

Supporting Information

Stabilization of Copper Iodide Hybrids with Increased Strength of Ionic Bonding for Lighting and X-ray Imaging

Qianqian Wang, Haibo Li,* Jiali Fan, Zhennan Zhou, Hua Tong, Jialin Zhu, Wei Liu* and Gangfeng Ouyang*

School of Chemical Engineering and Technology, Sun Yat-sen University & Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai, 519082, Guangdong, P. R. China

E-mail: lih63@mail.sysu.edu.cn, liuwei96@mail.sysu.edu.cn, cesoygf@mail.sysu.edu.cn

EXPERIMENTAL SECTION

Materials. CuI (>99.5%, Aladdin), triethylenediamine (ted, 98%, Macklin), 1-bromopropane (>99.0%, Macklin), 1-bromobutane (>99.0%, Macklin), 1-bromopentane (>99.0%, Macklin), potassium iodide (99.21%, Bidepharm), methanol (99.5%, Macklin), dimethyl sulfoxide-d₆ (DMSO-d₆, D.99.9% +0.03% TMS, Macklin), acetonitrile (AR, Macklin), polydimethylsiloxane (PDMS, AR, Macklin) and deionized water. All reagents were used as received without further purification.

Preparation of R-ted-R ligands. 10 mmol triethylenediamine (ted, 1.12 g) was dissolved in 5 mL of acetonitrile. Under magnetic stirring, 5 mL acetonitrile solution dissolved with 40 mmol of bromoalkane was dropwise added into the ted acetonitrile solution and stirred for 2 days to obtain the white precipitate. And the reaction solution is then poured out, leaving only the powder product, which is washed with cyclohexane and finally dried under vacuum. All ligands were dissolved in methanol at the concentration of 3 mL methanol/1 mmol ligand and prepared into methanol solution for use.

Synthesis of crystals of compounds 1-3. Single crystals were prepared by a slow diffusion method. In a glass sample bottle, 1 mmol CuI (0.19 g) was dissolved in 5 mL saturated KI solution, and then

2 mL acetonitrile was dropwise added. Finally, 3 mL methanol solution containing the ligand was slowly dribbled into the solution (the ligand dosage was 1 mmol). After a few days, transparent crystals grow out in the bottle, and the crystals emit bright yellow light under the ultraviolet lamp. Scoop out the crystals, and then add a small amount of ethanol to carefully rinse the crystals, and finally dry the crystals under vacuum.

Synthesis of powder of compounds 1-3. The 1 mmol R-*ted*-R ligand was dissolved in 3 mL methanol solution, and then 5 mL saturated KI solution dissolved with 1 mmol CuI was dropped into the solution to immediately produce a large amount of powder, which was illuminated with bright yellow light by 365 nm UV lamp. Then the product was centrifuged and washed with deionized water three times to remove KI in the solution, and then washed with anhydrous ethanol again and dried in vacuum. Finally, the powder was collected and weighed, and the product masses of compounds **1**, **2** and **3** were 168.4 mg, 545 mg and 284 mg, respectively.

LC-MS and ¹H-NMR analyses. Liquid chromatography-mass spectrometry (LC-MS, Thermo Fisher, UltiMate3000 ISQESI) and 600 M nuclear magnetic resonance hydrogen spectrum (¹H-NMR, Bruker Switzerland AG, AVANCE NEO 600) to verify the successful synthesis of the R-*ted* organic ligand and test the purity of the product. Mass spectrometry: All ligands were synthesized into 2 mg/mL methanol solution under direct injection and ESI+ detection mode, and the ion source was Electron Spray Ionization (ESI). ¹H-NMR spectroscopy: 5-10 mg ligand dissolved in 0.5 mL dimethyl sulfoxid-D₆ deuterium.

Microscope images. The crystal micrographs were obtained by using a MIT500 metallographic microscope. The glow micrographs were obtained in the dark under the illumination of a 365 nm ultraviolet LED.

Single-crystal X-ray diffraction (SCXRD). Single crystal data was collected on a Bruker D8 Venture METALJET Ga-Target SC-XRD under test temperature (*T*) of 100 K and radiation wavelength (λ) of 0.71073 Å. The structure was solved by direct method and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL package. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif. The structures of compounds **1-3** are deposited in CCDC with deposition number of 2368508, 2368509 and 23685010, respectively.

Powder X-ray diffraction (PXRD). PXRD data were collected on the Rigaku Ultima IV automated

diffraction system with an X-ray source of 1.54056 Å Cu K α 1 and a power of 40 kV/40 mA (5-50°, 10°/min).

