Supporting Information (SI)

for

**Synthesis and Luminescence of Optical Memory Active Tetramethylammonium Cyanocuprate(I) 3D Networks**

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**Figure S1.** Unit cell diagram of **1** viewed along the *b*-axis, 30% ellipsoids. Disordered atom positions and hydrogen atoms omitted.

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**Figure S2.** Unit cell diagram of **2** at 296 K viewed between the *a*- and *c*-axes, 30% ellipsoids. Disordered atom positions and hydrogen atoms omitted.

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**Figure S3.** Unit cell diagram of **2** at 100 K viewed along the *a*-axis, 30% ellipsoids. Disordered atom positions and hydrogen atoms omitted.

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**Figure S4.** Unit cell diagram of **3** at 100 K viewed along the *b*-axis, 30% ellipsoids. Disordered atom positions and hydrogen atoms omitted.

**Table S1.** Select bond lengths of **1**.

|  |  |  |  |
| --- | --- | --- | --- |
| Cu(1)-N(1B) | 1.960(4) | C(10)-H(10A) | 0.9800 |
| Cu(1)-C(1A) | 1.960(4) | C(10)-H(10B) | 0.9800 |
| Cu(1)-N(8) | 1.963(4) | C(10)-H(10C) | 0.9800 |
| Cu(1)-C(8) | 1.963(4) | C(11)-H(11A) | 0.9800 |
| Cu(1)-C(4)#1 | 2.089(4) | C(11)-H(11B) | 0.9800 |
| Cu(1)-C(3)#2 | 2.236(4) | C(11)-H(11C) | 0.9800 |
| Cu(1)-Cu(3)#2 | 2.5146(8) | N(10)-C(14) | 1.487(8) |
| Cu(3)-N(7) | 1.987(4) | N(10)-C(13)#8 | 1.492(5) |
| Cu(3)-C(7) | 1.987(4) | N(10)-C(13) | 1.492(5) |
| Cu(3)-C(3) | 2.007(4) | N(10)-C(12) | 1.497(7) |
| Cu(3)-N(2) | 2.023(4) | C(12)-H(12A) | 0.9800 |
| Cu(3)-C(4)#3 | 2.077(4) | C(12)-H(12B) | 0.9800 |
| Cu(3)-Cu(1)#4 | 2.5146(8) | C(12)-H(12C) | 0.9800 |
| Cu(4)-N(5) | 1.905(5) | C(13)-H(13A) | 0.9800 |
| Cu(4)-C(5) | 1.905(5) | C(13)-H(13B) | 0.9800 |
| Cu(4)-N(4) | 1.913(4) | C(13)-H(13C) | 0.9800 |
| Cu(4)-N(3) | 1.923(4) | C(14)-H(14A) | 0.9800 |
| N(2)-C(2) | 1.145(6) | C(14)-H(14B) | 0.9800 |
| C(2)-Cu(2B) | 1.934(15) | C(14)-H(14C) | 0.9800 |
| C(2)-Cu(2A) | 2.037(6) | N(11)-C(16) | 1.433(11) |
| C(2)-Cu(2A)#5 | 2.299(9) | N(11)-C(18) | 1.451(16) |
| N(3)-C(3) | 1.151(6) | N(11)-C(15) | 1.458(12) |
| C(3)-Cu(1)#4 | 2.236(4) | N(11)-C(17) | 1.595(17) |
| N(4)-C(4) | 1.152(6) | C(15)-H(15A) | 0.9800 |
| C(4)-Cu(3)#6 | 2.077(4) | C(15)-H(15B) | 0.9800 |
| C(4)-Cu(1)#1 | 2.089(4) | C(15)-H(15C) | 0.9800 |
| Cu(2A)-C(6) | 1.981(6) | C(16)-H(16A) | 0.9800 |
| Cu(2A)-N(1A) | 2.005(6) | C(16)-H(16B) | 0.9800 |
| Cu(2A)-C(2)#5 | 2.299(9) | C(16)-H(16C) | 0.9800 |
| Cu(2A)-Cu(2A)#5 | 2.436(12) | C(17)-H(17A) | 0.9800 |
| N(1A)-C(1A) | 1.161(6) | C(17)-H(17B) | 0.9800 |
| C(5)-C(5)#1 | 1.137(10) | C(17)-H(17C) | 0.9800 |
| C(6)-C(6)#7 | 1.180(8) | C(18)-H(18A) | 0.9800 |
| C(7)-C(7)#8 | 1.167(8) | C(18)-H(18B) | 0.9800 |
| C(8)-C(8)#8 | 1.151(8) | C(18)-H(18C) | 0.9800 |
| Cu(2B)-N(6) | 1.910(11) | N(12)-C(21) | 1.475(9) |
| Cu(2B)-C(1B) | 1.912(13) | N(12)-C(20)#8 | 1.491(5) |
| Cu(2B)-Cu(2B)#5 | 3.03(8) | N(12)-C(20) | 1.491(5) |
| C(1B)-N(1B) | 1.161(6) | N(12)-C(19) | 1.498(9) |
| N(5)-N(5)#1 | 1.137(10) | C(19)-H(19A) | 0.9800 |
| N(6)-N(6)#7 | 1.180(8) | C(19)-H(19B) | 0.9800 |
| N(7)-N(7)#8 | 1.167(8) | C(19)-H(19C) | 0.9800 |
| N(8)-N(8)#8 | 1.151(8) | C(20)-H(20A) | 0.9800 |
| N(9)-C(10) | 1.489(8) | C(20)-H(20B) | 0.9800 |
| N(9)-C(9) | 1.496(8) | C(20)-H(20C) | 0.9800 |
| N(9)-C(11)#7 | 1.499(5) | C(21)-H(21A) | 0.9800 |
| N(9)-C(11) | 1.499(5) | C(21)-H(21B) | 0.9800 |
| C(9)-H(9A) | 0.9800 | C(21)-H(21C) | 0.9800 |
| C(9)-H(9B) | 0.9800 | O(1)-H(1W) | 0.82(2) |
| C(9)-H(9C) | 0.9800 | O(1)-H(2W) | 0.82(2) |

