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# Halogen-induced Core Structural Evolution of Four Dinuclear Copper(I) Luminescent Coordination Compounds

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**Table S1.** Crystallographic data for complexes **1a**-**3b**.

| Complex | 1a | 2a | 2b | 3b |
|---|---|---|---|---|
| Formula | $C_{51}H_{44}N_3Cl_2O_5P_3Cu_2$ | $C_{51}H_{42}N_3ClBrO_4P_3Cu_2$ | $C_{51}H_{42}N_3Br_2P_3Cu_2$ | $C_{51}H_{42}N_3I_2P_3Cu_2$ |
| Mr | 1069.78 | 1096.22 | 1076.68 | 1170.66 |
| Cryst system | trigonal | trigonal | monoclinic | triclinic |
| Space group | *P*-3*c*1 | *P*-3*m*1 | $P2_1/n$ | *P*-1 |
| a/Å | 13(3) | 12.803(9) | 14.256(9) | 13.615(5) |
| b/Å | 13(3) | 12.803(9) | 18.240(1) | 13.933(7) |
| c/Å | 39(4) | 19.257(2) | 17.675(1) | 15.790(6) |
| $\alpha$/° | 90.000 | 90.000 | 90 | 103.40(2) |
| $\beta$/° | 90.000 | 90.000 | 98.596(1) | 102.005(2) |
| $\gamma$/° | 120.00 | 120.000 | 90 | 117.440(2) |
| $V$/Å$^3$ | 5708(5) | 2733(2) | 4544(5) | 2407.7(2) |
| Z | 4 | 2 | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.219 | 1.332 | 1.574 | 1.615 |
| $\mu$/mm$^{-1}$ | 0.945 | 1.688 | 2.840 | 2.303 |
| $F$(000) | 2144 | 1112 | 2168 | 1156 |
| $R$(int) | 0.0613 | 0.0675 | 0.0519 | 0.0427 |
| Total reflections | 17180 | 21482 | 34734 | 18618 |
| Unique reflections | 3660 | 2356 | 10258 | 10792 |
| $I > 2\sigma(I)$ | 2050 | 1986 | 7462 | 7023 |
| $R_1$ | 0.0930 | 0.0559 | 0.0497 | 0.0592 |
| $wR_2$ | 0.3235 | 0.1384 | 0.1078 | 0.1625 |
| $S$ | 1.096 | 1.136 | 1.050 | 1.077 |

**Table S2.** Selected Bond Distances (Å) and Angles (deg) of **$[Cu_2(\mu\text{-dppy})_3Cl]ClO_4\cdot H_2O$ (1a)**

| | | | |
|---|---|---|---|
| | | bond distances | |
| Cu(2)-N(1) | 1.992(6) | Cu(1)-Cl(2) | 2.304(2) |
| Cu(2)-Cu(1) | 2.782(2) | Cu(1)-P(1) | 2.324 (2) |
| | | angles | |
| N(1)#1-Cu(2)-N(1)#2 | 61.9(3) | P(1)#1-Cu(1)-Cu(2) | 75.21(3) |
| N(1)#1-Cu(2)-N(1) | 116.94(9) | C(1)-N(1)-Cu(2) | 119.7(5) |
| N(1)#2-Cu(2)-N(1) | 56.0(3) | C(5)-N(1)-Cu(2) | 121.5(5) |
| N(1)#1-Cu(2)-N(1)#4 | 159.4(3) | N(1)#2-N(1)-Cu(2) | 62.02(2) |
| N(1)#2-Cu(2)-N(1)#4 | 116.94(9) | C(17)#4-N(1)-Cu(2) | 143.5(5) |
| N(1)#5-Cu(2)-Cu(1) | 100.19(14) | C(12)-P(1)-Cu(1) | 121.9(2) |
| Cl(2)-Cu(1)-P(1)#1 | 104.79(3) | C(6)-P(1)-Cu(1) | 113.27(2) |
| P(1)#1-Cu(1)-P(1) | 113.72(3) | C(5)-P(1)-Cu(1) | 111.6(2) |
| Cl(2)-Cu(1)-Cu(2) | 180 | | |
| | | torsion angles | |
| N(1)-Cu(2)-Cu(1)-P(1) | 31.50(2) | | |

[a]Symmetry transformations used to generate equivalent atoms: #1 = -x+y, -x+1, z; #2 = x, x-y+1, z; #3 = -y+1, -x+1, z; #4 = -x+y, y, z; #5 = -y+1, x-y+1, z; #6 = -y, -x, z.