X-ray photoelectron spectroscopy (XPS) tests. The XPS spectra of compounds **1-3** were obtained by an X-ray photoelectron spectrometer (SHIMADZU AXIS SUPRA+).

Optical diffuse reflectance measurements. Optical diffuse reflectance spectrum was measured on the UV-2600 spectrophotometer from Shimadzu using BaSO₄ powder as the reflectivity reference. The optical bandgap was calculated by use of a typical Tauc method by employing the equation: $(\alpha h\nu)^n = A(h\nu - E_g)$, where α , h , ν , A , and E_g are the absorption coefficient, Planck's constant, light frequency, a constant, and band gap. The value of n here is 2 presuming that compounds **1-3** are direct transition semiconductors.

Thermogravimetric (TG) analysis. The TG analysis was performed on the TG analyzer (Netzsch TG 209 F1 Libra R) and was heated from room temperature to 800 °C under nitrogen flow at a rate of 10 °C/min.

Photoluminescence/radioluminescence related measurements. Photoluminescence emission (PL) and excitation (PLE) measurements, radioluminescence (RL), room temperature fluorescence decay curve and photoluminescence quantum yield (PLQY) tests were carried out on FLS1000 spectrofluorometer (Edinburgh Instruments). The fluorescent lifetime excitation source is Edinburgh EPLED-295/365 nm picosecond pulsed diode laser. An X-ray tube (Moxtek, TUB00154-9I-WO6, working condition: 50 kV, 20 μ A) was used to collect the RL spectra, and BGO (Bi₄Ge₃O₁₂ crystal, a known reference material) was used for comparison.

Fabrication of flexible scintillator screens. 0.50 g compound **3** and 1.00 g PDMS were mixed uniformly and then dropped on the glass substrate, and then a thin film with uniform thickness was prepared by spin coating. The spin-coated films can be peeled off the glass substrate after curing at 120 °C overnight.

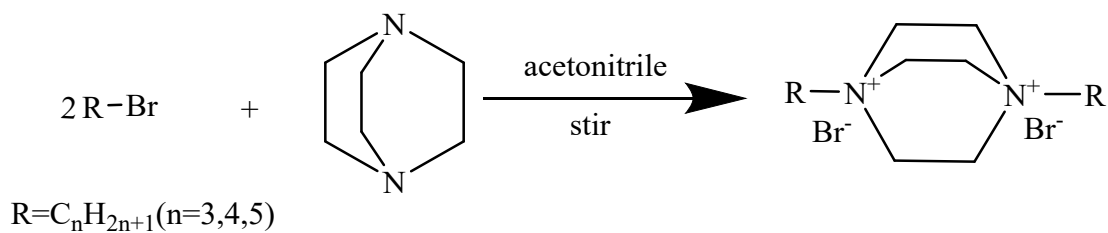


Figure S1. Synthesis of disubstituted ted derivative ligands.