**Table S2**. Selected bond angles of **1**.

|  |  |  |  |
| --- | --- | --- | --- |
| N(1B)-Cu(1)-N(8) | 114.59(15) | N(9)-C(10)-H(10B) | 109.5 |
| C(1A)-Cu(1)-C(8) | 114.59(15) | H(10A)-C(10)-H(10B) | 109.5 |
| N(1B)-Cu(1)-C(4)#1 | 111.26(16) | N(9)-C(10)-H(10C) | 109.5 |
| C(1A)-Cu(1)-C(4)#1 | 111.26(16) | H(10A)-C(10)-H(10C) | 109.5 |
| N(8)-Cu(1)-C(4)#1 | 113.11(15) | H(10B)-C(10)-H(10C) | 109.5 |
| C(8)-Cu(1)-C(4)#1 | 113.11(15) | N(9)-C(11)-H(11A) | 109.5 |
| N(1B)-Cu(1)-C(3)#2 | 111.54(16) | N(9)-C(11)-H(11B) | 109.5 |
| C(1A)-Cu(1)-C(3)#2 | 111.54(16) | H(11A)-C(11)-H(11B) | 109.5 |
| N(8)-Cu(1)-C(3)#2 | 103.14(16) | N(9)-C(11)-H(11C) | 109.5 |
| C(8)-Cu(1)-C(3)#2 | 103.14(16) | H(11A)-C(11)-H(11C) | 109.5 |
| C(4)#1-Cu(1)-C(3)#2 | 102.21(16) | H(11B)-C(11)-H(11C) | 109.5 |
| N(1B)-Cu(1)-Cu(3)#2 | 124.97(11) | C(14)-N(10)-C(13)#8 | 109.7(3) |
| C(1A)-Cu(1)-Cu(3)#2 | 124.97(11) | C(14)-N(10)-C(13) | 109.7(3) |
| N(8)-Cu(1)-Cu(3)#2 | 119.91(11) | C(13)#8-N(10)-C(13) | 109.3(5) |
| C(8)-Cu(1)-Cu(3)#2 | 119.91(11) | C(14)-N(10)-C(12) | 110.2(5) |
| C(4)#1-Cu(1)-Cu(3)#2 | 52.66(11) | C(13)#8-N(10)-C(12) | 108.9(3) |
| C(3)#2-Cu(1)-Cu(3)#2 | 49.56(11) | C(13)-N(10)-C(12) | 108.9(3) |
| N(7)-Cu(3)-C(3) | 110.75(16) | N(10)-C(12)-H(12A) | 109.5 |
| C(7)-Cu(3)-C(3) | 110.75(16) | N(10)-C(12)-H(12B) | 109.5 |
| N(7)-Cu(3)-N(2) | 105.75(15) | H(12A)-C(12)-H(12B) | 109.5 |
| C(7)-Cu(3)-N(2) | 105.75(15) | N(10)-C(12)-H(12C) | 109.5 |
| C(3)-Cu(3)-N(2) | 113.45(17) | H(12A)-C(12)-H(12C) | 109.5 |
| N(7)-Cu(3)-C(4)#3 | 106.79(16) | H(12B)-C(12)-H(12C) | 109.5 |
| C(7)-Cu(3)-C(4)#3 | 106.79(16) | N(10)-C(13)-H(13A) | 109.5 |
| C(3)-Cu(3)-C(4)#3 | 111.07(17) | N(10)-C(13)-H(13B) | 109.5 |
| N(2)-Cu(3)-C(4)#3 | 108.69(15) | H(13A)-C(13)-H(13B) | 109.5 |
| N(7)-Cu(3)-Cu(1)#4 | 123.84(11) | N(10)-C(13)-H(13C) | 109.5 |
| C(7)-Cu(3)-Cu(1)#4 | 123.84(11) | H(13A)-C(13)-H(13C) | 109.5 |
| C(3)-Cu(3)-Cu(1)#4 | 57.98(13) | H(13B)-C(13)-H(13C) | 109.5 |
| N(2)-Cu(3)-Cu(1)#4 | 129.85(10) | N(10)-C(14)-H(14A) | 109.5 |
| C(4)#3-Cu(3)-Cu(1)#4 | 53.09(11) | N(10)-C(14)-H(14B) | 109.5 |
| N(5)-Cu(4)-N(4) | 120.58(18) | H(14A)-C(14)-H(14B) | 109.5 |
| C(5)-Cu(4)-N(4) | 120.58(18) | N(10)-C(14)-H(14C) | 109.5 |
| N(5)-Cu(4)-N(3) | 119.12(18) | H(14A)-C(14)-H(14C) | 109.5 |
| C(5)-Cu(4)-N(3) | 119.12(18) | H(14B)-C(14)-H(14C) | 109.5 |
| N(4)-Cu(4)-N(3) | 120.28(15) | C(16)-N(11)-C(18) | 114.8(10) |
| C(2)-N(2)-Cu(3) | 174.4(3) | C(16)-N(11)-C(15) | 122.3(6) |
| N(2)-C(2)-Cu(2B) | 141.9(15) | C(18)-N(11)-C(15) | 106.3(10) |
| N(2)-C(2)-Cu(2A) | 153.2(5) | C(16)-N(11)-C(17) | 105.5(9) |
| N(2)-C(2)-Cu(2A)#5 | 138.7(4) | C(18)-N(11)-C(17) | 106.5(12) |
| Cu(2A)-C(2)-Cu(2A)#5 | 68.1(3) | C(15)-N(11)-C(17) | 99.3(9) |
| C(3)-N(3)-Cu(4) | 171.4(4) | N(11)-C(15)-H(15A) | 109.5 |
| N(3)-C(3)-Cu(3) | 158.9(4) | N(11)-C(15)-H(15B) | 109.5 |
| N(3)-C(3)-Cu(1)#4 | 128.2(4) | H(15A)-C(15)-H(15B) | 109.5 |
| Cu(3)-C(3)-Cu(1)#4 | 72.46(14) | N(11)-C(15)-H(15C) | 109.5 |
| C(4)-N(4)-Cu(4) | 177.7(4) | H(15A)-C(15)-H(15C) | 109.5 |
| N(4)-C(4)-Cu(3)#6 | 148.0(3) | H(15B)-C(15)-H(15C) | 109.5 |
| N(4)-C(4)-Cu(1)#1 | 137.7(3) | N(11)-C(16)-H(16A) | 109.5 |
| Cu(3)#6-C(4)-Cu(1)#1 | 74.25(14) | N(11)-C(16)-H(16B) | 109.5 |
| C(6)-Cu(2A)-N(1A) | 111.0(3) | H(16A)-C(16)-H(16B) | 109.5 |
| C(6)-Cu(2A)-C(2) | 110.1(3) | N(11)-C(16)-H(16C) | 109.5 |
| N(1A)-Cu(2A)-C(2) | 110.4(3) | H(16A)-C(16)-H(16C) | 109.5 |
| C(6)-Cu(2A)-C(2)#5 | 104.6(3) | H(16B)-C(16)-H(16C) | 109.5 |
| N(1A)-Cu(2A)-C(2)#5 | 108.6(3) | N(11)-C(17)-H(17A) | 109.5 |
| C(2)-Cu(2A)-C(2)#5 | 111.9(3) | N(11)-C(17)-H(17B) | 109.5 |
| C(6)-Cu(2A)-Cu(2A)#5 | 121.7(3) | H(17A)-C(17)-H(17B) | 109.5 |
| N(1A)-Cu(2A)-Cu(2A)#5 | 126.4(4) | N(11)-C(17)-H(17C) | 109.5 |
| C(2)-Cu(2A)-Cu(2A)#5 | 61.1(2) | H(17A)-C(17)-H(17C) | 109.5 |
| C(2)#5-Cu(2A)-Cu(2A)#5 | 50.9(3) | H(17B)-C(17)-H(17C) | 109.5 |
| C(1A)-N(1A)-Cu(2A) | 172.1(4) | N(11)-C(18)-H(18A) | 109.5 |
| N(1A)-C(1A)-Cu(1) | 174.1(3) | N(11)-C(18)-H(18B) | 109.5 |
| C(5)#1-C(5)-Cu(4) | 179.2(7) | H(18A)-C(18)-H(18B) | 109.5 |
| C(6)#7-C(6)-Cu(2A) | 175.12(18) | N(11)-C(18)-H(18C) | 109.5 |
| C(7)#8-C(7)-Cu(3) | 177.58(11) | H(18A)-C(18)-H(18C) | 109.5 |
| C(8)#8-C(8)-Cu(1) | 172.67(11) | H(18B)-C(18)-H(18C) | 109.5 |
| N(6)-Cu(2B)-C(1B) | 118.5(7) | C(21)-N(12)-C(20)#8 | 110.7(4) |
| N(6)-Cu(2B)-C(2) | 117.9(7) | C(21)-N(12)-C(20) | 110.7(4) |
| C(1B)-Cu(2B)-C(2) | 119.4(10) | C(20)#8-N(12)-C(20) | 110.4(5) |
| N(6)-Cu(2B)-Cu(2B)#5 | 110.2(18) | C(21)-N(12)-C(19) | 108.7(5) |
| C(1B)-Cu(2B)-Cu(2B)#5 | 115.1(16) | C(20)#8-N(12)-C(19) | 108.1(3) |
| C(2)-Cu(2B)-Cu(2B)#5 | 61.5(5) | C(20)-N(12)-C(19) | 108.1(4) |
| N(1B)-C(1B)-Cu(2B) | 173.2(11) | N(12)-C(19)-H(19A) | 109.5 |
| C(1B)-N(1B)-Cu(1) | 174.1(3) | N(12)-C(19)-H(19B) | 109.5 |
| N(5)#1-N(5)-Cu(4) | 179.2(7) | H(19A)-C(19)-H(19B) | 109.5 |
| N(6)#7-N(6)-Cu(2B) | 165.6(14) | N(12)-C(19)-H(19C) | 109.5 |
| N(7)#8-N(7)-Cu(3) | 177.58(11) | H(19A)-C(19)-H(19C) | 109.5 |
| N(8)#8-N(8)-Cu(1) | 172.67(11) | H(19B)-C(19)-H(19C) | 109.5 |
| C(10)-N(9)-C(9) | 109.9(5) | N(12)-C(20)-H(20A) | 109.5 |
| C(10)-N(9)-C(11)#7 | 109.7(3) | N(12)-C(20)-H(20B) | 109.5 |
| C(9)-N(9)-C(11)#7 | 109.2(3) | H(20A)-C(20)-H(20B) | 109.5 |
| C(10)-N(9)-C(11) | 109.7(3) | N(12)-C(20)-H(20C) | 109.5 |
| C(9)-N(9)-C(11) | 109.2(3) | H(20A)-C(20)-H(20C) | 109.5 |
| C(11)#7-N(9)-C(11) | 109.2(4) | H(20B)-C(20)-H(20C) | 109.5 |
| N(9)-C(9)-H(9A) | 109.5 | N(12)-C(21)-H(21A) | 109.5 |
| N(9)-C(9)-H(9B) | 109.5 | N(12)-C(21)-H(21B) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 | H(21A)-C(21)-H(21B) | 109.5 |
| N(9)-C(9)-H(9C) | 109.5 | N(12)-C(21)-H(21C) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 | H(21A)-C(21)-H(21C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 | H(21B)-C(21)-H(21C) | 109.5 |
| N(9)-C(10)-H(10A) | 109.5 | H(1W)-O(1)-H(2W) | 104(3) |

