Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Mechanochemical route toward rational, systematic, and cost-effective green synthesis of strongly luminescent copper iodide based hybrid phosphors

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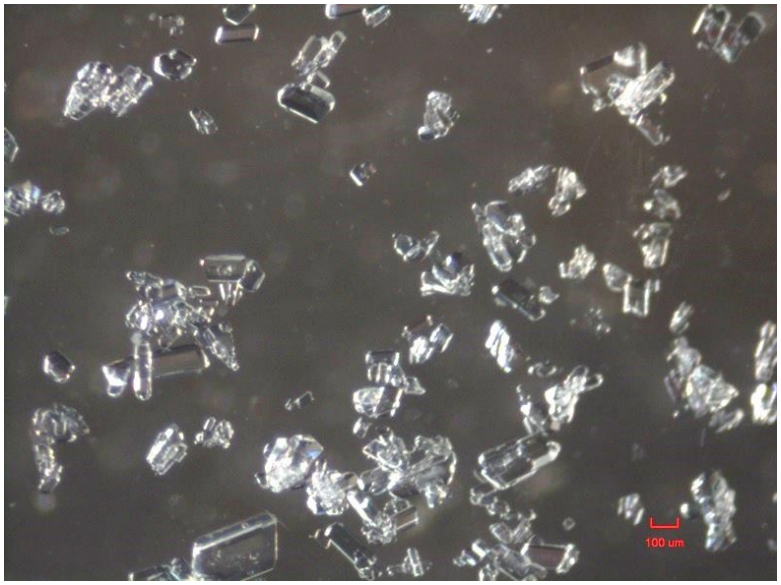


Fig. S1. Crystal image of 0D-CuI(*tpp*)$_2$(*4-me-pm*).

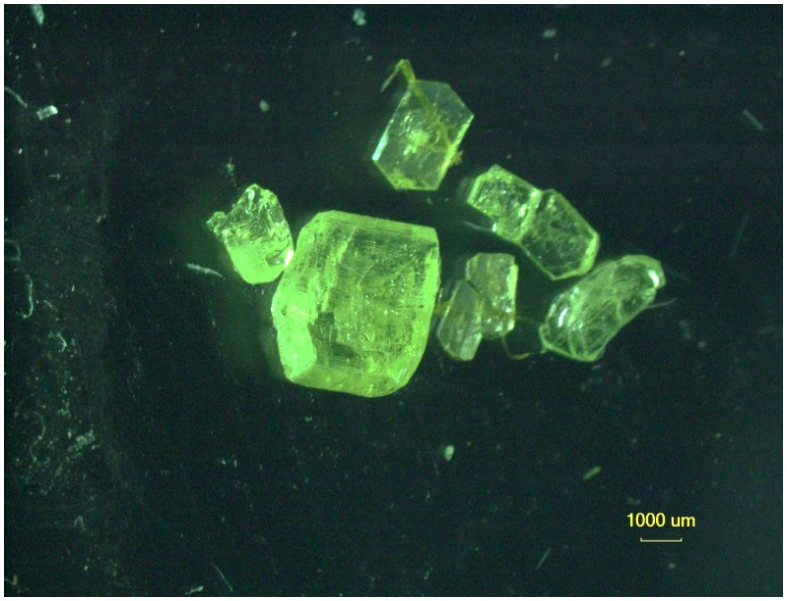


Fig. S2. Crystal image of 0D-Cu_2I_2(*tpp*)$_2$(*3-Br-py*)$_2$

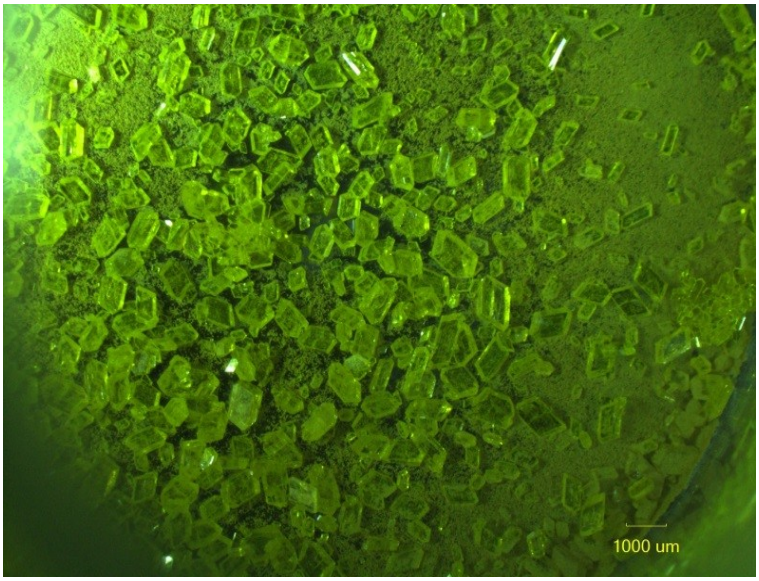


Fig. S3. Crystal image of 1D-Cu_2I_2(*tpp*)$_2$(*2,5-dm-pz*).

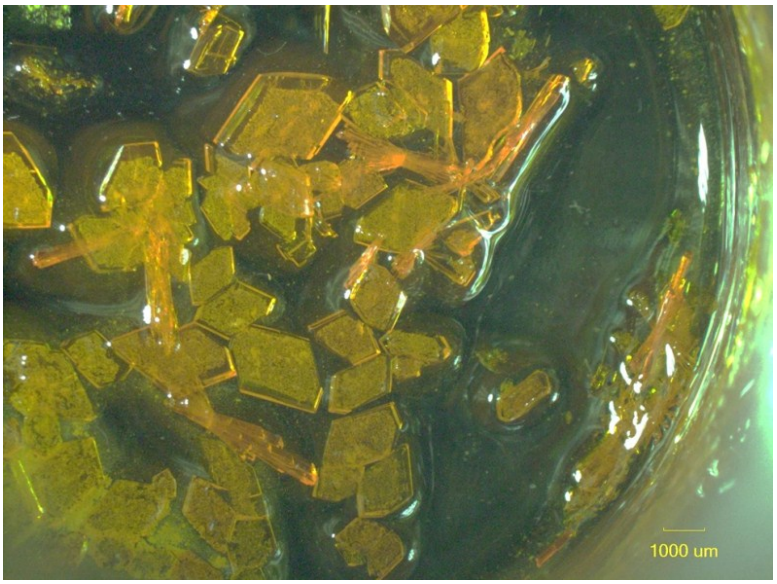


Fig. S4. Crystal image of 1D-Cu_2I_2(tpp)$_2$(*2-me-pz*).

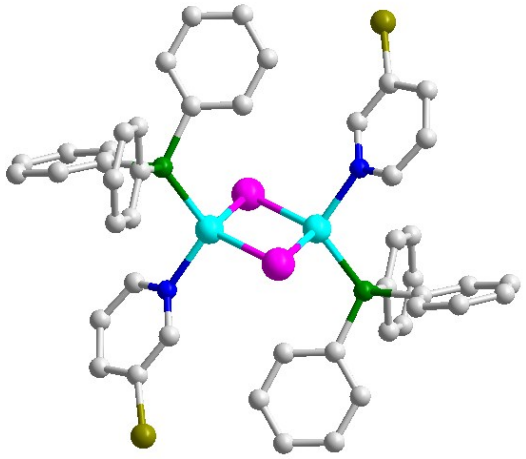


Fig. S5. Structure plot of 0D-CuI(*tpp*)$_2$(*3-Br-py*)$_2$.

