

Supplementary Information

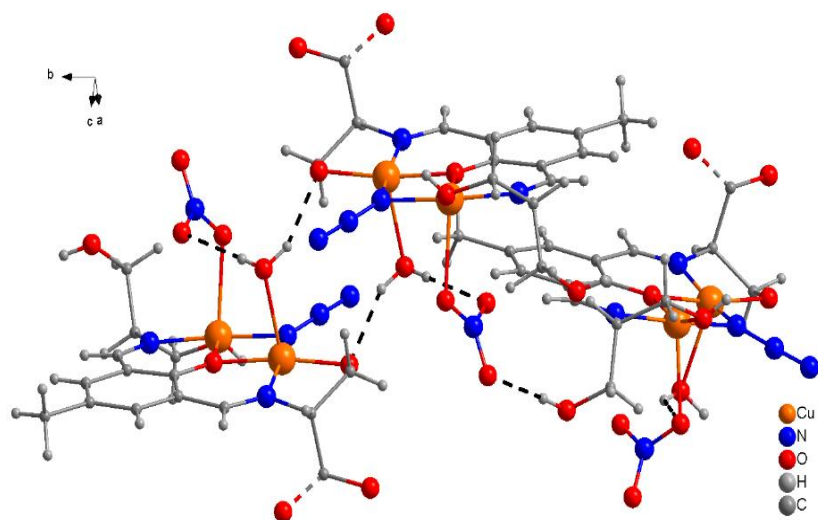


Figure S1. Perspective view of crystal packing of **3** along the *ab* axis, showing the formation of a 2D-sheet structure.

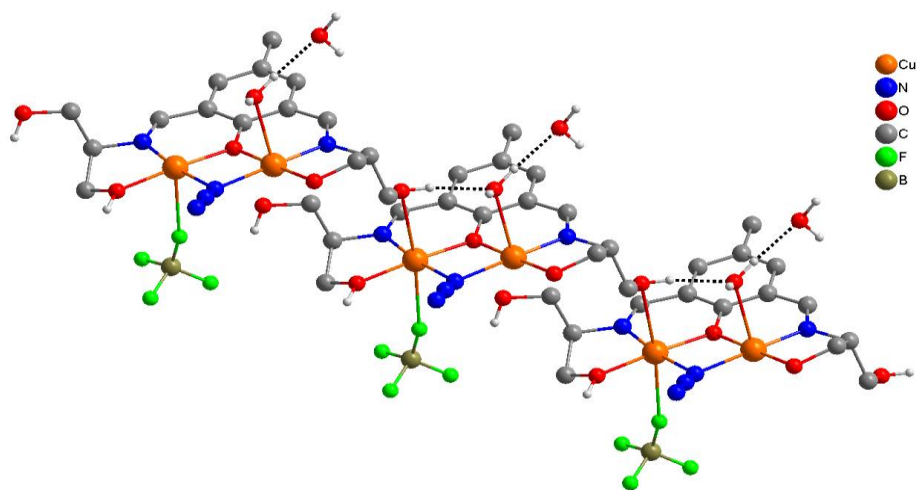


Figure S2. Perspective view of a portion of 1D-single chain in **4** along the *b*-axis.

Figures S3-S5 (XRD Pattern
Figures S3.