**Table S3.** Select bond length of **2** at 296 K.

|  |  |  |  |
| --- | --- | --- | --- |
| Cu(1)-N(1B) | 1.917(2) | N(3A)-C(4A)#4 | 1.522(6) |
| Cu(1)-C(1A) | 1.917(2) | N(3A)-C(4A) | 1.522(6) |
| Cu(1)-C(2B) | 1.934(3) | C(3A)-H(3AA) | 0.9600 |
| Cu(1)-N(2A) | 1.934(3) | C(3A)-H(3AB) | 0.9600 |
| Cu(1)-C(1B)#1 | 1.939(2) | C(3A)-H(3AC) | 0.9600 |
| Cu(1)-N(1A)#1 | 1.939(2) | C(4A)-C(4A)#4 | 1.957(16) |
| Cu(2)-N(2B) | 1.850(3) | C(4A)-H(4AA) | 0.9600 |
| Cu(2)-C(2A) | 1.850(3) | C(4A)-H(4AB) | 0.9600 |
| Cu(2)-N(2B)#2 | 1.850(3) | C(4A)-H(4AC) | 0.9600 |
| Cu(2)-C(2A)#2 | 1.850(3) | N(3B)-C(4B)#4 | 1.384(10) |
| N(1A)-C(1A) | 1.150(3) | N(3B)-C(4B) | 1.384(11) |
| N(1A)-Cu(1)#3 | 1.939(2) | N(3B)-C(3B) | 1.793(12) |
| C(2A)-N(2A) | 1.144(5) | N(3B)-C(3B)#4 | 1.793(12) |
| C(1B)-N(1B) | 1.150(3) | C(3B)-H(3BA) | 0.9600 |
| C(1B)-Cu(1)#3 | 1.939(2) | C(3B)-H(3BB) | 0.9600 |
| N(2B)-C(2B) | 1.144(5) | C(3B)-H(3BC) | 0.9600 |
| N(3A)-C(3A)#4 | 1.413(5) | C(4B)-H(4BA) | 0.9600 |
| N(3A)-C(3A) | 1.413(5) | C(4B)-H(4BB) | 0.9600 |
|  |  | C(4B)-H(4BC) | 0.9600 |