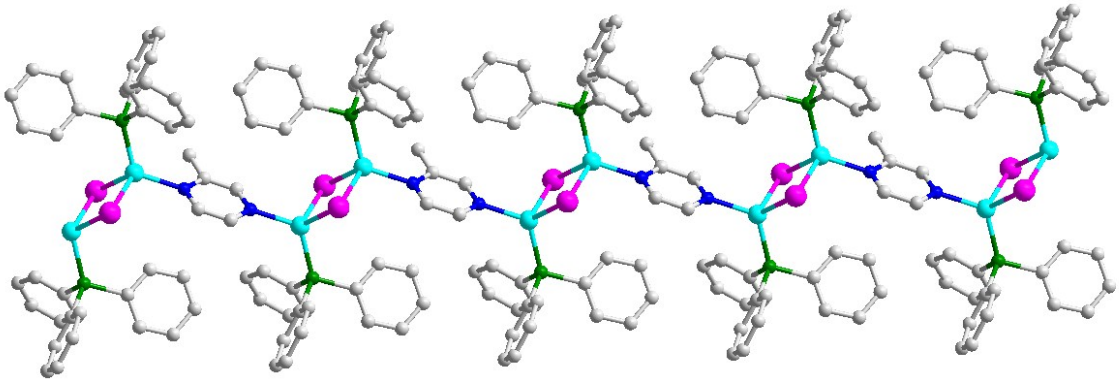


Fig. S6. Structure plot of 1D-Cu_2I_2(*tpp*)$_2$(*2-me-pz*).

S2. PXRD analysis of compounds 1-11.

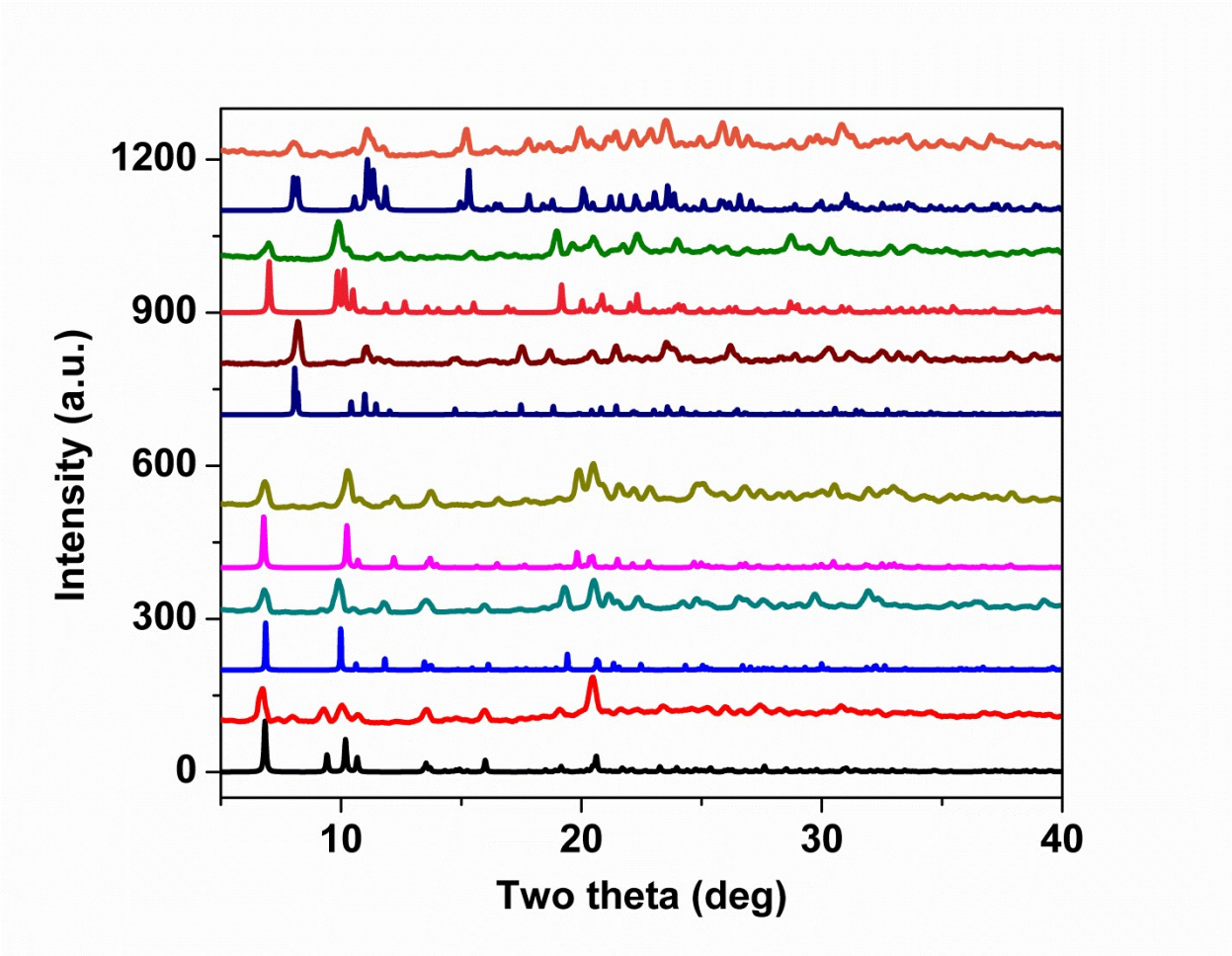


Fig. S7. PXRD patterns of **1**-**6**. From bottom to top: simulated **1**, as made **1**, simulated **2**, as made **2**, simulated **3**, as made **3**, simulated **4**, as made **4**, simulated **5**, as made **5**, simulated **6**, as made **6**.

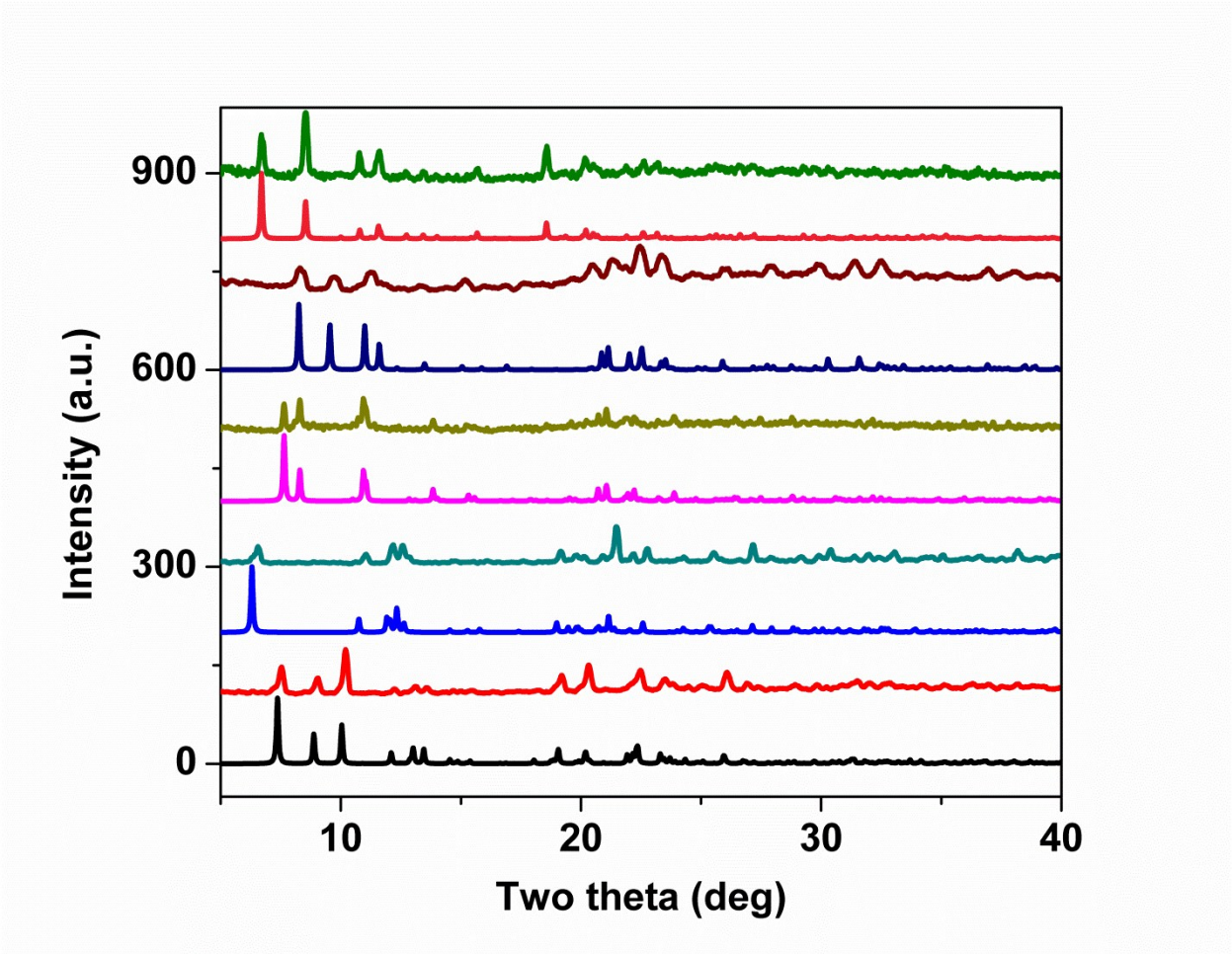


Fig. S8. PXRD patterns of **7**-**11**. From bottom to top: simulated **7**, as made **7**, simulated **8**, as made **8**, simulated **9**, as made **9**, simulated **10**, as made **10**, simulated **11**, as made **11**.

