em>{72}$H$</em>{96}$N$<em>4$O$</em>{15}$Cu$_2$ (1)</th>
<th>C$<em>{32}$H$</em>{28}$N$_2$O$_8$Cu (2)</th>
<th>C$<em>{42}$H$</em>{40}$N$_2$O$_8$Cu (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula Weight</strong></td>
<td>1374.52</td>
<td>632.10</td>
<td>764.30</td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td><strong>Wavelength (Å)</strong></td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td><strong>System, space group</strong></td>
<td>Monoclinic, C2/c</td>
<td>Monoclinic, P2$_1$/n</td>
<td>Monoclinic, P2$_1$/n</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>52.0046(17)</td>
<td>8.4342(3)</td>
<td>11.7498(5)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>5.9991(2)</td>
<td>8.6978(3)</td>
<td>10.8664(5)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>21.5105(8)</td>
<td>18.9953(7)</td>
<td>15.2007(8)</td>
</tr>
<tr>
<td><strong>α (°)</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>β (°)</strong></td>
<td>90.359(2)</td>
<td>96.953(2)</td>
<td>105.000(2)</td>
</tr>
<tr>
<td><strong>γ (°)</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>U (Å$^3$) / Z</strong></td>
<td>6710.7(4) / 4</td>
<td>1383.23(9) / 2</td>
<td>1874.66(15) / 2</td>
</tr>
<tr>
<td><strong>D$_{calc}$ (g cm$^{-3}$) / μ (mm$^{-1}$)</strong></td>
<td>1.360 / 0.704</td>
<td>1.518 / 0.848</td>
<td>1.354 / 0.639</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>2896</td>
<td>654</td>
<td>798</td>
</tr>
<tr>
<td><strong>Crystal size (mm$^3$)</strong></td>
<td>0.104x0.081x0.057</td>
<td>0.308x0.268x0.144</td>
<td>0.397x0.373x0.284</td>
</tr>
<tr>
<td><strong>hkl ranges</strong></td>
<td>-63≤h≤64, -7≤k≤7, -24≤l≤26</td>
<td>-12≤h≤12, -12≤k≤12, -27≤l≤27</td>
<td>-14≤h≤14, -13≤k≤13, -19≤l≤19</td>
</tr>
<tr>
<td><strong>2θ Range (°)</strong></td>
<td>2.350 to 25.994</td>
<td>2.539 to 30.601</td>
<td>2.536 to 26.424</td>
</tr>
<tr>
<td><strong>Reflections collected/unique/ [R$_{int}$]</strong></td>
<td>14428/4433/4433 [R$_{int}$=0.0717]</td>
<td>44501/4253/4253 [R$_{int}$=0.0494]</td>
<td>22324/3801/3801 [R$_{int}$=0.0296]</td>
</tr>
<tr>
<td><strong>Completeness to θ (%)</strong></td>
<td>65.0</td>
<td>99.9</td>
<td>99.2</td>
</tr>
<tr>
<td><strong>Absorption correction</strong></td>
<td>Semi-empirical from equivalents</td>
<td>Semi-empirical from equivalents</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td><strong>Max. and min. trans.</strong></td>
<td>0.7453 and 0.6123</td>
<td>0.7461 and 0.7069</td>
<td>0.7454 and 0.6782</td>
</tr>
<tr>
<td><strong>Data/restrains/parameters</strong></td>
<td>4429/4/439</td>
<td>4253/0/199</td>
<td>3801/0/246</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F$^2$</strong></td>
<td>0.995</td>
<td>1.044</td>
<td>1.092</td>
</tr>
<tr>
<td><strong>Final R indices [I&gt;2σ(I)]</strong></td>
<td>R$_1$ = 0.0451, wR$_2$ = 0.0906</td>
<td>R$_1$ = 0.0316, wR$_2$ = 0.0715</td>
<td>R$_1$ = 0.0330, wR$_2$ = 0.0856</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R$_1$ = 0.0868, wR$_2$ = 0.1171</td>
<td>R$_1$ = 0.0435, wR$_2$ = 0.0760</td>
<td>R$_1$ = 0.0387, wR$_2$ = 0.0925</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole (e Å$^{-3}$)</strong></td>
<td>+0.699, −0.477</td>
<td>+0.524, −0.285</td>
<td>+0.360, −0.417</td>
</tr>
</tbody>
</table>
# Table S2. Crystallographic Data for compound 4 and 5