[b]Torsion angle around the Cu2-Cu1-Cl1 axis in a four-membered ring $Cu_2NP$.

**Table S3.** Selected Bond Distances (Å) and Angles(deg) of **$[Cu_2(\mu\text{-dppy})_3Br]ClO_4 \cdot H_2O$ (2a)**

| | | | |
|---|---|---|---|
| bond distances | | | |
| Cu(2)-N(1) | 1.983(7) | Cu(1)-Br(1) | 2.441(2) |
| Cu(2)-Cu(1) | 2.751(2) | Cu(1)-P(1) | 2.326(2) |
| angles | | | |
| N(1)#1-Cu(2)-N(1)#2 | 61.3(4) | P(1)#1-Cu(1)-P(1) | 114.00(4) |
| N(1)#1-Cu(2)-N(1) | 117.10(11) | Br(1)-Cu(1)-Cu(2) | 180 |
| N(1)#2-Cu(2)-N(1) | 56.7(4) | P(1)-Cu(1)-Cu(2) | 75.57(5) |
| N(1)#1-Cu(2)-N(1)#3 | 56.7(4) | C(12)-P(1)-Cu(1) | 121.1(3) |
| N(1)-Cu(2)-N(1)#3 | 160.0(4) | C(6)-P(1)-Cu(1) | 113.6(2) |
| N(1)#1-Cu(2)-Cu(1) | 99.92(2) | C(5)-P(1)-Cu(1) | 110.8(3) |
| Br(1)-Cu(1)-P(1)#1 | 104.43(5) | | |
| torsion angles | | | |
| N(1)-Cu(2)-Cu(1)-P(1) | 31.19(2) | | |

[a]Symmetry transformations used to generate equivalentatoms: #1 = x+y, -x+1, z; #2 = x, x-y+1, z; #3 = -y+1, -x+1, z; #4 = -x+y, y, z; #5 = -y+1, x-y+1, z; #6 = -y, -x, z.

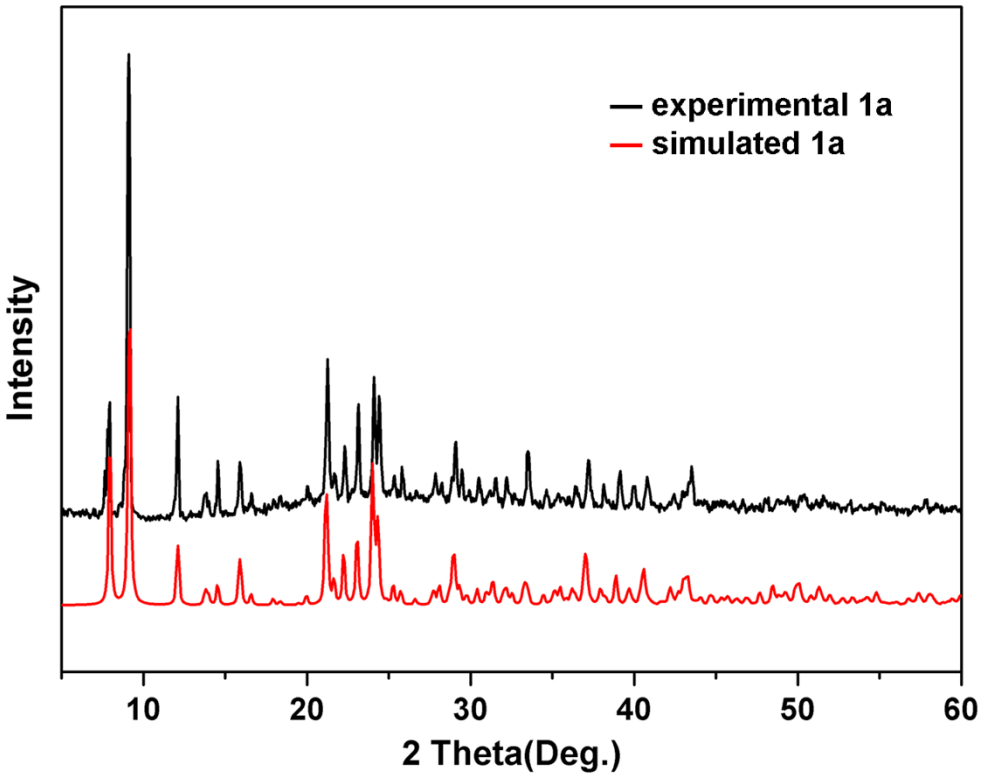
[b]Torsion angle around the Cu2-Cu1-Br1 axis in a four-membered ring $Cu_2NP$.