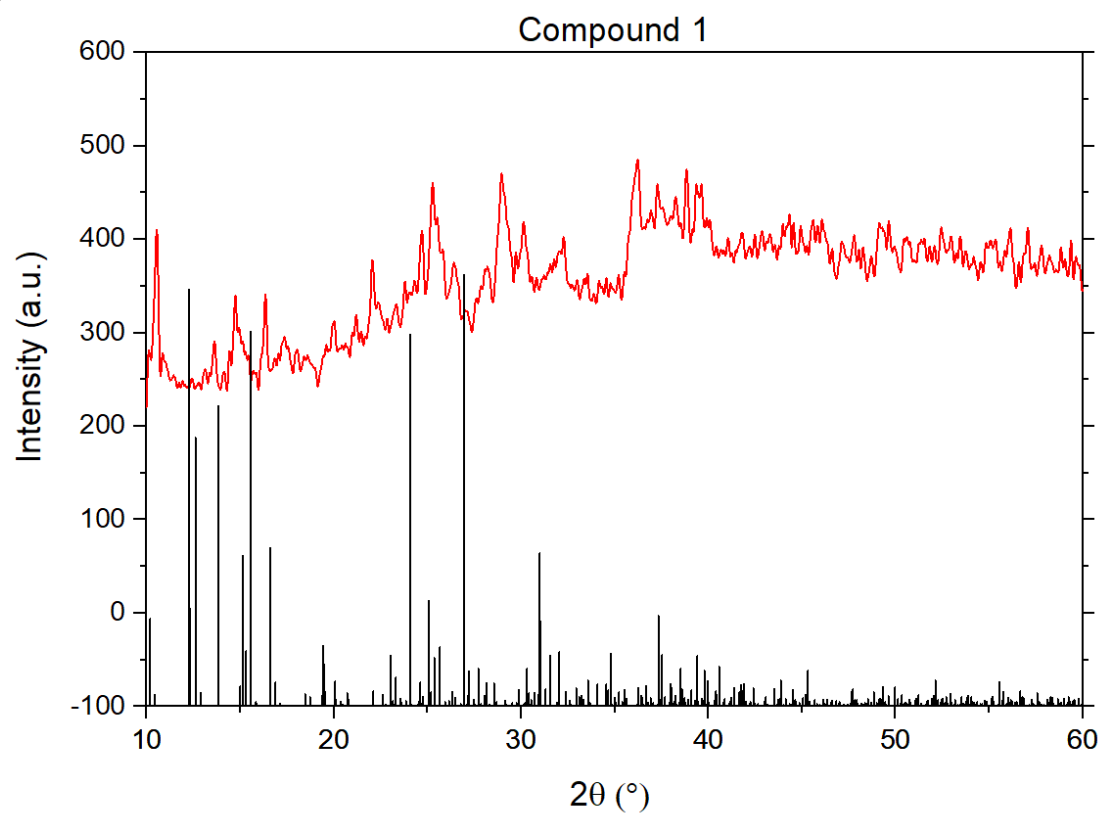


Figure S4.

