Strongly luminescent inorganic-organic hybrid semiconductors with tunable white light emissions by doping

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Supporting Information

- S1. Synthesis detail, crystal images and crystal structures
- S2. TG profiles and DFT calculation results
- S3. Optical analyses
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S1. Synthesis detail, crystal images and crystal structures

Various approaches have been developed for the syntheses of copper halide based structures and as far as we know, layered method is the most ideal one for the synthesis of staircase chain based structures. Various py derivatives with different functional groups were used in the syntheses for compounds **1-4**. Slow mixing of CuBr in saturated KBr solution with the ligands in ethanol at room temperature would quickly form the powder products. To slow down the reaction process for fine crystal growth, a third solvent acetonitrile was used between the above two solutions. It is worth mentioning that the amount of ligands added has notable influence on the final product. Staircase based structures would be formed preferably in ligand deficient conditions, so ligands must be added slowly into the CuBr solution in order to avoid the formation of other types of structures. Adding the ligand quickly or in excess amount might lead to the formation of Cu₂Br₂ dimer based structures, such as compound **5** and **6**.



Figure S1. Illustration of the design strategy of the parent and doped structures.



Figure S2. Layerd approach for growing single crystal of both parent and doped structure (left). Crystals fromed in the middle layer as shown in the photo (right).



Figure S3. White light emissions of the crystals under UV light.



Figure S4. Structural plot of 1D-CuBr(3,5-dm-py) (1).



Figure S5a. Structural plot of 1D-CuBr(*3-Cl-py*) (**3**).



Figure S5b. Structural plot of 2D-CuBr(*pz*)_{0.5.}



Figure S6. Crystal image of 1D-CuBr(*3*,*5-dm-py*) (1).



Figure S7. Crystal image of 1D-CuBr(*3-Cl-py*) (**3**)



Figure S8. Single crystals of 2c emitting white light under UV excitation (360 nm).



Figure S9. PXRD patterns of undoped structures. From bottom to top: simulated 1, as made 1, simulated 2, as made 2, simulated 3, as made 3, simulated 4, as made 4.

Compound	Method	C(%)	H(%)	N(%)
1D-CuBr(<i>3</i> , <i>5-dm-py</i>) (1)	Calculated	33.5	3.6	5.6
	Experimental	33.4	3.5	5.6
1D-CuBr(<i>py</i>)	Calculated	26.9	2.2	6.3
	Experimental	26.7	2.1	6.2
1D-CuBr(3-Cl-py) (3)	Calculated	23.3	1.6	5.4
	Experimental	23.5	1.5	5.5
1D-CuBr(3-Br-py) (4)	Calculated	19.9	1.3	4.6
	Experimental	19.7	1.2	4.5

 Table S1. Summary of elemental analysis of compounds 1-4.

S2. TG profiles and DFT calculation results

The thermogravimetric (TG) analyses were performed on selected compounds. A single-step weight loss profile is found for all these samples. Based on their TG profiles, these structures, including the doped samples, have similar thermal stability and are thermally stable up to approximately 100 °C. The weight loss is due to the loss of ligand molecules, and the experimental weight loss is in agreement with the calculated results. The residues were analyzed to be CuBr.



Figure S10. TG profiles of 2 (black), 4 (red) and 2c (blue).

The BS of 1D-CuBr(py) was calculated by CASTEP package (Materials Studio 5.0). Generalized gradient approximations (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional (xc) were used in all calculations.¹⁻³



Figure S11. Band structure plot of 1D-CuBr(*py*).

DGDZVP^{4,5} and $6-311++G(3df,3pd)^{6-13}$ were used for the calculation of the HUMO/LUMO energy of the ligands and the results are listed in Table S2. There is a correlation between electronic affinity of the functional groups and the energy level, as shown in the table.

Basis Set		DGDZVP		6-311++G(3df,3pd)	
Name	Structure	HOMO	LUMO	HOMO	LUMO (eV)
		(eV)	(eV)	(eV)	
3,5-dimethylpyridine (<i>3,5-dm-py</i>)		-6.869	-0.933	-6.924	-1.039
pyridine (<i>py</i>)		-7.175	-1.041	-7.213	-1.120
3-cloro-pyridine (3-Cl-py)	CI	-7.340	-1.428	-7.361	-1.473
3-bromo-pyridine (3-Br-py)	Br	-7.228	-1.441	-7.264	-1.492
2-ethyl-prazine (2-et-pz)					
		-6.912	-1.632	-6.876	-1.690
2-methyl-prazine (2-me-pz)		-6.971	-1.668	-6.988	-1.726
Pyrazine (<i>pz</i>)	∕ <mark>N</mark> ∖				
		-7.146	-1.857	-7.125	-1.795
2-cloro-prazine (2- <i>Cl-pz</i>)		-7.529	-2.097	-7.467	-2.056

Table S2. Calculated HOMO-LUMO energy levels of ligands.

2-bromo-prazine (2-Br-pz)	R R R R R R R R R R R R R R R R R R R	-7.558	-2.146	-7.575	-2.171
5-bromopyrimidine (5-Br-pm)		-7.550	-1.943	-7.538	-1.970
4-acetyl-pyridine (4-ac-py)		-7.362	-2.406	-7.378	-2.425
4-cyano-pyridine (4-cy-py)		-7.908	-2.437	-7.922	-2.453

S3. Optical analyses

The optical absorption spectra for compounds **1-4** were recorded at room temperature and converted to the Kubelka-Munk function. Their band gaps were estimated by their absorption edges, and are 3.1, 2.8, 2.7 and 2.5 eV, respectively. This trend corresponds with the decreasing LUMO energies of the organic ligands in the structures, which are -1.039, -1.120, -1.473 and - 1.492 eV for *3,5-dm-py, py, 3-Cl-py* and *3-Br-py*, respectively.



Figure S12. Optical absorption of 1 (black), 2 (red), 3 (blue) and 4 (green).



Figure S13. The absorption spectra for doped structures 2a (black), 2c (red), 2f (blue), 2e (green).



Figure S14. Optical absorption of 1% doped 1D-CuBr(py). Inset: optical absorption of 2D-CuBr(pz)_{0.5}.



Figure S15. QY scaled PL spectra of 1 (black), 2 (red), 3 (blue) and 4 (green).

Table S3. Estimated band gaps, emission energies, IQYs, emission color of 1-4.

#	Structure	Band gap (eV)	λ _{em} (nm) (298K)	Emission color	IQYs (%) 360nm
1	1D-CuBr(<i>3</i> , <i>5-dm-py</i>)	3.1	482	Blue	56
2	1D-CuBr(<i>py</i>)	2.8	494	Cyan	48
3	1D-CuBr(<i>3-Cl-py</i>)	2.7	505	Blue-green	27
4	1D-CuBr(<i>3-Br-py</i>)	2.5	514	Green	21

 Table S4. Unit cell data of compound 2c at room temperature and at 150 K.

	а	b	С	α	β	γ
RT	8.8861 (16)	3.9571 (8)	9.3985 (2)	90.0000	107.8154 (17)	90.0000
150 K	8.8659 (9)	3.9176 (3)	9.2461 (7)	90.000	107.774 (14)	90.000



Figure S16. PL spectra of 2c (black), 2f (red) and 2e (blue). $\lambda_{ex} = 360$ nm.



Figure S17. PL spectra of *pm* (black) and *tz* (red) doped 1D-CuBr(*py*). $\lambda_{ex} = 360$ nm.

S4. References

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