<table>
<thead>
<tr>
<th></th>
<th>C_{121.50}H_{106}N_{6}O_{21.50}Cu_{3} (4)</th>
<th>C_{71}H_{50}N_{4}O_{6}Cu_{2} (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula Weight</strong></td>
<td>2184.74</td>
<td>1236.27</td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
<td>293(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td><strong>Wavelength (Å)</strong></td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td><strong>System, space group</strong></td>
<td>Triclinic, P-1</td>
<td>Monoclinic, C2/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.9562(6)</td>
<td>13.6289(6)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>15.7183(7)</td>
<td>25.4524(13)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>16.1429(7)</td>
<td>34.1595(17)</td>
</tr>
<tr>
<td>α (°)</td>
<td>78.243(2)</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>71.856(2)</td>
<td>92.4530(10)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>66.888(2)</td>
<td>90</td>
</tr>
<tr>
<td>U (Å³ / Z)</td>
<td>2860.8(2) / 1</td>
<td>11838.7(10) / 8</td>
</tr>
<tr>
<td><strong>Dcalc (g cm⁻³) / µ (mm⁻¹)</strong></td>
<td>1.268 / 0.623</td>
<td>1.387 / 0.783</td>
</tr>
<tr>
<td>F(000)</td>
<td>1136</td>
<td>5120</td>
</tr>
<tr>
<td><strong>Crystal size (mm³)</strong></td>
<td>0.772x0.088x0.039</td>
<td>0.145x0.071x0.060</td>
</tr>
<tr>
<td>hkl ranges</td>
<td>-16≤h≤16, -19≤k≤19, -20≤l≤20</td>
<td>-17≤h≤14, -31≤k≤31, -42≤l≤42</td>
</tr>
<tr>
<td>2θ Range (°)</td>
<td>1.890 to 26.405</td>
<td>2.111 to 26.448</td>
</tr>
<tr>
<td><strong>Reflections collected/unique/ [Rint]</strong></td>
<td>66611/11680 / [R(int)=0.0912]</td>
<td>156209/12168 / [R(int)=0.0817]</td>
</tr>
<tr>
<td>Completeness to θ (%)</td>
<td>99.8</td>
<td>99.9</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. trans.</td>
<td>0.7454 and 0.6937</td>
<td>0.7454 and 0.7068</td>
</tr>
<tr>
<td>Data/restrains/parameters</td>
<td>11678/24/698</td>
<td>12168/0/777</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.017</td>
<td>1.024</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ (I)]</td>
<td>R₁ = 0.0832</td>
<td>R₁ = 0.0404</td>
</tr>
<tr>
<td></td>
<td>wR₂ = 0.22013</td>
<td>wR₂ = 0.0769</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1277</td>
<td>R₁ = 0.0709</td>
</tr>
<tr>
<td></td>
<td>wR₂ =0.2534</td>
<td>wR₂ =0.08065</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e Å⁻³)</td>
<td>+1.755, −1.985</td>
<td>+0.727, −0.397</td>
</tr>
</tbody>
</table>
PXRD patterns and Phase Purity Calculations

**Figure S1.** X-ray diffractogram of [Cu(µ-pOHcinn)₂(4-tBupy)₂(H₂O)][Cu(µ-pOHcinn)₂(4-tBupy)₂(H₂O)]₂ (1, up) measured at room temperature. Calculated pattern from resolved crystal structure is also included (down) as a reference, from monocystal XRD measured at 100 K.
Figure S2. X-ray diffractogram of [Cu(µ-pOHcinn)₂(4-Acpy)₂]ₙ (2, up) measured at room temperature. Calculated pattern from resolved crystal structure is also included (down) as a reference, from monocystal XRD measured at 100 K.
Figure S3. X-ray diffractogram of \([\text{Cu(pOHcinn)}_2(4\text{-Phpy})_2]_2\cdot[\text{Cu(pOHcinn)}_2(4\text{-Phpy})_2] \cdot 1.5\text{MeOH}\cdot\text{H}_2\text{O}\) (4, up) measured at room temperature. Calculated pattern from resolved crystal structure is also included (down) as a reference, from monocystal XRD measured at 100 K.
Figure S4. X-ray diffractogram of \([\text{Cu}_2(\text{pOHcinn})_2(\text{trans-4-Phpy})_4(\mu-\text{pOcinn})_2\text{Cu}_2(\text{pOHcinn})_2(\text{cis-4-Phpy})_4)_n \) (5, up) measured at room temperature. Calculated pattern from resolved crystal structure is also included (down) as a reference, from monocrystal XRD measured at 100 K.
FTIR-ATR spectra

Figure S5. ATR-FTIR spectra of compound 1.

Figure S6. ATR-FTIR spectra of compound 2.
Figure S7. ATR-FTIR spectra of compound 3.

Figure S8. ATR-FTIR spectra of compound 4.
Figure S9. ATR-FTIR spectra of compound 5.
Figure S10. Temporal FTIR-ATR spectra of compound 3. Note that the band at 3396 cm$^{-1}$ corresponding to $\nu_{st}$(OH) of MeOH decreases over time. Conversely, a band at 3570 cm$^{-1}$ corresponding to $\nu_{st}$(OH) of H$_2$O appears. Lastly, note that after exposure to vacuum, the 3500 cm$^{-1}$-3200 cm$^{-1}$ region shows no bands related to $\nu_{st}$(OH).