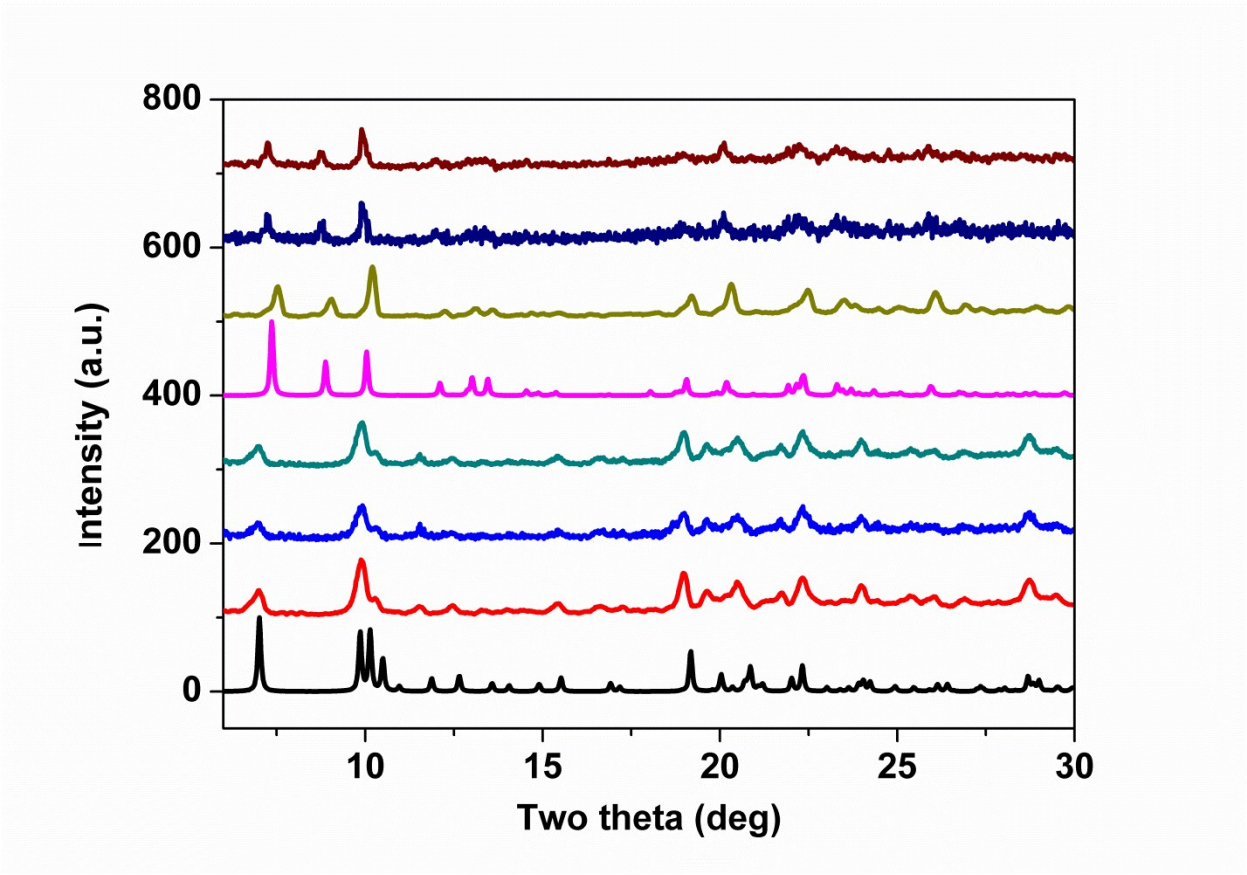
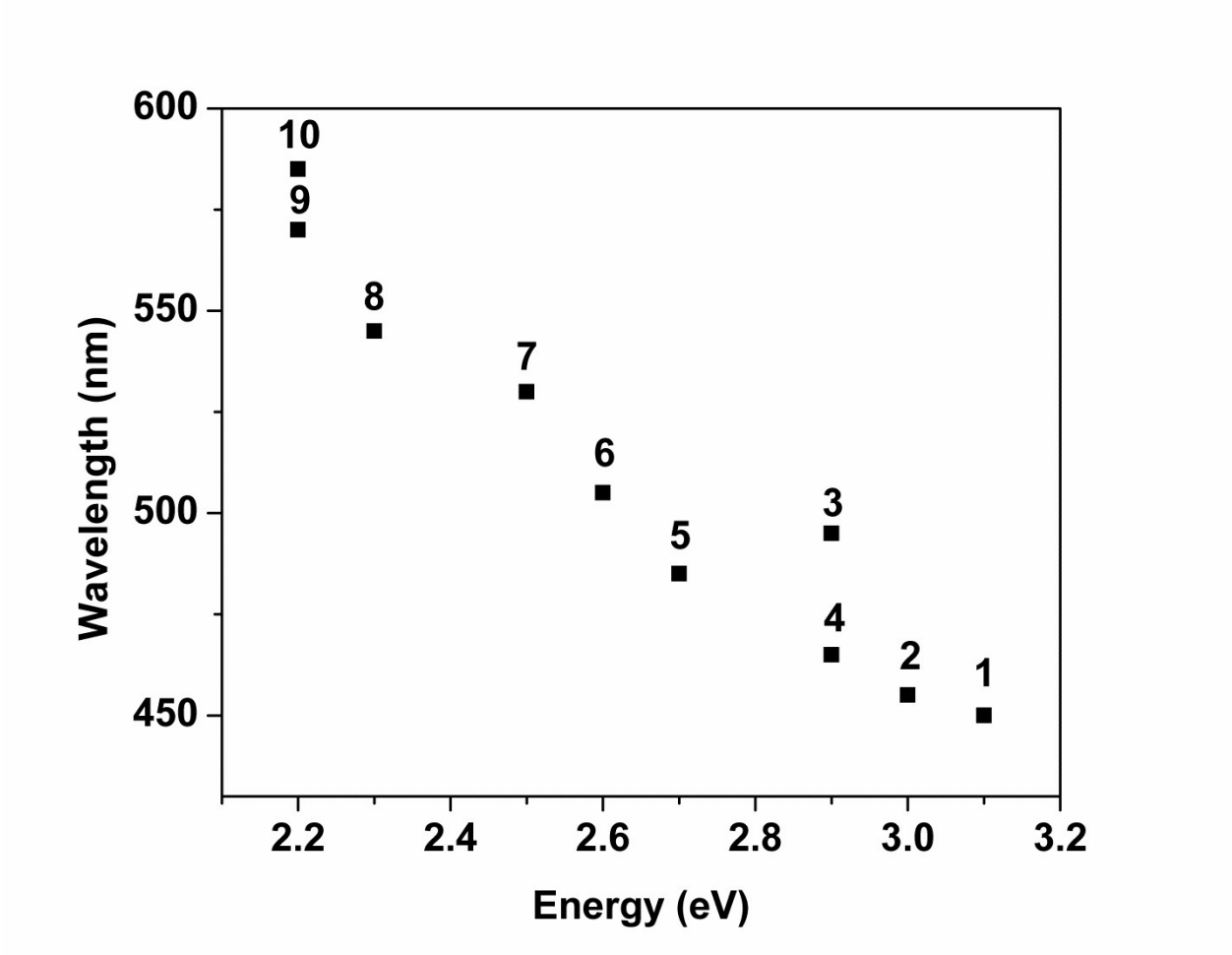


Fig. S9. PXRD patterns. From bottom to top: simulated **5**, as made **5**, **5** after immersed in water for 24 h, **5** after exposed to UV for 24 h, simulated **7**, as made **7**, **7** after immersed in water for 24 h**, 7** after exposed to UV for 24 h,

S3. Optical band gaps, emission energies, IQYs and thermal stability assessment of compounds 1-10.