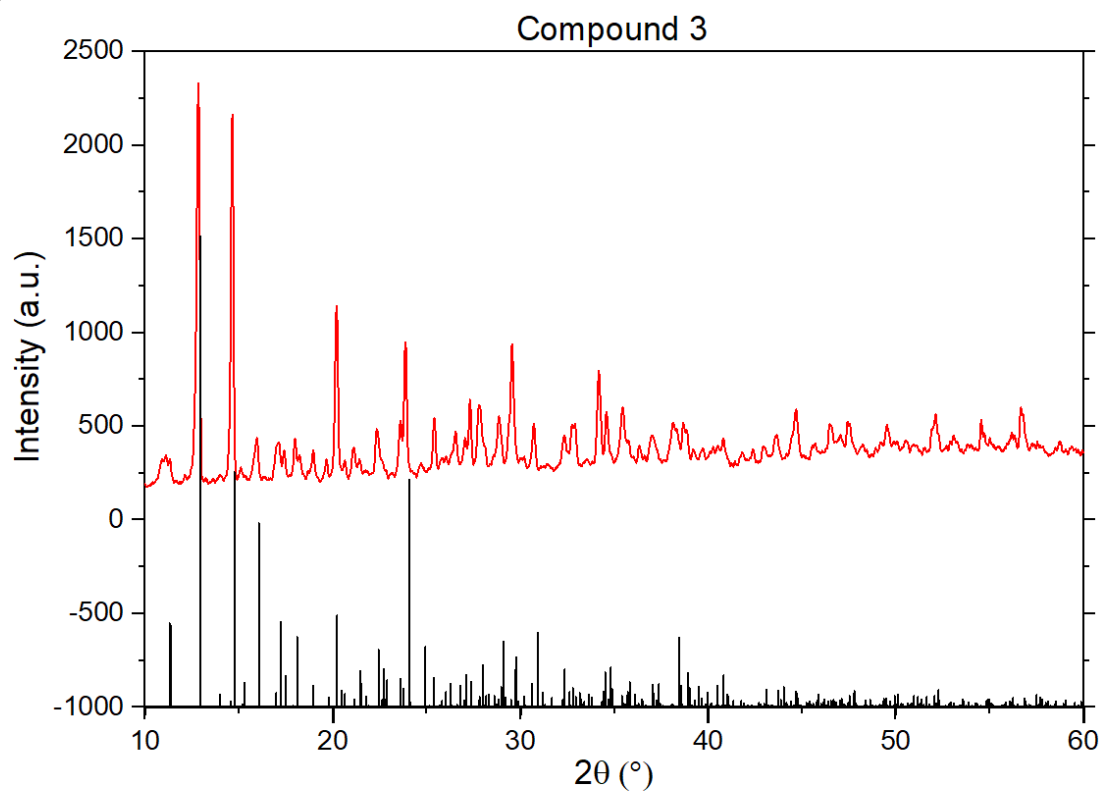
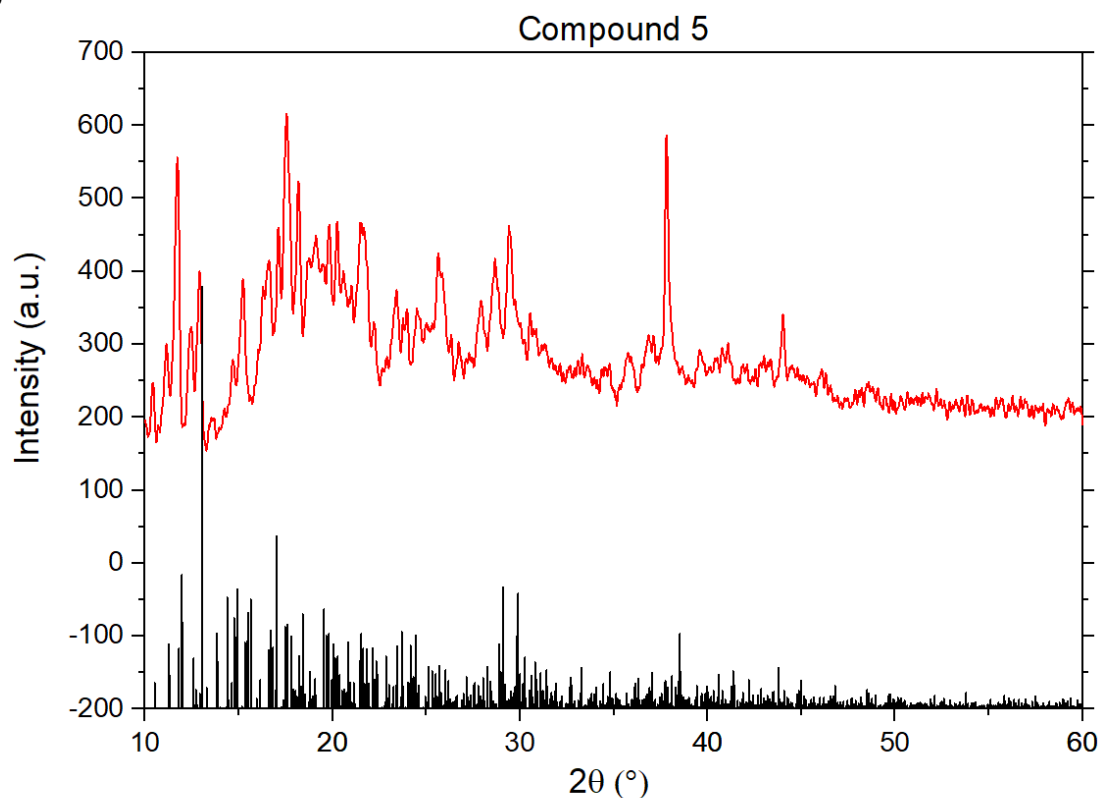


Figure S5.