**Table S4.** Selected bond angles of **2** at 298 K.

|  |  |  |  |
| --- | --- | --- | --- |
| N(1B)-Cu(1)-C(2B) | 122.94(10) | N(3A)-C(4A)-C(4A)#4 | 50.0(4) |
| C(1A)-Cu(1)-N(2A) | 122.94(10) | N(3A)-C(4A)-H(4AA) | 109.5 |
| N(1B)-Cu(1)-C(1B)#1 | 119.21(9) | C(4A)#4-C(4A)-H(4AA) | 75.7 |
| C(2B)-Cu(1)-C(1B)#1 | 117.53(9) | N(3A)-C(4A)-H(4AB) | 109.5 |
| C(1A)-Cu(1)-N(1A)#1 | 119.21(9) | C(4A)#4-C(4A)-H(4AB) | 87.9 |
| N(2A)-Cu(1)-N(1A)#1 | 117.53(9) | H(4AA)-C(4A)-H(4AB) | 109.5 |
| N(2B)-Cu(2)-N(2B)#2 | 180 | N(3A)-C(4A)-H(4AC) | 109.5 |
| C(2A)-Cu(2)-C(2A)#2 | 180 | C(4A)#4-C(4A)-H(4AC) | 157.8 |
| C(1A)-N(1A)-Cu(1)#3 | 174.7(3) | H(4AA)-C(4A)-H(4AC) | 109.5 |
| N(1A)-C(1A)-Cu(1) | 175.0(2) | H(4AB)-C(4A)-H(4AC) | 109.5 |
| N(2A)-C(2A)-Cu(2) | 177.7(3) | C(4B)#4-N(3B)-C(4B) | 176.9(14) |
| C(2A)-N(2A)-Cu(1) | 173.0(3) | C(4B)#4-N(3B)-C(3B) | 97.7(7) |
| N(1B)-C(1B)-Cu(1)#3 | 174.7(3) | C(4B)-N(3B)-C(3B) | 83.6(7) |
| C(1B)-N(1B)-Cu(1) | 175.0(2) | C(4B)#4-N(3B)-C(3B)#4 | 83.6(7) |
| C(2B)-N(2B)-Cu(2) | 177.7(3) | C(4B)-N(3B)-C(3B)#4 | 97.7(7) |
| N(2B)-C(2B)-Cu(1) | 173.0(3) | C(3B)-N(3B)-C(3B)#4 | 128.7(14) |
| C(3A)#4-N(3A)-C(3A) | 114.1(6) | N(3B)-C(3B)-H(3BA) | 109.5 |
| C(3A)#4-N(3A)-C(4A)#4 | 120.1(5) | N(3B)-C(3B)-H(3BB) | 109.5 |
| C(3A)-N(3A)-C(4A)#4 | 109.4(4) | H(3BA)-C(3B)-H(3BB) | 109.5 |
| C(3A)#4-N(3A)-C(4A) | 109.4(4) | N(3B)-C(3B)-H(3BC) | 109.5 |
| C(3A)-N(3A)-C(4A) | 120.1(5) | H(3BA)-C(3B)-H(3BC) | 109.5 |
| C(4A)#4-N(3A)-C(4A) | 80.1(7) | H(3BB)-C(3B)-H(3BC) | 109.5 |
| N(3A)-C(3A)-H(3AA) | 109.5 | N(3B)-C(4B)-H(4BA) | 109.5 |
| N(3A)-C(3A)-H(3AB) | 109.5 | N(3B)-C(4B)-H(4BB) | 109.5 |
| H(3AA)-C(3A)-H(3AB) | 109.5 | H(4BA)-C(4B)-H(4BB) | 109.5 |
| N(3A)-C(3A)-H(3AC) | 109.5 | N(3B)-C(4B)-H(4BC) | 109.5 |
| H(3AA)-C(3A)-H(3AC) | 109.5 | H(4BA)-C(4B)-H(4BC) | 109.5 |
| H(3AB)-C(3A)-H(3AC) | 109.5 | H(4BB)-C(4B)-H(4BC) | 109.5 |