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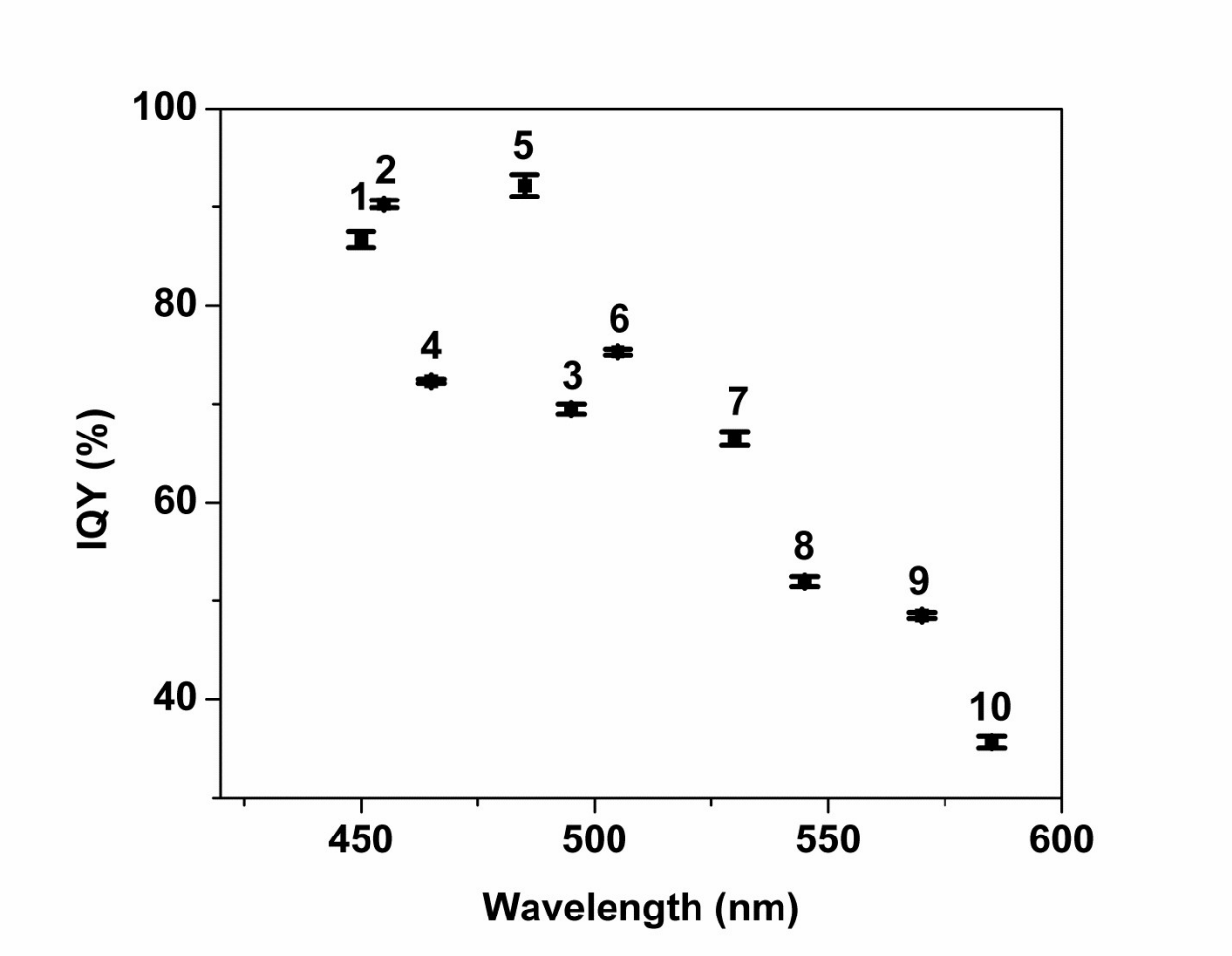


Fig. S11. Emission wavelengths and IQY values of compounds **1**-**10**.

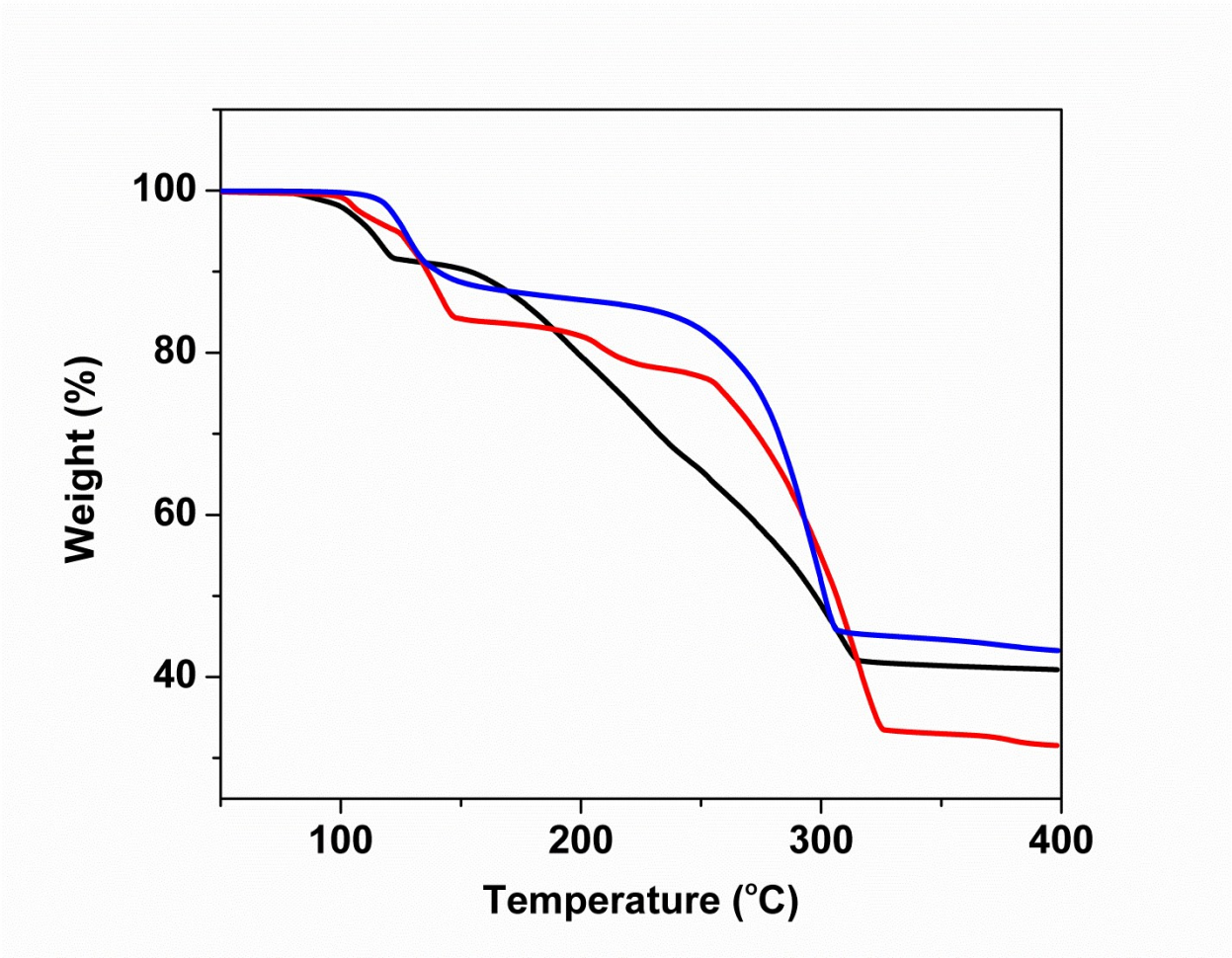


Fig. S12. TG profiles of **2** (blue), **6** (black), **10** (red).