Electronic Supplementary Information

Tables S1-S6 for bond lengths and angles

Table S1. Bond lengths [\AA] and angles [$^\circ$] for **1**.

| Bond lengths | [\AA] | Bond angles | [$^\circ$] |
|--------------|------------------|-------------------|--------------|
| Cu(1)-O(1) | 1.984(5) | N(1)-Cu(1)-O(1) | 92.3(3) |
| Cu(1)-N(1) | 1.944(7) | N(1)-Cu(1)-O(2) | 85.6(4) |
| Cu(1)-N(6) | 1.965(6) | O(2)-Cu(1)-N(6) | 103.1(4) |
| Cu(1)-O(2) | 1.943(7) | N6(1)-Cu(1)-O(1) | 78.4(2) |
| Cu(1)-N(3) | 2.422(7) | N(1)-Cu(1)-N(6) | 169.4(3) |
| Cu(2)-O(1) | 1.998(5) | O(1)-Cu(1)-O(2) | 173.3(3) |
| Cu(2)-N(2) | 1.959(6) | Cu(1)-O(1)-Cu(2) | 101.88 |
| Cu(2)-N(3) | 1.968(7) | Cu(1)-N(6)-Cu(2) | 102.4(3) |
| Cu(2)-N(6) | 2.001(7) | N(2)-Cu(2)-O(1) | 91.5(3) |
| Cu(1)-Cu(2) | 3.092 | N(2)-Cu(2)-N(3A) | 95.1(3) |
| | | N(3A)-Cu(2)-N(6) | 94.4(3) |
| | | N(6)-Cu(2)-O(1) | 77.2(2) |
| | | O(1)-Cu(2)-N(3A) | 160.6(3) |
| | | N(2)-Cu(2)-N(6) | 167.6(3) |
| | | Cu(1)-O(1)-Cu(2) | 101.9(2) |
| | | Cu(1)-N(3)-Cu(2A) | 108.9(3) |

Table S2. Bond lengths [\AA] and angles [$^\circ$] for **2**.

| Bond lengths | [Å] | Bond angles | [°] |
|--------------|----------|--------------------|------------|
| Cu(1)-O(1) | 1.951(3) | O(1)-Cu(1)-O(4) | 162.30(15) |
| Cu(1)-O(3) | 1.944(3) | O(3)-Cu(1)-O(1) | 81.52(14) |
| Cu(1)-O(4) | 1.993(3) | O(3)-Cu(1)-O(4) | 102.72(14) |
| Cu(1)-N(2) | 1.938(4) | N2(1)-Cu(1)-O(1) | 89.89(16) |
| Cu(2)-O(1) | 1.979(3) | N(2)-Cu(1)-O(2) | 168.32(17) |
| Cu(2)-O(2) | 2.038(4) | N(2)-Cu(1)-O(4) | 83.19(19) |
| Cu(2)-O(3) | 1.956(3) | Cu(1)-O(1)-Cu(2) | 98.02(14) |
| Cu(2)-O(3A) | 2.360(3) | Cu(1)-O(3)-Cu(2) | 92.05(16) |
| Cu(2)-O(5) | 2.393(4) | Cu(1)-O(3)-Cu((2A) | 110.07(15) |
| Cu(2)-N(1) | 1.936(4) | Cu(2)-O(3)-Cu(2A) | 95.07(13) |
| Cu(1)-Cu(2) | 2.967 | O(3)-Cu(2)-O(1) | 80.54(13) |
| | | O(3)-Cu(2)-O(2) | 105.09(14) |
| | | N(1)-Cu(2)-O(1) | 91.00(16) |
| | | N(1)-Cu(2)-O(2) | 83.35(16) |
| | | O(1)-Cu(2)-O(2) | 174.08(14) |
| | | N(1)-Cu(2)-O(3) | 171.53(16) |
| | | O(3A)-Cu(2)-O(5) | 173.61(13) |

Table S3. Bond distances [Å] and angles [°] for **3**.