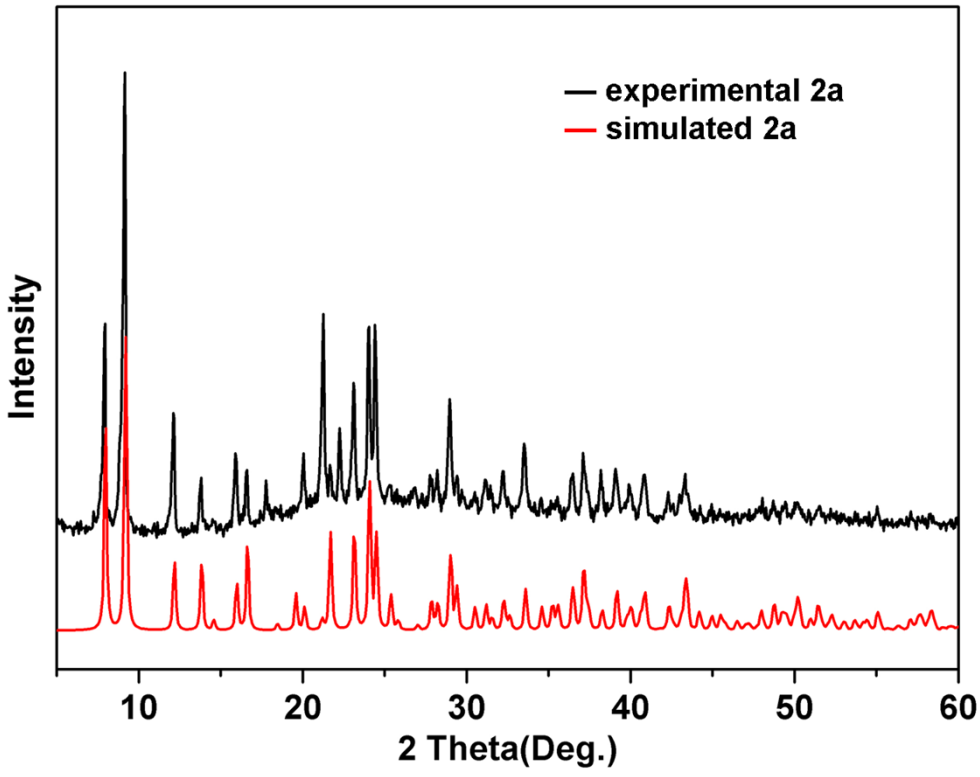
**Table S4 .** Selected Bond Distances (Å) and Angles (deg) of **$Cu_2(\mu\text{-}Br)_2(\mu\text{-}dppy)(dppy)_2$(2b)**