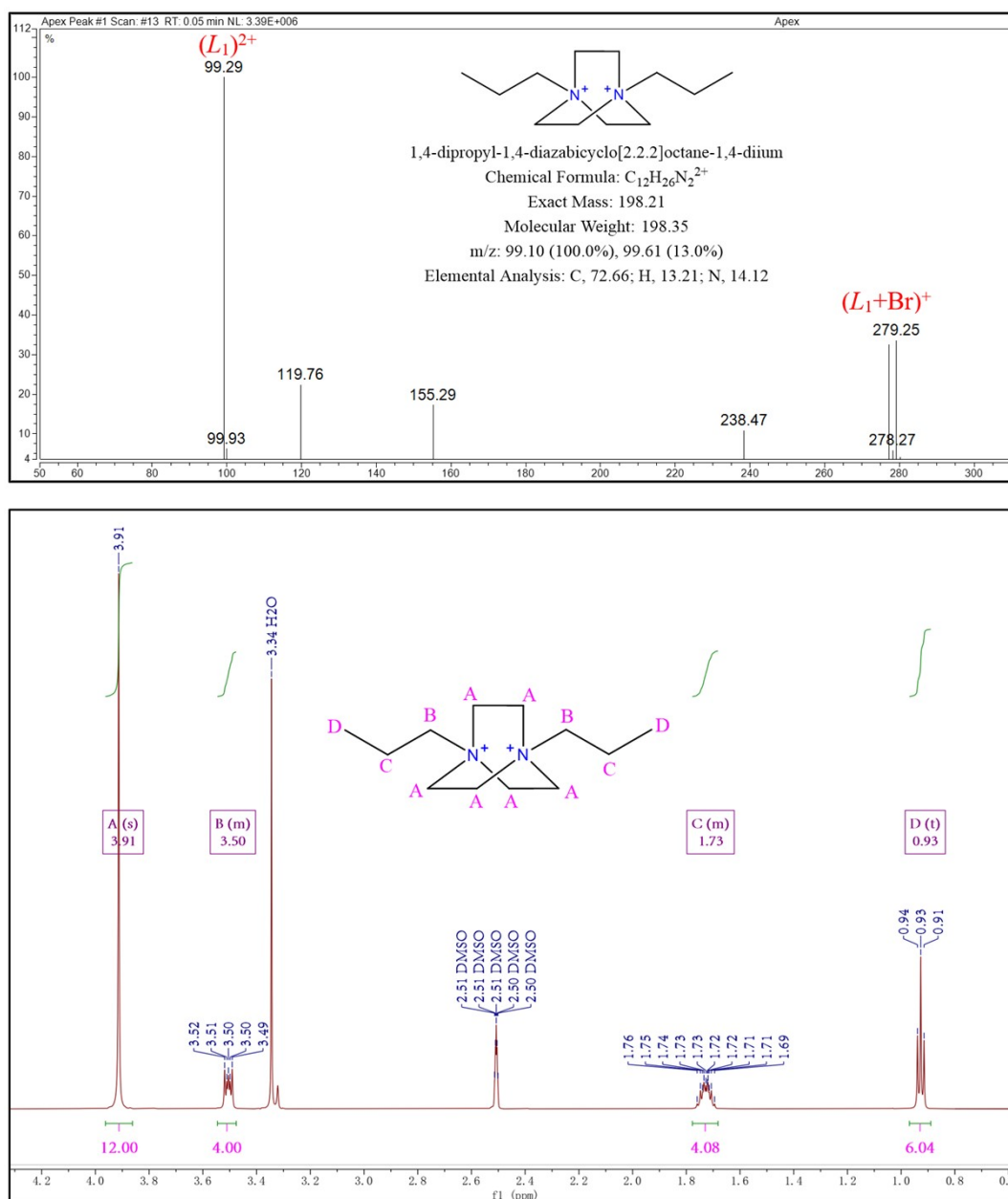


Figure S2. MS (top) and 1H -NMR (bottom) spectra of R-ted-R organic ligand L_1 . The inset is for its molecular structure. 1H NMR (600 MHz, $DMSO-d_6$) δ 3.91 (s, 12H), 3.55 – 3.48 (m, 4H), 1.78 – 1.68 (m, 4H), 0.93 (t, $J = 7.3$ Hz, 6H).