| Bond lengths | Å | Bond angles | [°] |
|--------------|------------|------------------|-----------|
| Cu(1)-O(1) | 1.9506(17) | N(1)-Cu(1)-O(1) | 92.15(8) |
| Cu(1)-N(1) | 1.915(2) | N(1)-Cu(1)-O(8) | 84.67(9) |
| Cu(1)-N(3) | 1.959(2) | O(8)-Cu(1)-N(3) | 102.28(8) |
| Cu(1)-O(8) | 1.9786(19) | N(3)-Cu(1)-O(1) | 79.98(8) |
| Cu(1)-O(5) | 2.384(2) | N(1)-Cu(1)-N(3) | 172.06(8) |
| Cu(2)-O(1) | 1.9680(17) | O(1)-Cu(1)-O(8) | 158.96(8) |
| Cu(2)-N(2) | 1.928(2) | N(2)-Cu(2)-O(1) | 90.76(8) |
| Cu(2)-N(3) | 1.980(2) | N(2)-Cu(2)-O(3) | 86.84(8) |
| Cu(2)-O(3) | 1.9341(17) | O(3)-Cu(2)-N(3) | 102.02(8) |
| Cu(2)-O(4) | 2.337(2) | N(3)-Cu(2)-O(1) | 79.06(8) |
| Cu(1)-Cu(2) | 3.019 | O(1)-Cu(2)-O(3) | 173.03(7) |
| | | N(2)-Cu(2)-N(3) | 165.33(9) |
| | | Cu(1)-O(1)-Cu(2) | 100.80(8) |
| | | Cu(1)-N(3)-Cu(2) | 100.07(9) |

Table S4. Bond distances [Å] and angles [°] for **4**.

| Bond lengths | Å | Bond angles | [°] |
|--------------|----------|-----------------|------------|
| Cu(1)-O(1) | 1.943(4) | N(1)-Cu(1)-O(1) | 92.60(18) |
| Cu(1)-N(1) | 1.928(5) | N(1)-Cu(1)-O(4) | 86.10(19) |
| Cu(1)-N(3) | 1.992(4) | O(4)-Cu(1)-N(3) | 100.80(18) |
| Cu(1)-O(4) | 1.916(4) | N(3)-Cu(1)-O(1) | 80.47(18) |

| | | | |
|-------------|----------|------------------|------------|
| Cu(1)-O(6) | 2.505(6) | N(1)-Cu(1)-N(3) | 171.3(2) |
| Cu(2)-O(1) | 1.941(4) | O(1)-Cu(1)-O(4) | 178.67(18) |
| Cu(2)-N(2) | 1.920(4) | N(2)-Cu(2)-O(1) | 92.28(18) |
| Cu(2)-N(3) | 1.971(5) | N(2)-Cu(2)-O(3) | 85.10(18) |
| Cu(2)-O(3) | 1.929(4) | O(3)-Cu(2)-N(3) | 101.84(18) |
| Cu(2)-O(5) | 2.797(4) | N(3)-Cu(2)-O(1) | 81.02(17) |
| Cu(4)-F(4) | 2.728(3) | O(1)-Cu(2)-O(3) | 173.05(19) |
| Cu(1)-Cu(2) | 2.985 | N(2)-Cu(2)-N(3) | 172.86(19) |
| | | Cu(1)-O(1)-Cu(2) | 100.44(17) |
| | | Cu(1)-N(3)-Cu(2) | 97.8(2) |

Table S5. Bond distances [Å] and angles [°] for **5**.