| | | | |
|---|---|---|---|
| bond distances | | | |
| Cu(1)-N(3) | 2.095(4) | Cu(2)-P(3) | 2.2488(7) |
| Cu(1)-P(1) | 2.2377(8) | Cu(2)-P(2) | 2.2618(6) |
| Cu(1)-Br(1) | 2.5104(5) | Cu(2)-Br(2) | 2.5287(3) |
| Cu(1)-Br(2) | 2.5434(2) | Cu(2)-Br(1) | 2.5686(3) |
| Cu(1)-Cu(2) | 2.8937(8) | | |
| angles | | | |
| N(3)-Cu(1)-P(1) | 123.28(10) | P(2)-Cu(2)-Cu(1) | 150.47(4) |
| N(3)-Cu(1)-Br(1) | 111.35(10) | Br(2)-Cu(2)-Cu(1) | 55.45(3) |
| P(1)-Cu(1)-Br(1) | 104.73(5) | Br(1)-Cu(2)-Cu(1) | 54.33(4) |
| N(3)-Cu(1)-Br(2) | 99.60(11) | C(1)-P(1)-Cu(1) | 116.04(5) |
| P(1)-Cu(1)-Br(2) | 113.35(5) | C(7)-P(1)-Cu(1) | 118.83(5) |
| Br(1)-Cu(1)-Br(2) | 102.92(5) | C(12)-P(1)-Cu(1) | 113.38(6) |
| N(3)-Cu(1)-Cu(2) | 90.41(10) | C(24)-P(2)-Cu(2) | 114.16(6) |
| P(1)-Cu(1)-Cu(2) | 146.30(5) | C(29)-P(2)-Cu(2) | 118.09(6) |
| Br(1)-Cu(1)-Cu(2) | 56.22(2) | C(18)-P(2)-Cu(2) | 113.61(6) |
| Br(2)-Cu(1)-Cu(2) | 54.98(3) | C(35)-P(3)-Cu(2) | 116.63(5) |
| P(3)-Cu(2)-P(2) | 124.42(6) | C(41)-P(3)-Cu(2) | 114.94(5) |
| P(3)-Cu(2)-Br(2) | 104.20(4) | C(47)-P(3)-Cu(2) | 115.80(4) |
| P(2)-Cu(2)-Br(2) | 108.90(5) | C(51)-N(3)-Cu(1) | 114.1(3) |
| P(3)-Cu(2)-Br(1) | 100.04(4) | C(47)-N(3)-Cu(1) | 128.7(3) |
| P(2)-Cu(2)-Br(1) | 114.90(5) | Cu(1)-Br(1)-Cu(2) | 69.45(5) |
| Br(2)-Cu(2)-Br(1) | 101.70(5) | Cu(2)-Br(2)-Cu(1) | 69.57(4) |
| P(3)-Cu(2)-Cu(1) | 85.05(4) | | |

**Table S5.** Selected Bond Distances (Å) and Angles (deg) of **$Cu_2(\mu\text{-}I)_2(\mu\text{-}dppy)(dppy)_2$(3b)**

| | | | |
|---|---|---|---|
| bond distances | | | |
| Cu(1)-N(3) | 2.122(5) | Cu(2)-P(3) | 2.260(2) |
| Cu(1)-P(1) | 2.261(2) | Cu(2)-P(2) | 2.264(2) |
| Cu(1)-I(2) | 2.648(2) | Cu(2)-I(1) | 2.689(2) |
| Cu(1)-I(1) | 2.745(1) | Cu(2)-I(2) | 2.695(2) |
| Cu(1)-Cu(2) | 2.796(2) | | |
| angles | | | |
| N(3)-Cu(1)-P(1) | 117.6(2) | C(1)-P(1)-C(6) | 102.8(3) |
| N(3)-Cu(1)-I(2) | 113.9(2) | C(12)-P(1)-C(6) | 100.4(3) |
| P(1)-Cu(1)-I(2) | 108.6(6) | C(1)-P(1)-Cu(1) | 117.2(2) |
| N(3)-Cu(1)-I(1) | 100.2(2) | C(12)-P(1)-Cu(1) | 115.8(2) |
| P(1)-Cu(1)-I(1) | 108.4(6) | C(6)-P(1)-Cu(1) | 114.4(2) |
| I(2)-Cu(1)-I(1) | 107.3(4) | C(29)-P(2)-Cu(2) | 111.4(2) |
| N(3)-Cu(1)-Cu(2) | 90.96(2) | C(23)-P(2)-Cu(2) | 117.0(2) |
| P(1)-Cu(1)-Cu(2) | 151.06(6) | C(18)-P(2)-Cu(2) | 115.6(2) |
| I(2)-Cu(1)-Cu(2) | 59.27(4) | C(35)-P(3)-Cu(2) | 116.1(2) |
| I(1)-Cu(1)-Cu(2) | 58.06(4) | C(41)-P(3)-Cu(2) | 116.7(2) |
| P(3)-Cu(2)-P(2) | 120.81(7) | C(47)-P(3)-Cu(2) | 113.7(2) |
| P(3)-Cu(2)-I(1) | 105.93(6) | P(2)-Cu(2)-Cu(1) | 152.22(6) |
| P(2)-Cu(2)-I(1) | 109.95(7) | I(1)-Cu(2)-Cu(1) | 60.03(4) |
| P(3)-Cu(2)-I(2) | 103.71(6) | I(2)-Cu(2)-Cu(1) | 57.63(4) |
| P(2)-Cu(2)-I(2) | 108.10(6) | Cu(2)-I(1)-Cu(1) | 61.91(4) |
| I(1)-Cu(2)-I(2) | 107.57(4) | Cu(1)-I(2)-Cu(2) | 63.10(3) |
| P(3)-Cu(2)-Cu(1) | 86.80(6) | | |