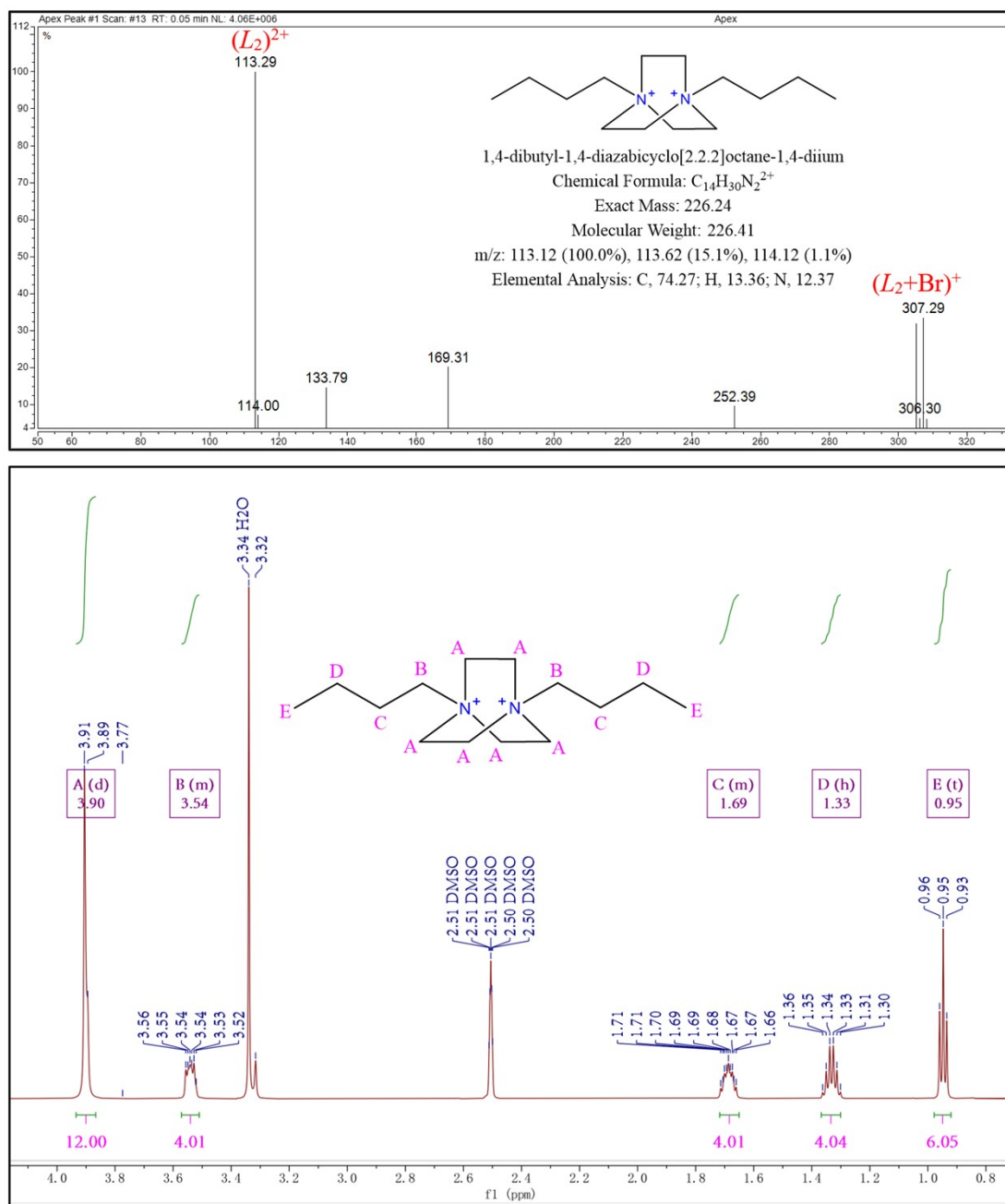


Figure S3. MS (top) and ^1H -NMR (bottom) spectra of R-*ted*-R organic ligand L_2 . The inset is for its molecular structure. ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 3.90 (d, $J = 6.8$ Hz, 12H), 3.57 – 3.51 (m, 4H), 1.73 – 1.65 (m, 4H), 1.33 (h, $J = 7.4$ Hz, 4H), 0.95 (t, $J = 7.4$ Hz, 6H).