| Bond lengths | Å | Bond angles | [°] |
|--------------|------------|-------------------|------------|
| Cu(4)-Cu(5) | 2.8650(13) | O(4)-Cu(4)-O(15) | 89.1(2) |
| Cu(4)-O(4) | 1.940(5) | O(4)-Cu(4)-O(11) | 85.9(2) |
| Cu(4)-O(5) | 2.162(5) | O(5)-Cu(4)-Cu(5) | 160.28(17) |
| Cu(4)-O(13) | 1.920(5) | O(13)-Cu(4)-O(4) | 176.2(2) |
| Cu(4)-O(15) | 1.967(5) | O(13)-Cu(4)-O(15) | 91.9(2) |
| Cu(4)-O(11) | 2.004(5) | O(13)-Cu(4)-O(11) | 94.8(2) |
| Cu(5)-O(20) | 1.948(5) | O(15)-Cu(4)-O(11) | 154.6(2) |
| Cu(5)-O(12) | 1.984(5) | O(20)-Cu(5)-O(12) | 88.1(2) |
| Cu(5)-O(16) | 1.983(6) | O(20)-Cu(5)-O(16) | 87.8(2) |
| Cu(5)-O(14) | 1.920(5) | O(16)-Cu(5)-O(12) | 156.8(2) |
| Cu(5)-O(21) | 2.163(5) | O(14)-Cu(5)-O(20) | 177.4(2) |
| Cu(7)-Cu(6) | 2.9428(15) | O(14)-Cu(5)-O(12) | 91.3(2) |
| Cu(7)-O(22) | 1.933(5) | O(14)-Cu(5)-O(16) | 93.7(2) |
| Cu(7)-O(17) | 1.934(5) | O(21)-Cu(5)-Cu(4) | 163.60(16) |
| Cu(7)-O(18) | 1.975(6) | O(22)-Cu(7)-O(17) | 81.2(2) |
| Cu(7)-O(10) | 2.174(6) | O(22)-Cu(7)-O(18) | 99.7(2) |
| Cu(7)-N(4) | 1.935(7) | O(22)-Cu(7)-N(4) | 166.3(2) |
| Cu(6)-O(20) | 1.939(5) | O(17)-Cu(7)-O(18) | 164.2(2) |
| Cu(6)-O(22) | 1.966(5) | O(17)-Cu(7)-N(4) | 91.1(2) |
| Cu(6)-O(17) | 1.916(5) | N(4)-Cu(7)-O(18) | 84.6(3) |
| Cu(6)-N(3) | 1.914(6) | O(20)-Cu(6)-O(22) | 101.9(2) |
| Cu(6)-O(23) | 2.509(6) | O(17)-Cu(6)-O(20) | 174.2(2) |
| Cu(6)-O(16) | 2.483(5) | O(17)-Cu(6)-O(22) | 80.8(2) |
| Cu(2)-Cu(1) | 2.9389(15) | N(3)-Cu(6)-O(20) | 85.0(2) |
| Cu(2)-O(4) | 1.930(5) | N(3)-Cu(6)-O(22) | 170.6(3) |
| Cu(2)-O(6) | 1.983(5) | N(3)-Cu(6)-O(17) | 92.9(2) |
| Cu(2)-O(1) | 1.920(5) | O(4)-Cu(2)-O(6) | 100.7(2) |
| Cu(2)-O(11) | 2.363(6) | O(1)-Cu(2)-O(4) | 177.1(2) |
| Cu(2)-N(2) | 1.901(6) | O(1)-Cu(2)-O(6) | 81.3(2) |
| Cu(3)-O(22) | 2.258(5) | N(2)-Cu(2)-O(4) | 86.2(2) |