experimental 1a
simulated 1a
Intensity
10
20
30
40
50
60
2 Theta(Deg.)


experimental 2a
simulated 2a
Intensity
10
20
30
40
50
60
2 Theta(Deg.)

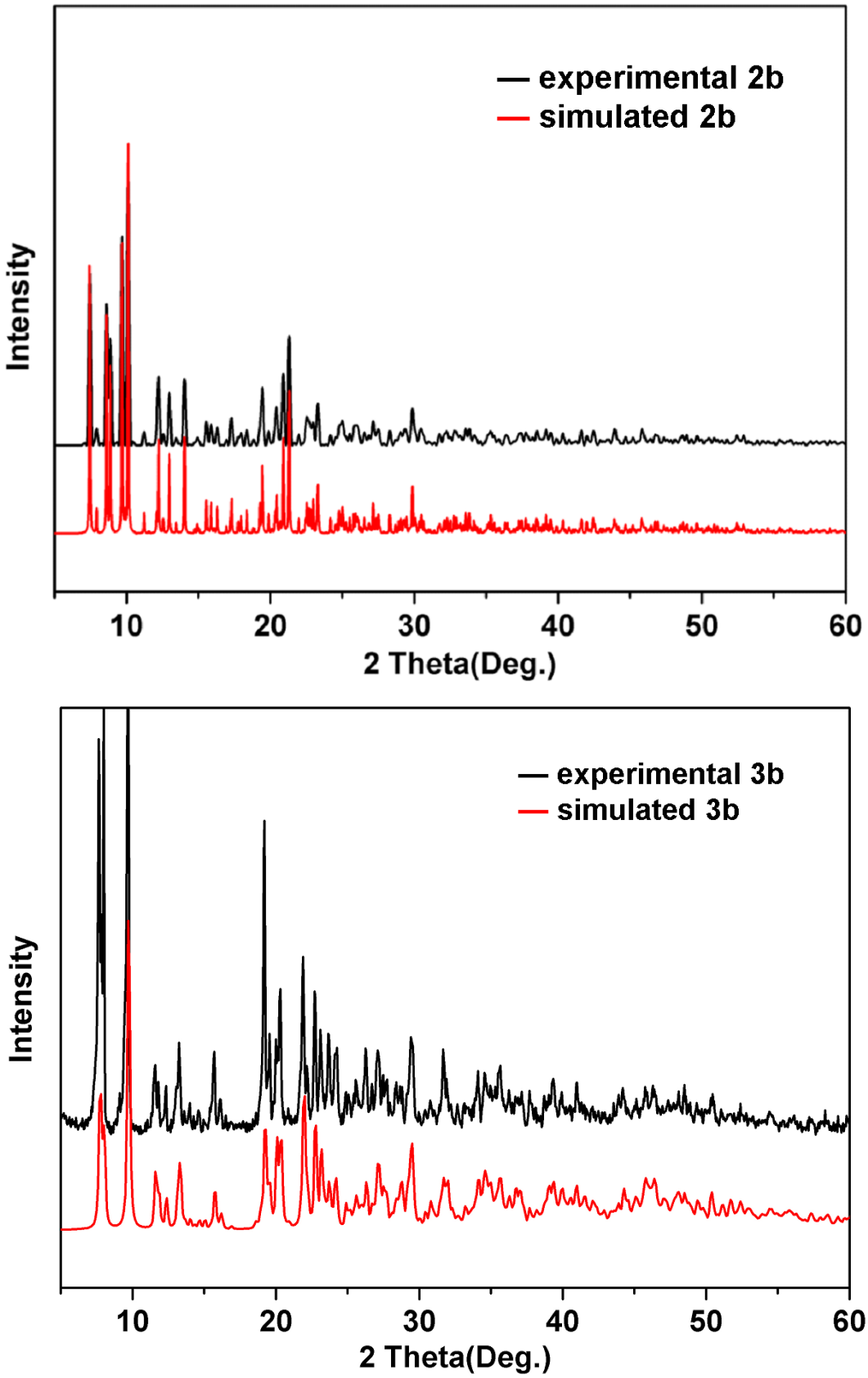



**Fig. S1** Powder X-ray diffractions for simulated and experimental **1a-3b**.