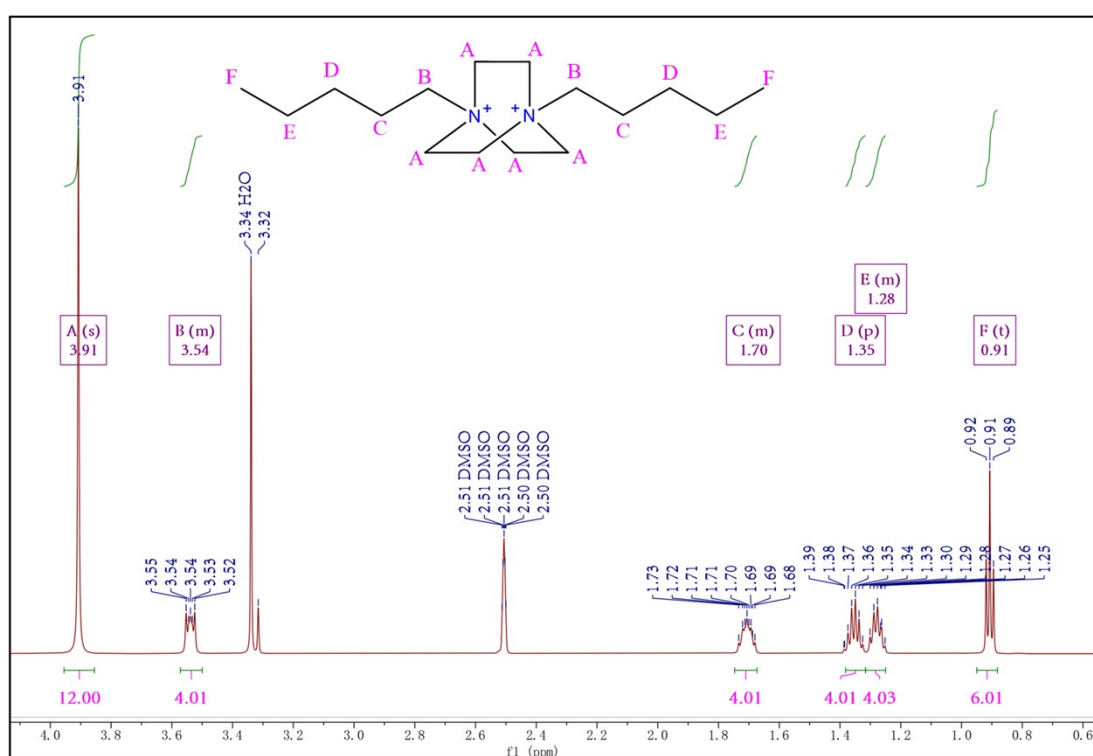
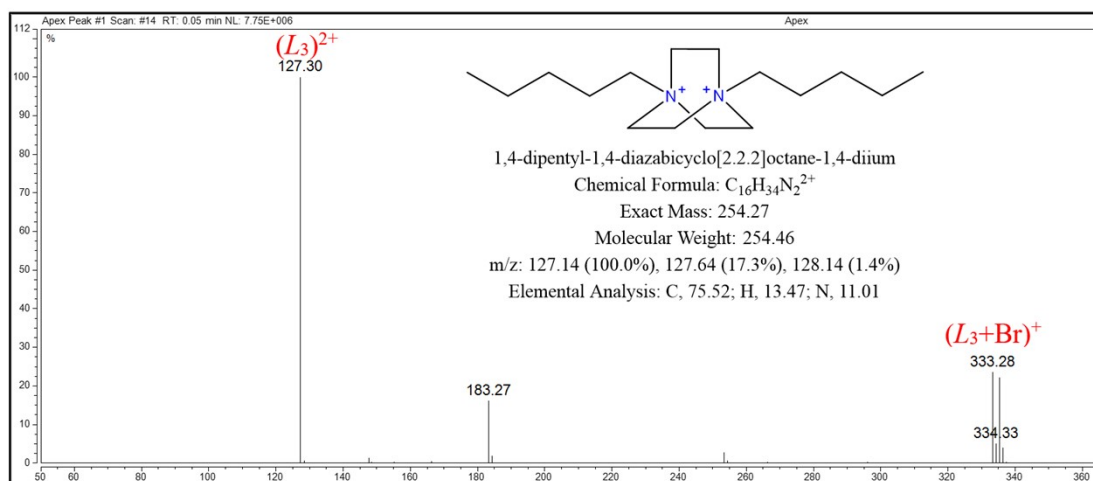


Figure S4. MS (top) and ^1H -NMR (bottom) spectra of R-ted-R organic ligand L_3 . The inset is for its molecular structure. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 3.91 (s, 12H), 3.57 – 3.50 (m, 4H), 1.75 – 1.67 (m, 4H), 1.35 (p, $J = 7.2$ Hz, 4H), 1.32 – 1.25 (m, 4H), 0.91 (t, $J = 7.2$ Hz, 6H).