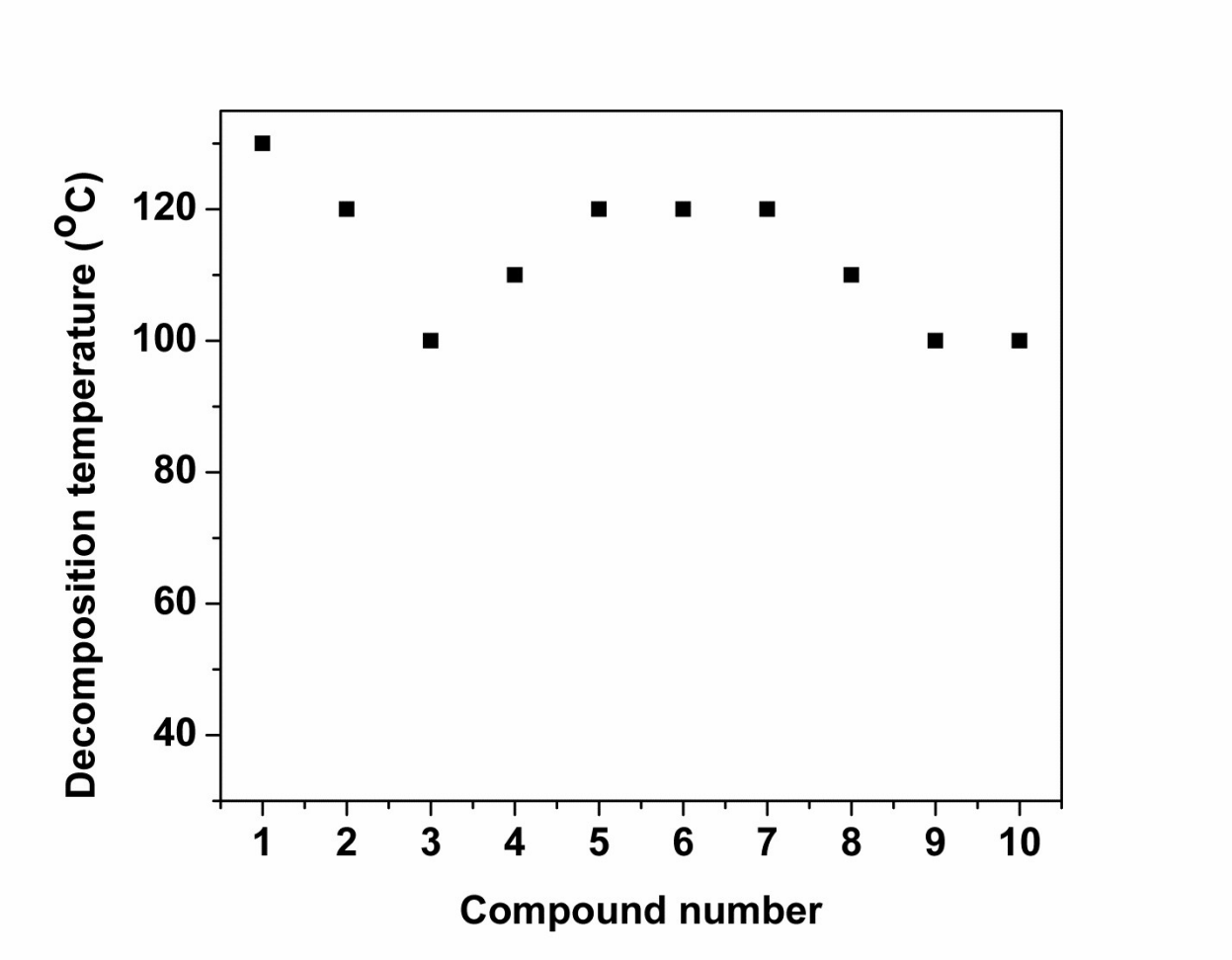


Fig. S13. Thermal decomposition temperatures for **1**-**10**.

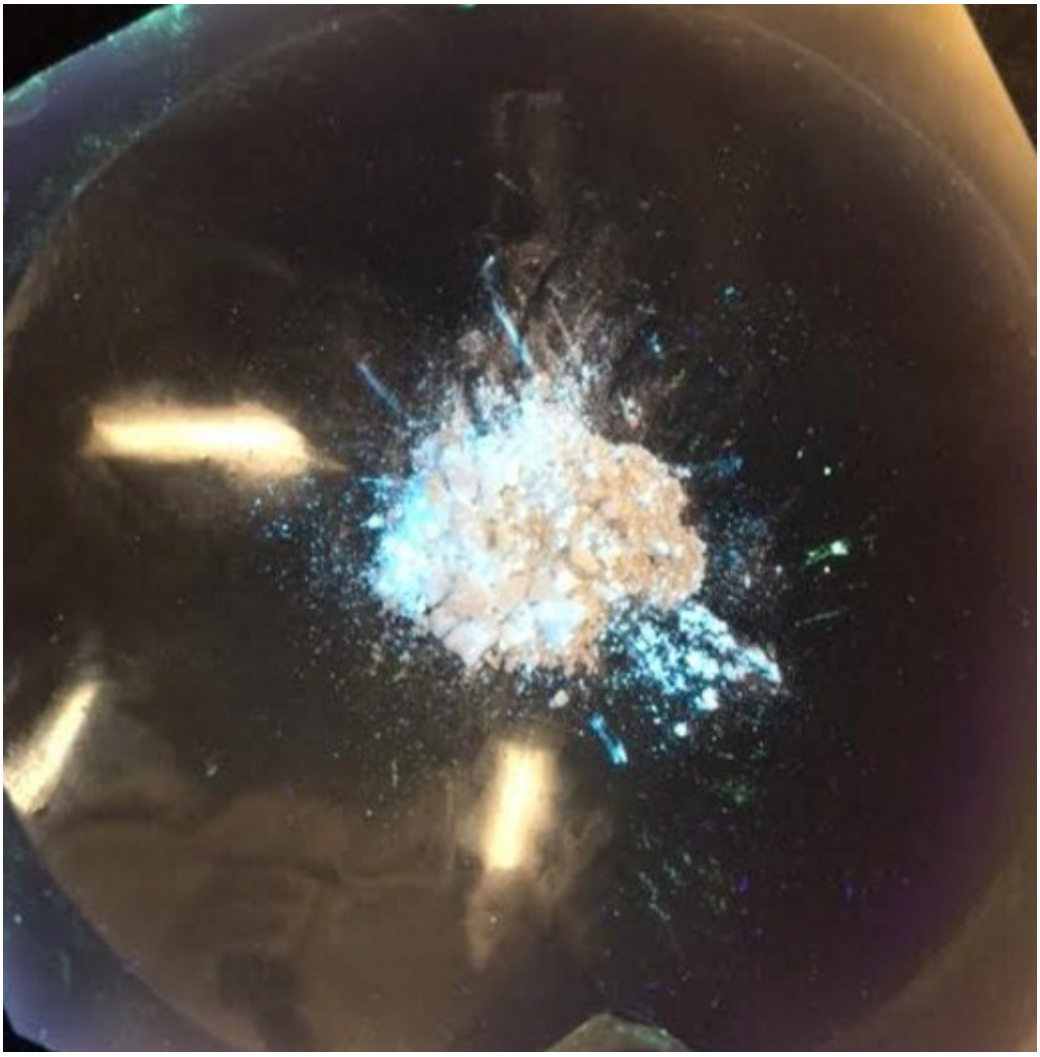


Fig. S14. Mixture of CuI, *tpp* and *4,6-dm-pm* without applying mechanochemical force. Image was taken under UV bar (365nm) after the liquid N-ligand was completely dried.