| | | | |
|-------------|----------|-------------------|----------|
| Cu(3)-O(6) | 2.012(5) | N(2)-Cu(2)-O6 | 167.1(2) |
| Cu(3)-O(7) | 1.995(6) | N(2)-Cu(2)-O(1) | 92.3(3) |
| Cu(3)-O(23) | 1.964(6) | O(7)-Cu(2)-O(11) | 156.4(6) |
| Cu(3)-O(9) | 1.919(6) | O(7)-Cu(3)-O(6) | 86.9(2) |
| Cu(3)-O(8) | 2.592(6) | O(23)-Cu(3)-O(6) | 92.5(2) |
| Cu(1)-O(6) | 1.945(5) | O(23)-Cu(3)-O(7) | 172.5(2) |
| Cu(1)-O(1) | 1.926(5) | O(9)-Cu(3)-O(6) | 167.4(2) |
| Cu(1)-O(8) | 2.382(7) | O(9)-Cu(3)-O(7) | 88.7(2) |
| Cu(1)-N(1) | 1.915(7) | O(9)-Cu(3)-O(23) | 90.3(3) |
| Cu(1)-O(2) | 1.928(7) | O(8)-Cu(3)-O(22) | 154.8(4) |
| | | O(1)-Cu(1)-O(6) | 82.1(2) |
| | | O(1)-Cu(1)-O(2) | 168.9(4) |
| | | N(1)-Cu(1)-O(6) | 174.8(3) |
| | | N(1)-Cu(1)-O(1) | 92.9(3) |
| | | N(1)-Cu(1)-O(2) | 86.1(3) |
| | | O(2)-Cu(1)-O(6) | 98.6(3) |
| | | Cu(7)-O(22)-Cu(6) | 98.0(2) |
| | | Cu(7)-O(22)-Cu(3) | 117.3(2) |
| | | Cu(6)-O(22)-Cu(3) | 102.1(2) |
| | | Cu(6)-O(17)-Cu(7) | 99.7(2) |
| | | C(68)-O(17)-Cu(7) | 130.6(5) |
| | | C(68)-O(17)-Cu(6) | 129.5(5) |
| | | Cu(2)-O(6)-Cu(3) | 109.3(3) |
| | | Cu(1)-O(6)-Cu(2) | 96.9(2) |
| | | Cu(1)-O(6)-Cu(3) | 109.6(2) |
| | | Cu(2)-O(1)-Cu(1) | 99.7(2) |
| | | C(5)-O(1)-Cu(2) | 130.8(6) |
| | | C(5)-O(1)-Cu(1) | 128.8(5) |

Table S6. Bond distances [Å] and angles [°] for **6**.

| Bond lengths | Å | Bond angles | [°] |
|---------------------------|-----------|------------------|----------|
| Cu(2)-Cu(3 ¹) | 3.004(4) | O(4)-Cu(2)-O(1) | 171.6(4) |
| Cu(2)-O(8) | 2.373(10) | O(6)-Cu(2)-O(1) | 83.7(4) |
| Cu(2)-O(1) | 1.938(10) | O(6)-Cu(2)-O(4) | 95.8(4) |
| Cu(2)-O(4) | 1.923(10) | N(2)-Cu(2)-O(1) | 91.6(5) |
| Cu(2)-O(6) | 1.920(10) | N(2)-Cu(2)-O(4) | 87.2(5) |
| Cu(2)-N(2) | 1.888(13) | N(2)-Cu(2)-O(6) | 167.8(4) |
| Cu(2)-O(9) | 2.59(2) | Cu(8)-Cu(2)-O(9) | 165.2(3) |
| Cu(1)-O(1) | 1.952(10) | O(1)-Cu(1)-O(6) | 81.7(4) |
| Cu(1)-O(2) | 1.874(10) | O(2)-Cu(1)-O(1) | 174.5(4) |
| Cu(1)-O(6) | 1.982(9) | O(2)-Cu(1)-O(6) | 100.3(4) |
| Cu(1)-N(1) | 1.912(12) | O(2)-Cu(1)-N(1) | 87.8(5) |
| Cu(1)-O(10) | 2.55(6) | N(1)-Cu(1)-O(1) | 90.4(5) |