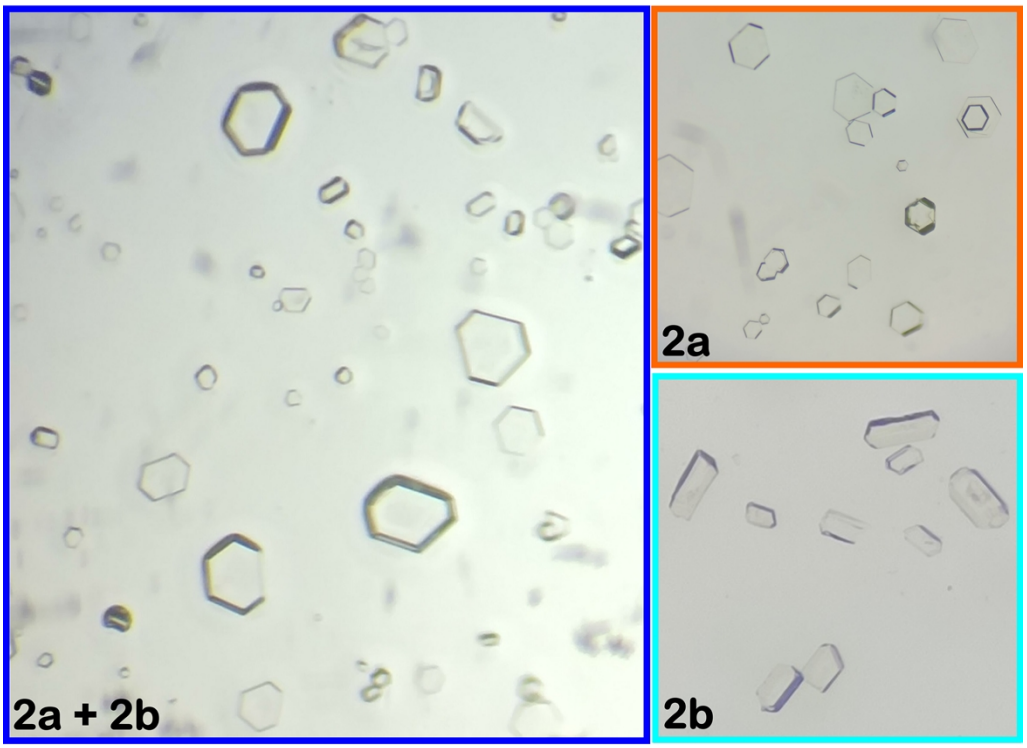



**Fig. S2**. one-pot synthesized rod crystal **2a** and hexagonal crystal **2b (**in the blue box); purified and separated crystal **2a (**in the orange box); purified and separated crystal **2b (**in the turquoise box).