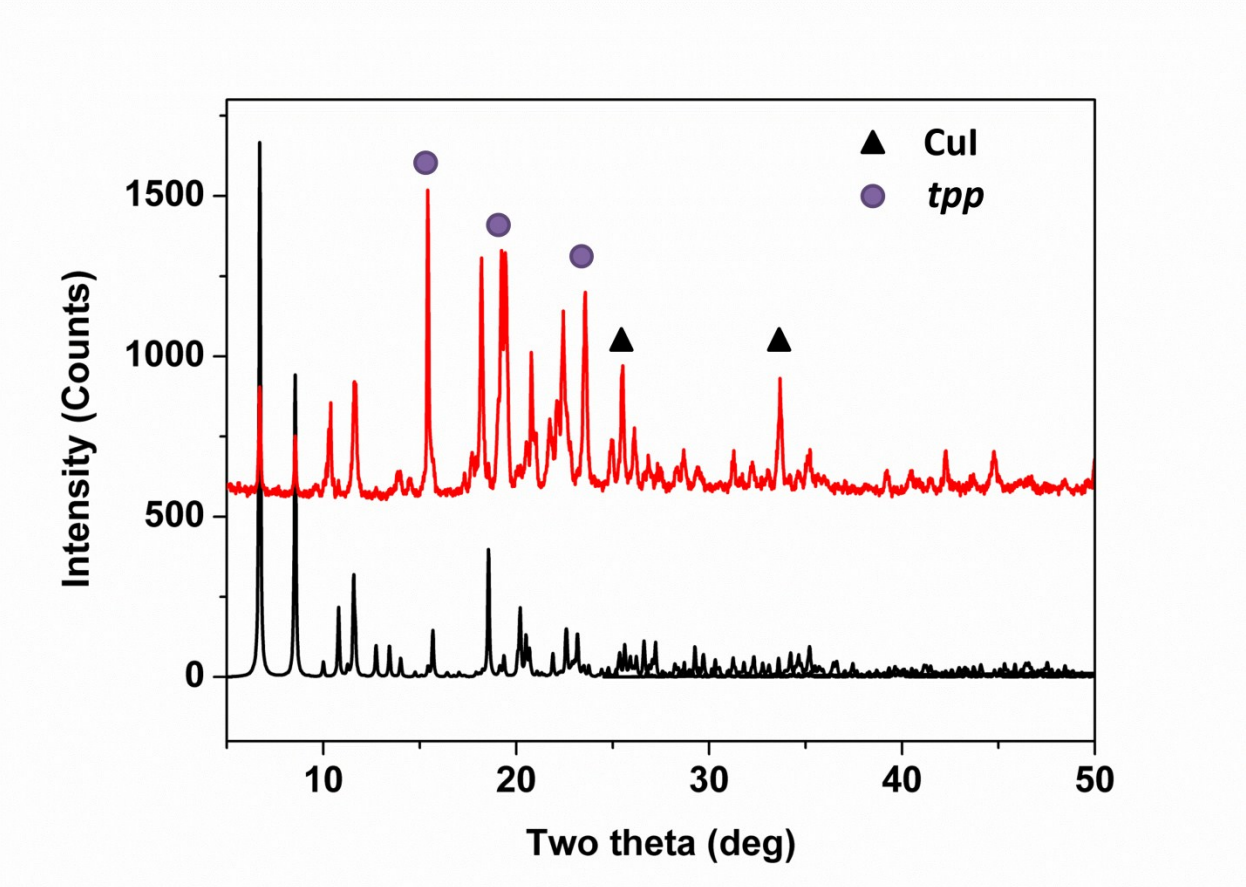


Fig. S15. PXRD patterns of simulated **11** (black) and **11** obtained after (solvent-free) manual grinding for 10 min (red).

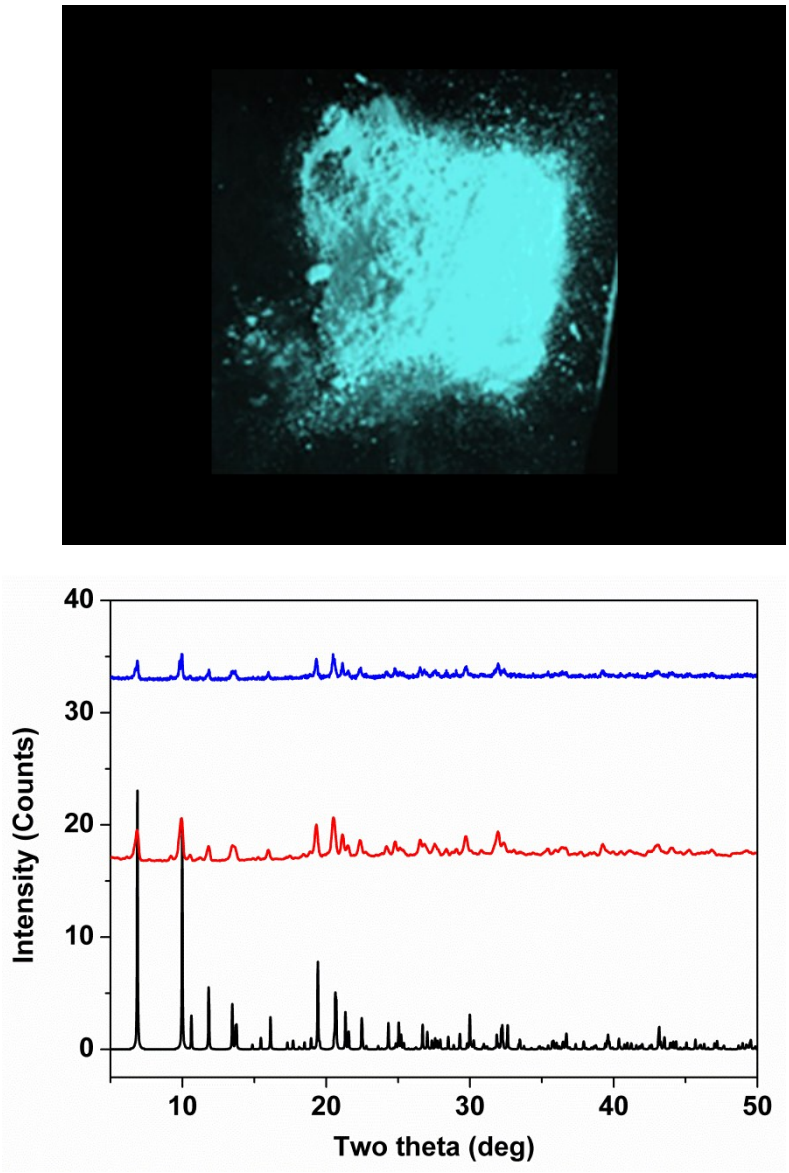


Fig. S16. Top: Product of **2** prepared by ball-milling under UV radiation. Bottom: PXRD patterns of **2**, from bottom to top: simulated pattern, sample prepared by manual grinding, and sample prepared by ball milling.