**Table S5.** Selected bond lengths of **2** at 100 K.

|  |  |  |  |
| --- | --- | --- | --- |
| Cu(1A)-C(1A) | 1.830(5) | C(8B)-Cu(3)#5 | 1.944(4) |
| Cu(1A)-C(2A) | 1.877(5) | Cu(2)-Cu(4B)#1 | 3.015(10) |
| Cu(1A)-Cu(5)#1 | 2.913(4) | Cu(2)-Cu(4A)#1 | 3.059(3) |
| Cu(4A)-C(5A) | 1.821(5) | Cu(3)-C(8B)#5 | 1.944(4) |
| Cu(4A)-C(6A) | 1.873(5) | Cu(3)-N(8A)#5 | 1.944(4) |
| Cu(4A)-Cu(6)#2 | 3.000(3) | Cu(3)-Cu(1B)#6 | 2.971(13) |
| Cu(4A)-Cu(2)#1 | 3.059(3) | Cu(5)-C(3B)#4 | 1.948(4) |
| N(1A)-C(1A) | 1.157(5) | Cu(5)-N(3A)#4 | 1.948(4) |
| N(1A)-Cu(6)#3 | 1.942(3) | Cu(5)-Cu(1A)#1 | 2.913(4) |
| N(2A)-C(2A) | 1.155(5) | Cu(5)-Cu(1B)#1 | 3.016(11) |
| N(2A)-Cu(2) | 1.929(4) | Cu(6)-C(1B)#7 | 1.942(3) |
| C(3A)-N(3A) | 1.158(5) | Cu(6)-N(1A)#7 | 1.942(3) |
| C(3A)-Cu(2) | 1.923(4) | Cu(6)-Cu(4A)#2 | 3.000(3) |
| N(3A)-Cu(5)#4 | 1.948(4) | Cu(6)-Cu(4B)#2 | 3.004(10) |
| N(4A)-C(4A) | 1.164(5) | C(9A)-N(9) | 1.461(7) |
| N(4A)-Cu(2) | 1.950(3) | C(9A)-H(9A1) | 0.9800 |
| C(4A)-Cu(3) | 1.911(4) | C(9A)-H(9A2) | 0.9800 |
| C(5A)-N(5A) | 1.162(5) | C(9A)-H(9A3) | 0.9800 |
| N(5A)-Cu(3) | 1.931(3) | C(11A)-N(9) | 1.527(8) |
| C(6A)-N(6A) | 1.166(5) | C(11A)-H(11A) | 0.9800 |
| N(6A)-Cu(5) | 1.926(3) | C(11A)-H(11B) | 0.9800 |
| N(7A)-C(7A) | 1.173(5) | C(11A)-H(11C) | 0.9800 |
| N(7A)-Cu(6) | 1.934(3) | C(9B)-N(9) | 1.637(18) |
| C(7A)-Cu(5) | 1.916(4) | C(9B)-H(9A) | 0.9800 |
| C(8A)-N(8A) | 1.155(5) | C(9B)-H(9AB) | 0.9800 |
| C(8A)-Cu(6) | 1.921(4) | C(9B)-H(9AC) | 0.9800 |
| N(8A)-Cu(3)#5 | 1.944(4) | C(11B)-N(9) | 1.388(18) |
| Cu(1B)-N(2B) | 1.784(9) | C(11B)-H(11D) | 0.9800 |
| Cu(1B)-N(1B) | 1.930(10) | C(11B)-H(11E) | 0.9800 |
| Cu(1B)-Cu(3)#6 | 2.971(13) | C(11B)-H(11F) | 0.9800 |
| Cu(1B)-Cu(5)#1 | 3.016(11) | N(9)-C(12) | 1.478(5) |
| Cu(4B)-N(6B) | 1.770(10) | N(9)-C(10) | 1.484(5) |
| Cu(4B)-N(5B) | 1.933(12) | C(10)-H(10A) | 0.9800 |
| Cu(4B)-Cu(6)#2 | 3.004(10) | C(10)-H(10B) | 0.9800 |
| Cu(4B)-Cu(2)#1 | 3.015(10) | C(10)-H(10C) | 0.9800 |
| C(1B)-N(1B) | 1.157(5) | C(12)-H(12A) | 0.9800 |
| C(1B)-Cu(6)#3 | 1.942(3) | C(12)-H(12B) | 0.9800 |
| C(2B)-N(2B) | 1.155(5) | C(12)-H(12C) | 0.9800 |
| C(2B)-Cu(2) | 1.929(4) | N(10)-C(13) | 1.484(5) |
| N(3B)-C(3B) | 1.158(5) | N(10)-C(15) | 1.485(6) |
| N(3B)-Cu(2) | 1.923(4) | N(10)-C(16) | 1.486(5) |
| C(3B)-Cu(5)#4 | 1.948(4) | N(10)-C(14) | 1.497(5) |
| C(4B)-N(4B) | 1.164(5) | C(13)-H(13A) | 0.9800 |
| C(4B)-Cu(2) | 1.950(3) | C(13)-H(13B) | 0.9800 |
| N(4B)-Cu(3) | 1.911(4) | C(13)-H(13C) | 0.9800 |
| N(5B)-C(5B) | 1.162(5) | C(14)-H(14A) | 0.9800 |
| C(5B)-Cu(3) | 1.931(3) | C(14)-H(14B) | 0.9800 |
| N(6B)-C(6B) | 1.166(5) | C(14)-H(14C) | 0.9800 |
| C(6B)-Cu(5) | 1.926(3) | C(15)-H(15A) | 0.9800 |
| C(7B)-N(7B) | 1.173(5) | C(15)-H(15B) | 0.9800 |
| C(7B)-Cu(6) | 1.934(3) | C(15)-H(15C) | 0.9800 |
| N(7B)-Cu(5) | 1.916(4) | C(16)-H(16A) | 0.9800 |
| N(8B)-C(8B) | 1.155(5) | C(16)-H(16B) | 0.9800 |
| N(8B)-Cu(6) | 1.921(4) | C(16)-H(16C) | 0.9800 |