| | | | |
|--------------------------|-----------|--------------------------------|-----------|
| Cu(3)-O(2) | 1.931(9) | N(1)-Cu(1)-O(6) | 171.6(5) |
| Cu(3)-O(6 ¹) | 1.947(9) | O(2)-Cu(3)-O(6 ¹) | 93.3(4) |
| Cu(3)-O(12) | 1.897(9) | O(2)-Cu(3)-O(9) | 162.7(4) |
| Cu(3)-O(9) | 1.948(10) | O(6 ¹)-Cu(3)-O(9) | 86.9(4) |
| Cu(5)-O(7) | 2.243(12) | O(12)-Cu(3)-O(2) | 92.1(4) |
| Cu(5)-O(16) | 1.954(10) | O(12)-Cu(3)-O(6 ¹) | 165.8(4) |
| Cu(5)-O(11) | 1.952(9) | O(12)-Cu(3)-O(9) | 91.8(4) |
| Cu(5)-O(12) | 1.936(9) | O(11)-Cu(5)-O(16) | 81.5(4) |
| Cu(5)-N(4) | 1.932(12) | O(12)-Cu(5)-O(16) | 101.2(4) |
| Cu(4)-O(8) | 2.403(10) | O(12)-Cu(5)-O(11) | 171.6(4) |
| Cu(4)-O(16) | 1.953(9) | N(4)-Cu(5)-O(16) | 167.7(4) |
| Cu(4)-O(11) | 1.956(11) | N(4)-Cu(5)-O(11) | 90.7(5) |
| Cu(4)-O(14) | 1.944(10) | N(4)-Cu(5)-O(12) | 85.3(5) |
| Cu(4)-N(3) | 1.934(11) | O(16)-Cu(4)-O(11) | 81.4(4) |
| | | O(14)-Cu(4)-O(16) | 102.6(4) |
| | | O(14)-Cu(4)-O(11) | 174.5(4) |
| | | N(3)-Cu(4)-O(16) | 167.7(4) |
| | | N(3)-Cu(4)-O(11) | 89.6(5) |
| | | N(3)-Cu(4)-O(14) | 85.9(5) |
| | | Cu(2)-O(8)-Cu(4) | 106.6(4) |
| | | C(16)-O(8)-Cu(2) | 113.8(9) |
| | | C(16)-O(8)-Cu(4) | 116.4(9) |
| | | Cu(2)-O(1)-Cu(1) | 97.5(4) |
| | | C(5)-O(1)-Cu(2) | 129.7(10) |
| | | C(5)-O(1)-Cu(1) | 131.9(10) |
| | | Cu(1)-O(2)-Cu(3) | 123.5(5) |
| | | C(10)-O(2)-Cu(1) | 108.9(8) |
| | | C(10)-O(2)-Cu(3) | 113.6(9) |
| | | Cu(2)-O(6)-Cu(1) | 97.1(4) |
| | | Cu(2)-O(6)-Cu(3 ¹) | 102.0(5) |
| | | Cu(3 ¹)-O(6)-Cu(1) | 118.9(4) |
| | | Cu(4)-O(16)-Cu(5) | 97.4(4) |
| | | Cu(5)-O(11)-Cu(4) | 97.3(4) |
| | | C(34)-O(11)-Cu(5) | 128.0(9) |
| | | C(34)-O(11)-Cu(4) | 128.0(10) |
| | | Cu(3)-O(12)-Cu(5) | 117.6(5) |
| | | C(39)-O(12)-Cu(3) | 122.8(8) |
| | | C(39)-O(12)-Cu(5) | 106.5(7) |

IR and UV-Vis Spectroscopy

In the IR spectrum (experimental section) of **1** which has EO intradimer and interdimer (μ -1,1-N₃) bridging azide groups, and **3**, **4**, and **7** which have only intradimer μ -1,1-N₃ ion, one, two, or three strong bands are observed at (cm⁻¹) 2093, 2037(**1**), 2110, 2074, 2050 (**3**), 2114, 2080 (**4**) and 2035 cm⁻¹ (**7**), typical for such bridging moieties.^{40,48,49} The IR spectra of **1-6** show one to three bands in the regions 3137-3423 cm⁻¹ and two bands in the region 1608-1645 cm⁻¹ due to ν (OH) (H₂O and CH₃OH) or ν (NH₂) and ν (C=N)/ ν (C=O) of coordinated imine/carbonyl of benzoate groups respectively.

The UV-Vis spectra of **1-6** compounds, recorded in DMF solution, are characterized by a very strong band in the region 320-378 nm and a low energy shoulder in the region 370-420 nm, which are assigned to metal-azide/metal-ligand charge transfer transitions. The d-d transition, characteristic for Cu(II) is observed as a broad band in the region 620-665 nm, typical for square

pyramidal/octahedrally-based geometry.⁶⁷ A typical UV-Vis spectrum of complex **5** is shown in Fig. S1

Fig S1. UV-Vis spectrum of **5** in DMF