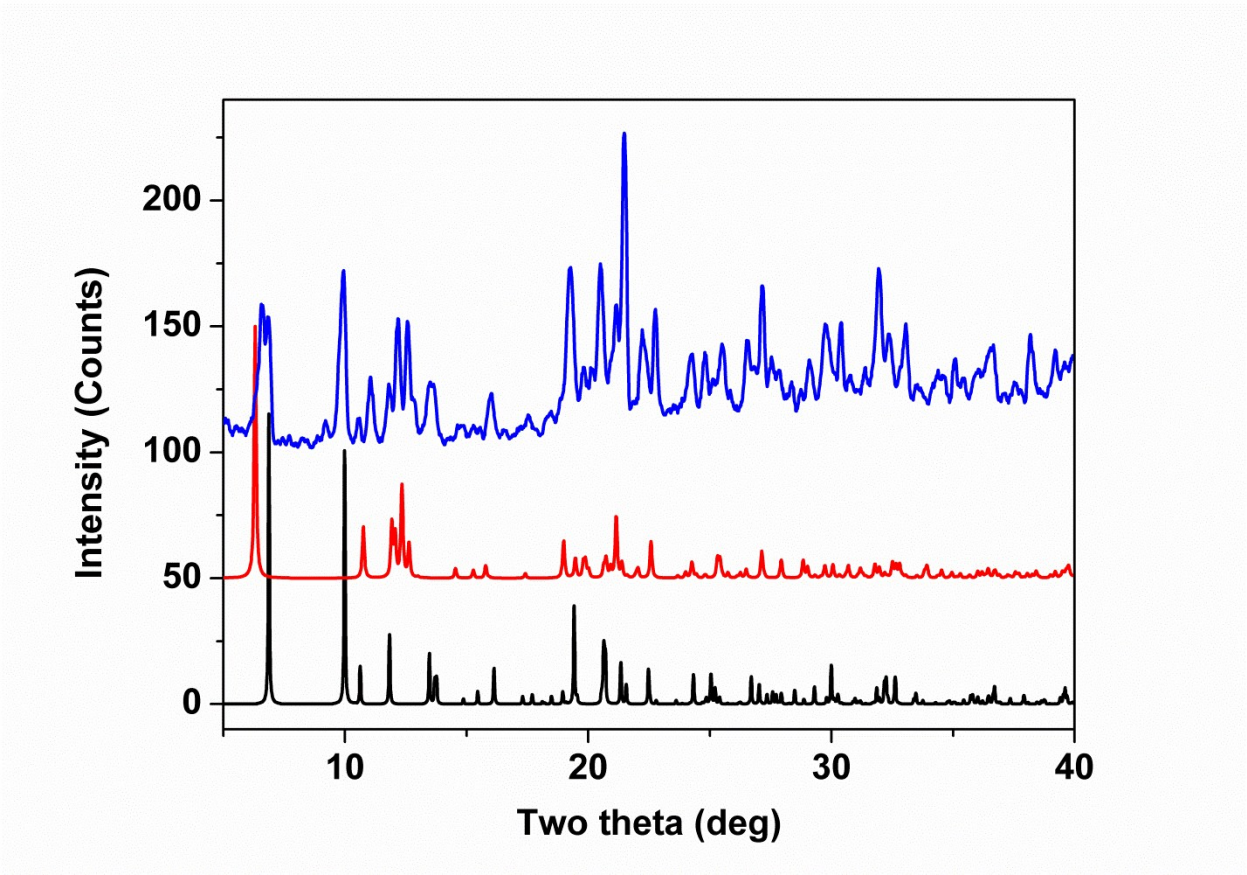


Fig. S17. PXRD pattern of simulated **2** (black), simulated **8** (red) and white phosphor composite **12** (blue).

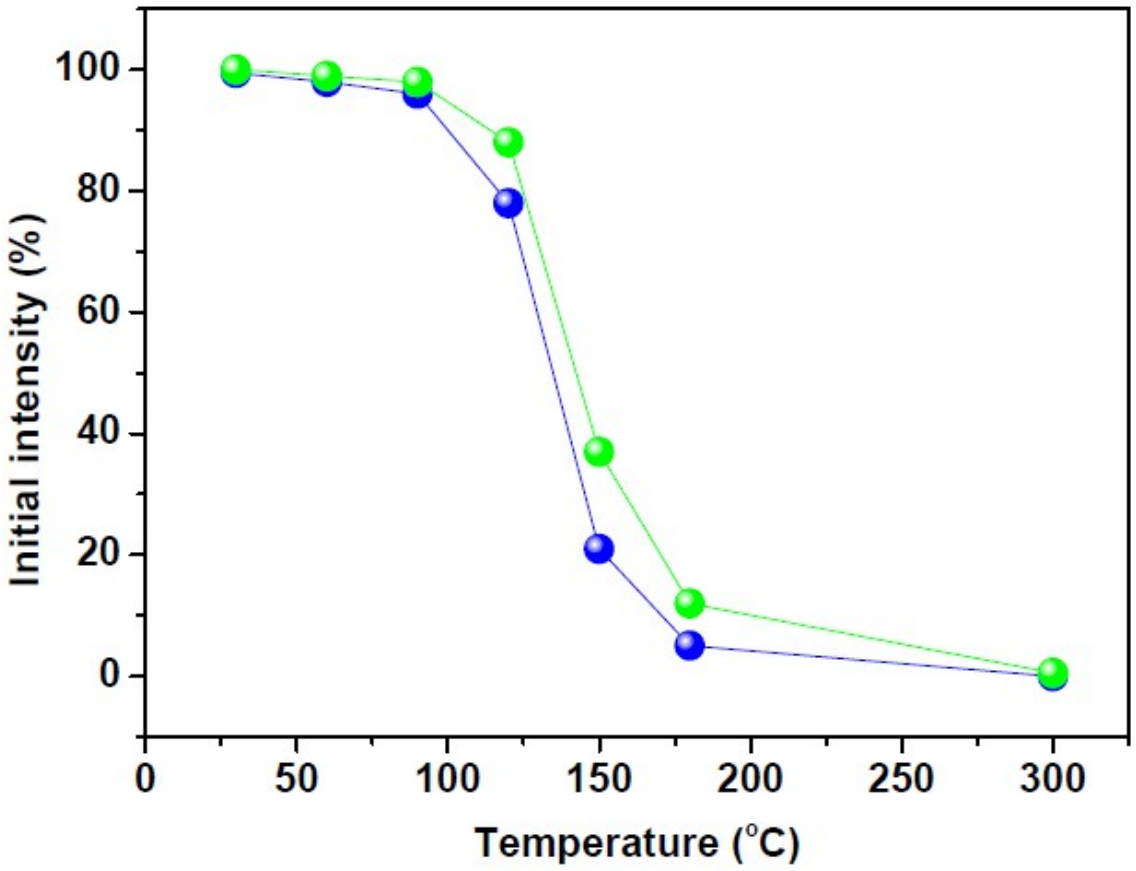
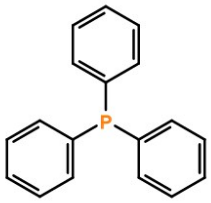
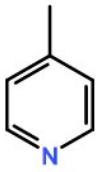
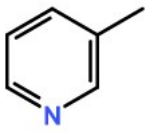
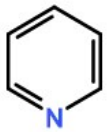
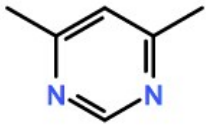


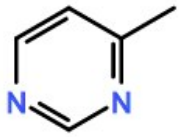
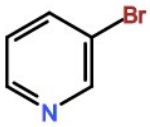
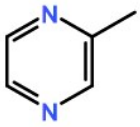
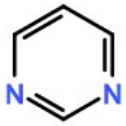
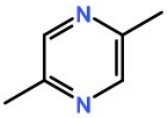
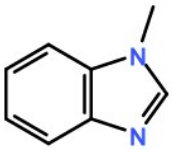
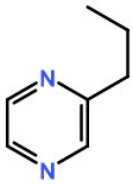
Fig. S18. Photoluminescence intensity as a function of temperature for selected compounds. Each point represents measured internal quantum yield value after sample being heated at the given temperature for some time. Blue: 0D-Cu_2I_2(*tpp*)$_2$(*3-pc*)$_2$, Green: 1D-Cu_2I_2(*tpp*)$_2$(*pm*).

S4. Molecular orbital (MO) energy calculations of the ligands and Density of States (DOS) calculation of selective structure

DGDZVP[1,2] and 6-311++G(3df,3pd)[3-10] were used for the calculation of the HUMO/LUMO energies of the ligands and the results are listed in Table S1.

Table S1. Calculated HOMO-LUMO energy levels of ligands.