**Table S6.** Selected bond angles of **2** at 100 K.

|  |  |  |  |
| --- | --- | --- | --- |
| C(1A)-Cu(1A)-C(2A) | 174.7(4) | N(8B)-Cu(6)-C(7B) | 119.57(14) |
| C(1A)-Cu(1A)-Cu(5)#1 | 102.7(2) | N(8B)-Cu(6)-C(1B)#7 | 123.83(15) |
| C(2A)-Cu(1A)-Cu(5)#1 | 81.40(15) | C(7B)-Cu(6)-C(1B)#7 | 116.24(14) |
| C(5A)-Cu(4A)-C(6A) | 176.9(3) | C(8A)-Cu(6)-N(1A)#7 | 123.83(15) |
| C(5A)-Cu(4A)-Cu(6)#2 | 87.95(16) | N(7A)-Cu(6)-N(1A)#7 | 116.24(14) |
| C(6A)-Cu(4A)-Cu(6)#2 | 90.74(15) | C(8A)-Cu(6)-Cu(4A)#2 | 83.50(12) |
| C(5A)-Cu(4A)-Cu(2)#1 | 101.25(16) | N(7A)-Cu(6)-Cu(4A)#2 | 91.10(13) |
| C(6A)-Cu(4A)-Cu(2)#1 | 79.45(15) | N(1A)#7-Cu(6)-Cu(4A)#2 | 101.54(12) |
| Cu(6)#2-Cu(4A)-Cu(2)#1 | 164.99(17) | N(8B)-Cu(6)-Cu(4B)#2 | 86.0(3) |
| C(1A)-N(1A)-Cu(6)#3 | 171.5(3) | C(7B)-Cu(6)-Cu(4B)#2 | 87.1(4) |
| N(1A)-C(1A)-Cu(1A) | 178.2(4) | C(1B)#7-Cu(6)-Cu(4B)#2 | 102.8(2) |
| C(2A)-N(2A)-Cu(2) | 171.9(3) | N(9)-C(9A)-H(9A1) | 109.5 |
| N(2A)-C(2A)-Cu(1A) | 176.6(4) | N(9)-C(9A)-H(9A2) | 109.5 |
| N(3A)-C(3A)-Cu(2) | 172.3(3) | H(9A1)-C(9A)-H(9A2) | 109.5 |
| C(3A)-N(3A)-Cu(5)#4 | 171.9(3) | N(9)-C(9A)-H(9A3) | 109.5 |
| C(4A)-N(4A)-Cu(2) | 170.8(3) | H(9A1)-C(9A)-H(9A3) | 109.5 |
| N(4A)-C(4A)-Cu(3) | 172.3(3) | H(9A2)-C(9A)-H(9A3) | 109.5 |
| N(5A)-C(5A)-Cu(4A) | 177.5(4) | N(9)-C(11A)-H(11A) | 109.5 |
| C(5A)-N(5A)-Cu(3) | 173.5(3) | N(9)-C(11A)-H(11B) | 109.5 |
| N(6A)-C(6A)-Cu(4A) | 177.8(4) | H(11A)-C(11A)-H(11B) | 109.5 |
| C(6A)-N(6A)-Cu(5) | 171.7(3) | N(9)-C(11A)-H(11C) | 109.5 |
| C(7A)-N(7A)-Cu(6) | 173.2(3) | H(11A)-C(11A)-H(11C) | 109.5 |
| N(7A)-C(7A)-Cu(5) | 172.9(3) | H(11B)-C(11A)-H(11C) | 109.5 |
| N(8A)-C(8A)-Cu(6) | 172.7(3) | N(9)-C(9B)-H(9A) | 109.5 |
| C(8A)-N(8A)-Cu(3)#5 | 172.1(3) | N(9)-C(9B)-H(9AB) | 109.5 |
| N(2B)-Cu(1B)-N(1B) | 171.2(11) | H(9A)-C(9B)-H(9AB) | 109.5 |
| N(2B)-Cu(1B)-Cu(3)#6 | 95.0(5) | N(9)-C(9B)-H(9AC) | 109.5 |
| N(1B)-Cu(1B)-Cu(3)#6 | 89.2(4) | H(9A)-C(9B)-H(9AC) | 109.5 |
| N(2B)-Cu(1B)-Cu(5)#1 | 79.8(4) | H(9AB)-C(9B)-H(9AC) | 109.5 |
| N(1B)-Cu(1B)-Cu(5)#1 | 96.7(5) | N(9)-C(11B)-H(11D) | 109.5 |
| Cu(3)#6-Cu(1B)-Cu(5)#1 | 172.3(6) | N(9)-C(11B)-H(11E) | 109.5 |
| N(6B)-Cu(4B)-N(5B) | 171.4(11) | H(11D)-C(11B)-H(11E) | 109.5 |
| N(6B)-Cu(4B)-Cu(6)#2 | 92.7(4) | N(9)-C(11B)-H(11F) | 109.5 |
| N(5B)-Cu(4B)-Cu(6)#2 | 85.9(4) | H(11D)-C(11B)-H(11F) | 109.5 |
| N(6B)-Cu(4B)-Cu(2)#1 | 82.2(4) | H(11E)-C(11B)-H(11F) | 109.5 |
| N(5B)-Cu(4B)-Cu(2)#1 | 100.0(4) | C(11B)-N(9)-C(12) | 123.5(9) |
| Cu(6)#2-Cu(4B)-Cu(2)#1 | 172.7(6) | C(9A)-N(9)-C(12) | 112.6(4) |
| N(1B)-C(1B)-Cu(6)#3 | 171.5(3) | C(11B)-N(9)-C(10) | 117.8(8) |
| C(1B)-N(1B)-Cu(1B) | 171.5(6) | C(9A)-N(9)-C(10) | 115.3(4) |
| N(2B)-C(2B)-Cu(2) | 171.9(3) | C(12)-N(9)-C(10) | 110.4(3) |
| C(2B)-N(2B)-Cu(1B) | 176.0(7) | C(9A)-N(9)-C(11A) | 107.5(5) |
| C(3B)-N(3B)-Cu(2) | 172.3(3) | C(12)-N(9)-C(11A) | 105.7(4) |
| N(3B)-C(3B)-Cu(5)#4 | 171.9(3) | C(10)-N(9)-C(11A) | 104.6(4) |
| N(4B)-C(4B)-Cu(2) | 170.8(3) | C(11B)-N(9)-C(9B) | 105.3(12) |
| C(4B)-N(4B)-Cu(3) | 172.3(3) | C(12)-N(9)-C(9B) | 96.7(7) |
| C(5B)-N(5B)-Cu(4B) | 174.5(6) | C(10)-N(9)-C(9B) | 96.1(8) |
| N(5B)-C(5B)-Cu(3) | 173.5(3) | N(9)-C(10)-H(10A) | 109.5 |
| C(6B)-N(6B)-Cu(4B) | 172.2(7) | N(9)-C(10)-H(10B) | 109.5 |
| N(6B)-C(6B)-Cu(5) | 171.7(3) | H(10A)-C(10)-H(10B) | 109.5 |
| N(7B)-C(7B)-Cu(6) | 173.2(3) | N(9)-C(10)-H(10C) | 109.5 |
| C(7B)-N(7B)-Cu(5) | 172.9(3) | H(10A)-C(10)-H(10C) | 109.5 |
| C(8B)-N(8B)-Cu(6) | 172.7(3) | H(10B)-C(10)-H(10C) | 109.5 |
| N(8B)-C(8B)-Cu(3)#5 | 172.1(3) | N(9)-C(12)-H(12A) | 109.5 |
| C(3A)-Cu(2)-N(2A) | 125.09(15) | N(9)-C(12)-H(12B) | 109.5 |
| N(3B)-Cu(2)-C(2B) | 125.09(15) | H(12A)-C(12)-H(12B) | 109.5 |
| N(3B)-Cu(2)-C(4B) | 116.23(14) | N(9)-C(12)-H(12C) | 109.5 |
| C(2B)-Cu(2)-C(4B) | 118.30(15) | H(12A)-C(12)-H(12C) | 109.5 |
| C(3A)-Cu(2)-N(4A) | 116.23(14) | H(12B)-C(12)-H(12C) | 109.5 |
| N(2A)-Cu(2)-N(4A) | 118.30(15) | C(13)-N(10)-C(15) | 109.2(4) |
| N(3B)-Cu(2)-Cu(4B)#1 | 85.2(3) | C(13)-N(10)-C(16) | 110.5(3) |
| C(2B)-Cu(2)-Cu(4B)#1 | 106.0(2) | C(15)-N(10)-C(16) | 108.7(3) |
| C(4B)-Cu(2)-Cu(4B)#1 | 84.0(4) | C(13)-N(10)-C(14) | 109.8(3) |
| C(3A)-Cu(2)-Cu(4A)#1 | 87.37(12) | C(15)-N(10)-C(14) | 110.1(4) |
| N(2A)-Cu(2)-Cu(4A)#1 | 107.46(12) | C(16)-N(10)-C(14) | 108.5(3) |
| N(4A)-Cu(2)-Cu(4A)#1 | 80.09(14) | N(10)-C(13)-H(13A) | 109.5 |
| N(4B)-Cu(3)-C(5B) | 122.41(14) | N(10)-C(13)-H(13B) | 109.5 |
| C(4A)-Cu(3)-N(5A) | 122.41(14) | H(13A)-C(13)-H(13B) | 109.5 |
| N(4B)-Cu(3)-C(8B)#5 | 119.29(14) | N(10)-C(13)-H(13C) | 109.5 |
| C(5B)-Cu(3)-C(8B)#5 | 117.95(14) | H(13A)-C(13)-H(13C) | 109.5 |
| C(4A)-Cu(3)-N(8A)#5 | 119.29(14) | H(13B)-C(13)-H(13C) | 109.5 |
| N(5A)-Cu(3)-N(8A)#5 | 117.95(14) | N(10)-C(14)-H(14A) | 109.5 |
| N(4B)-Cu(3)-Cu(1B)#6 | 87.9(3) | N(10)-C(14)-H(14B) | 109.5 |
| C(5B)-Cu(3)-Cu(1B)#6 | 102.0(2) | H(14A)-C(14)-H(14B) | 109.5 |
| C(8B)#5-Cu(3)-Cu(1B)#6 | 85.7(2) | N(10)-C(14)-H(14C) | 109.5 |
| C(7A)-Cu(5)-N(6A) | 126.22(14) | H(14A)-C(14)-H(14C) | 109.5 |
| N(7B)-Cu(5)-C(6B) | 126.22(14) | H(14B)-C(14)-H(14C) | 109.5 |
| N(7B)-Cu(5)-C(3B)#4 | 116.56(14) | N(10)-C(15)-H(15A) | 109.5 |
| C(6B)-Cu(5)-C(3B)#4 | 116.84(14) | N(10)-C(15)-H(15B) | 109.5 |
| C(7A)-Cu(5)-N(3A)#4 | 116.56(14) | H(15A)-C(15)-H(15B) | 109.5 |
| N(6A)-Cu(5)-N(3A)#4 | 116.84(14) | N(10)-C(15)-H(15C) | 109.5 |
| C(7A)-Cu(5)-Cu(1A)#1 | 78.50(14) | H(15A)-C(15)-H(15C) | 109.5 |
| N(6A)-Cu(5)-Cu(1A)#1 | 109.32(14) | H(15B)-C(15)-H(15C) | 109.5 |
| N(3A)#4-Cu(5)-Cu(1A)#1 | 87.88(12) | N(10)-C(16)-H(16A) | 109.5 |
| N(7B)-Cu(5)-Cu(1B)#1 | 82.6(3) | N(10)-C(16)-H(16B) | 109.5 |
| C(6B)-Cu(5)-Cu(1B)#1 | 106.4(2) | H(16A)-C(16)-H(16B) | 109.5 |
| C(3B)#4-Cu(5)-Cu(1B)#1 | 86.5(2) | N(10)-C(16)-H(16C) | 109.5 |
| C(8A)-Cu(6)-N(7A) | 119.57(14) | H(16A)-C(16)-H(16C) | 109.5 |
|  |  | H(16B)-C(16)-H(16C) | 109.5 |