Basis Set		DGDZVP		6-311++G(3df,3pd)	
Name	Structure	HOMO (eV)	LUMO (eV)	HOMO (eV)	LUMO (eV)
Triphenylphosphine (*tpp*)		-5.962	-0.874	-6.032	-0.985
4-picoline (*4-pc*)		-7.089	-0.872	-7.117	-0.965
3-picoline (*3-pc*)		-7.056	-0.982	-7.089	-1.073
pyridine (*py*)		-7.175	-1.041	-7.213	-1.120
4,6-dimethyl-pyridimine (*4,6-dm-pm*)		-7.001	-1.208	-7.021	-1.257

4-methyl-pyrimidine (*4-me-pm*)		-7.112	-1.381	-7.128	-1.429
3-bromo-pyridine (*3-Br-py*)		--7.228	-1.441	-7.264	-1.492
2-methyl-pyrazine (*2-me-pz*)		-6.971	-1.668	-6.988	-1.726
Pyrimidine (*pm*)		-7.237	-1.549	-7.255	-1.599
2,5-dimethyl-pyrazine (*2,5-dm-pz*)		-6.830	-1.560	-6.868	-1.583
1-methyl-benzimidazole (*1-me-bzim*)		-6.249	-0.739	-6.260	-0.771
2-propyl-pyrazine (*2-pr-pz*)		-6.925	-1.623	-6.945	-1.683

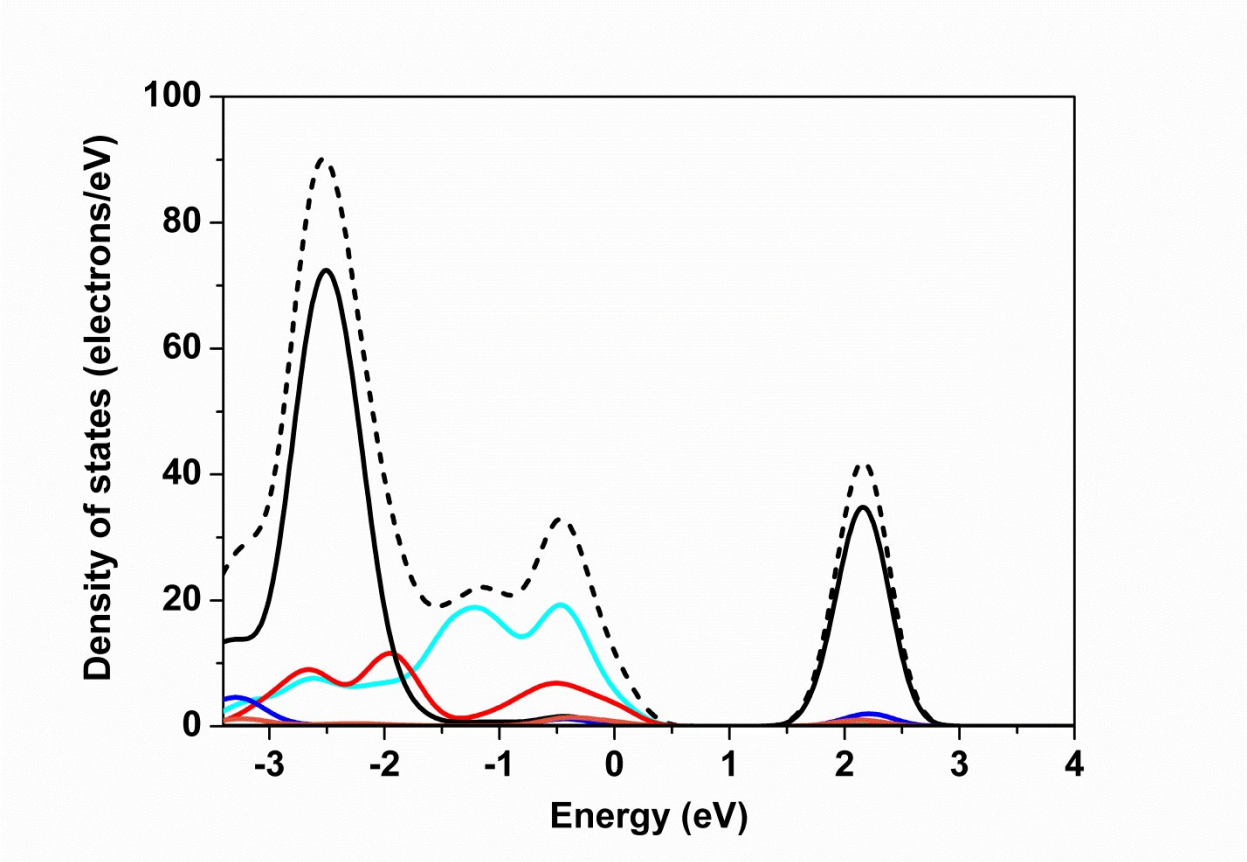


Fig. S19. Calculated density of states (DOS) of **2** by DFT method: total DOS (dotted black); Cu 3d orbitals (light blue); I 5p orbitals (red); C 2p orbitals (black); N 2p orbitals (blue); P 3p orbitals (orange).

S5. Elemental analysis results of selected compounds.

Table S2. Summary of elemental analysis of compounds **1-10**.

Compound		C%	H%	N%
0D-Cu_2I_2(*tpp*)$_2$(*4-pc*)$_2$	Calculated	52.7	4.0	2.6
	Experimental	52.6	3.8	2.5
0D-Cu_2I_2(*tpp*)$_2$(*3-pc*)$_2$	Calculated	52.7	4.0	2.6
	Experimental	54.3	3.4	2.2
0D-Cu_2I_2(*tpp*)$_2$(*py*)$_2$	Calculated	51.9	3.8	2.6
	Experimental	52.4	3.7	3.0
0D-Cu_2I_2(*tpp*)$_2$(*4,6-dm-pm*)$_2$	Calculated	51.4	4.1	5.0
	Experimental	48.6	4.1	5.2
0D-Cu_2I_2(*tpp*)$_2$(*4-me-pm*)$_4$	Calculated	50.3	3.8	5.1
	Experimental	49.8	3.9	3.7
0D-Cu_2I_2(*tpp*)$_2$(*3-Br-py*)$_2$	Calculated	45.2	3.1	2.3
	Experimental	45.7	3.7	1.7
1D-Cu_2I_2(*tpp*)$_2$(*pm*)	Calculated	48.7	3.4	2.8
	Experimental	51.9	3.2	2.7
1D-Cu_2I_2(*tpp*)$_2$(*2,5-dm-pz*)	Calculated	49.7	3.7	2.7
	Experimental	47.0	3.5	2.8
1D-Cu_2I_2(*tpp*)$_2$(*2-pr-pz*)	Calculated	50.9	4.0	2.3
	Experimental	50.4	3.6	2.4
1D-Cu_2I_2(*tpp*)$_2$(*2-me-pz*)	Calculated	51.8	3.8	2.8
	Experimental	51.2	4.1	2.7

S6. References.

(1) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Canadian Journal of Chemistry* **1992**, *70*, 560.

(2) Sosa, C.; Andzelm, J.; Elkin, B. C.; Wimmer, E.; Dobbs, K. D.; Dixon, D. A. *The Journal of Physical Chemistry* **1992**, *96*, 6630.

(3) Gordon, M. S. *Chemical Physics Letters* **1980**, *76*, 163.

(4) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *The Journal of Chemical Physics* **1982**, *77*, 3654.

(5) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. *Journal of Computational Chemistry* **1983**, *4*, 294.

(6) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *The Journal of Chemical Physics* **1984**, *80*, 3265.

(7) Binning, R. C.; Curtiss, L. A. *Journal of Computational Chemistry* **1990**, *11*, 1206.

(8) Blaudeau, J.-P.; McGrath, M. P.; Curtiss, L. A.; Radom, L. *The Journal of Chemical Physics* **1997**, *107*, 5016.

(9) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. *The Journal of Chemical Physics* **1998**, *109*, 1223.

(10) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *The Journal of Chemical Physics* **1972**, *56*, 2257.