**Figure S5.** Vibrational infrared spectra of solid samples of **1** and **2** at 298 K.

**Figure S6.** Luminescence spectrum of (left) **1** and (right) **2** at 78 K and 298 K.

**Figure S7.** Lifetime measurements of **1** at (left) 298 K (𝜆em = 522 nm) and (right) 78 K. An excitation wavelength of 350 nm was used for both lifetime measurements.

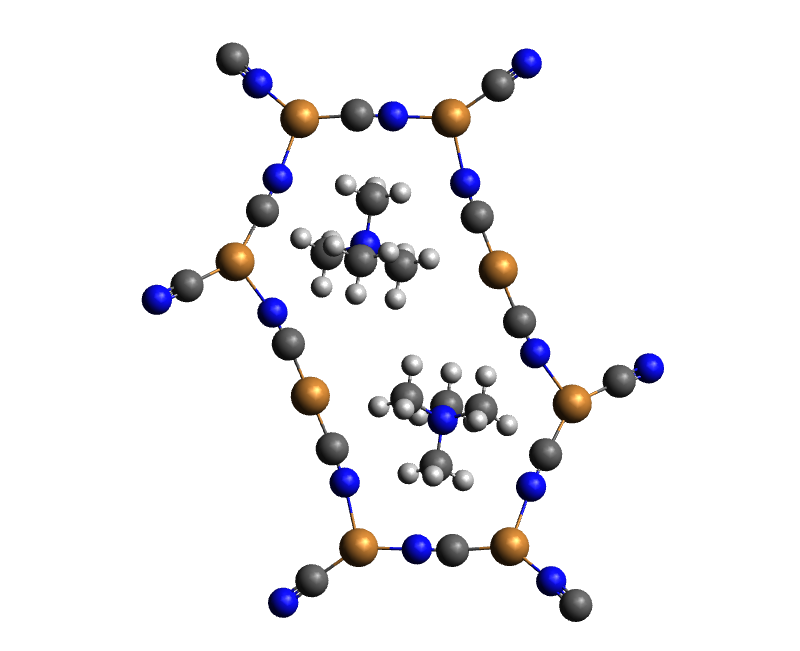
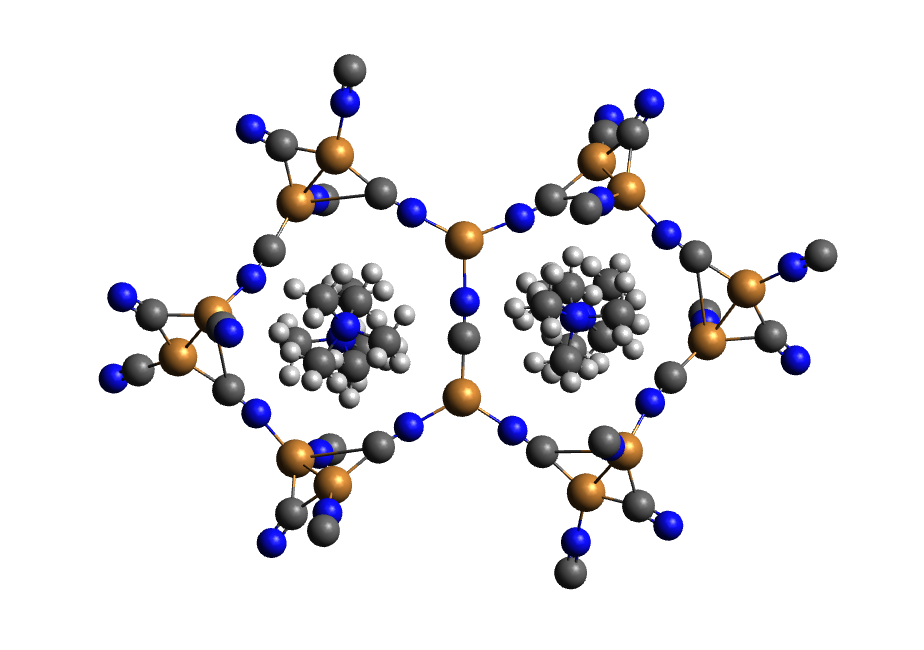
**Figure S8.** Lifetime measurements of **2** at (left) 298 K (𝜆em = 420 nm) and (right) 78 K (𝜆em = 440 nm). An excitation wavelength of 350 nm was used for both lifetime measurements.

**Table S7.** DFT ground state parameters of **1** compared to experimental values.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Distances (Å)/Angles(o) | | |
|  | M06/CEP-31G(d) | B3LYP/SDD | Experimental |
| Cu⋯Cu (Rhomboid) | 2.673 | 2.806 | 2.489 |
| CuC3v⋯NMe4+ | 5.349 | 5.674 | 5.718 |
| NC-CuC3v-CN | 120.0 | 120.0 | 120.0 |
| (𝜇2-CN)-Cu-(𝜇2-CN) | 110.7 | 107.2 | 108.4 |

**Table S8.** DFT ground state parameters of **2** compared to experimental values.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Distances (Å)/Angles(o) | | |
|  | M06/CEP-31G(d) | B3LYP/SDD | Experimental |
| CuC3v⋯CuC3v | 5.127 | 5.116 | 4.980 |
| CuC3v⋯CuC∞v | 5.223 | 5.166 | 4.926 |
| CuC∞v⋯NMe4+ | 4.935 | 5.510 | 5.141 |
| Cu-Cu-Cu | 166.1 | 172.0 | 175.4 |
| NC-CuC3v-CN | 107.3 | 107.6 | 118.5 |



**Figure S9.** M06/CEP-31G(d) ground state structure of **1**(left) and **2** (right).

**Table S9**. M06/CEP-31G(d) TD-DFT calculation excited state transitions for **1** at 300 nm. Percent contributions noted.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Transition | | | Contribution | Percent Contribution |
| HOMO-5 | ➝ | LUMO+4 | 0.29692 | 27% |
| HOMO-5 | ➝ | LUMO | 0.2794 | 24% |
| HOMO | ➝ | LUMO | 0.25509 | 20% |
| HOMO-8 | ➝ | LUMO+4 | 0.1319 | 5% |
| HOMO-5 | ➝ | LUMO+6 | 0.12917 | 5% |
| HOMO-5 | ➝ | LUMO+2 | 0.12013 | 4% |
| HOMO | ➝ | LUMO+8 | –0.10686 | 4% |
| HOMO | ➝ | LUMO+5 | 0.10579 | 3% |
| HOMO | ➝ | LUMO+1 | 0.10518 | 3% |
| HOMO-2 | ➝ | LUMO | –0.10325 | 3% |

**Table S10**. M06/CEP-31G(d) TD-DFT calculation excited state transitions for **2** at 330 nm. Percent contributions noted.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Transition | | | Contribution | Percent Contribution |
| HOMO-8 | ➝ | LUMO | 0.32687 | 24% |
| HOMO-9 | ➝ | LUMO | –0.2935 | 19% |
| HOMO-8 | ➝ | LUMO+1 | –0.2126 | 10% |
| HOMO-4 | ➝ | LUMO+1 | –0.1919 | 8% |
| HOMO-6 | ➝ | LUMO+1 | –0.17759 | 7% |
| HOMO-6 | ➝ | LUMO+3 | –0.14608 | 5% |
| HOMO-7 | ➝ | LUMO+1 | 0.14025 | 4% |
| HOMO-6 | ➝ | LUMO | 0.13889 | 4% |
| HOMO-3 | ➝ | LUMO+1 | –0.13586 | 4% |
| HOMO-9 | ➝ | LUMO+1 | –0.13421 | 4% |
| HOMO-2 | ➝ | LUMO+1 | –0.12752 | 4% |
| HOMO-7 | ➝ | LUMO | 0.12265 | 3% |
| HOMO-6 | ➝ | LUMO+2 | 0.11918 | 3% |

**Figure S10.** Uncorrected optical memory results of (left) **1** and (right) **2**.