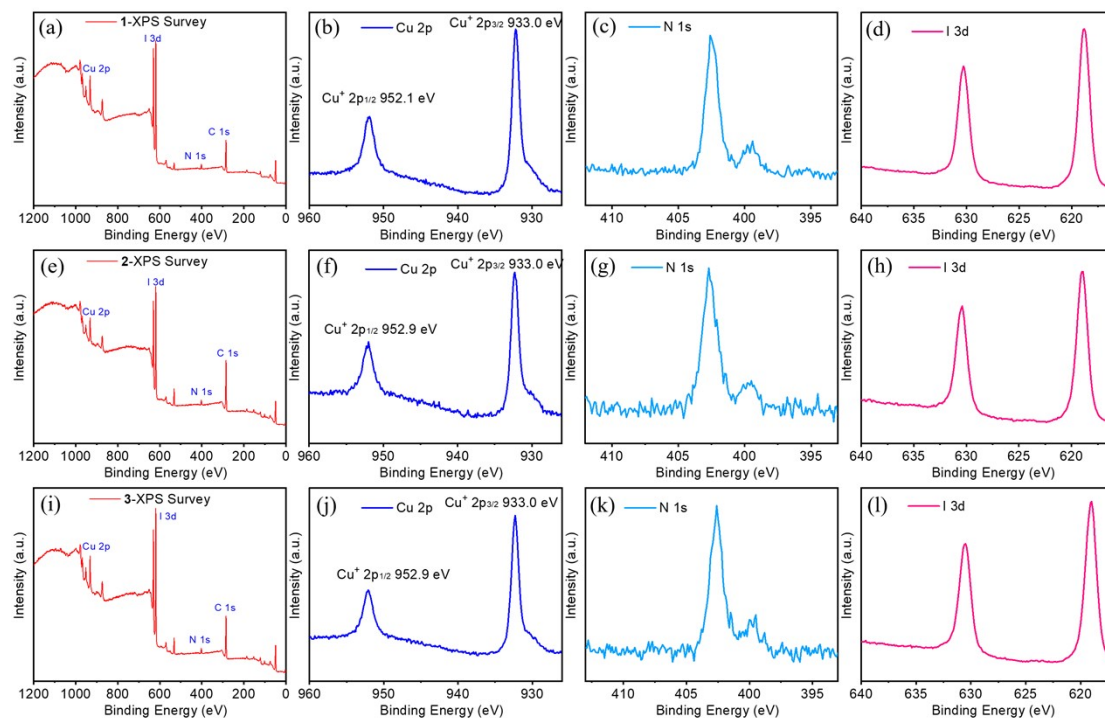


Figure S5. X-ray photoelectron spectroscopy (XPS) survey spectra and high-resolution XPS spectra of Cu 2p, N 1s and I 3d of compounds (a-d) **1**, (e-h) **2** and (i-l) **3**, respectively.

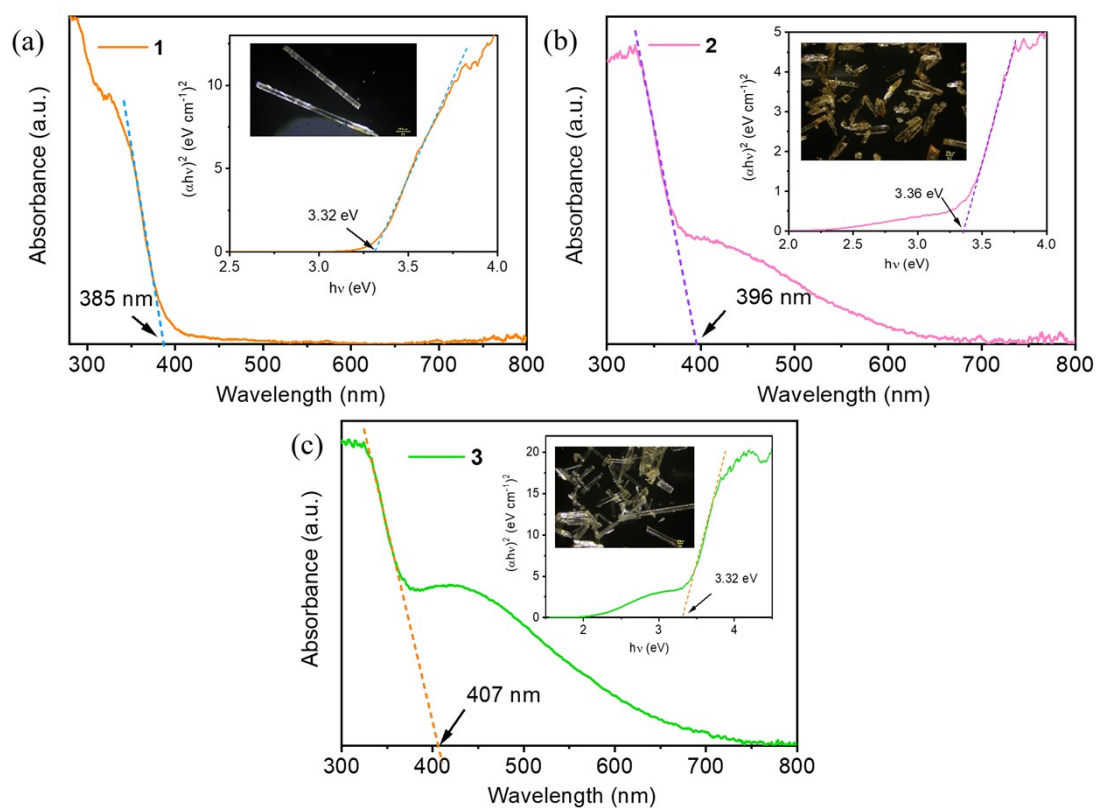


Figure S6. (a-c) UV-Vis diffuse reflectance spectra of compounds **1-3** (insets are Tauc curves and microscope images of crystals under natural light), respectively.

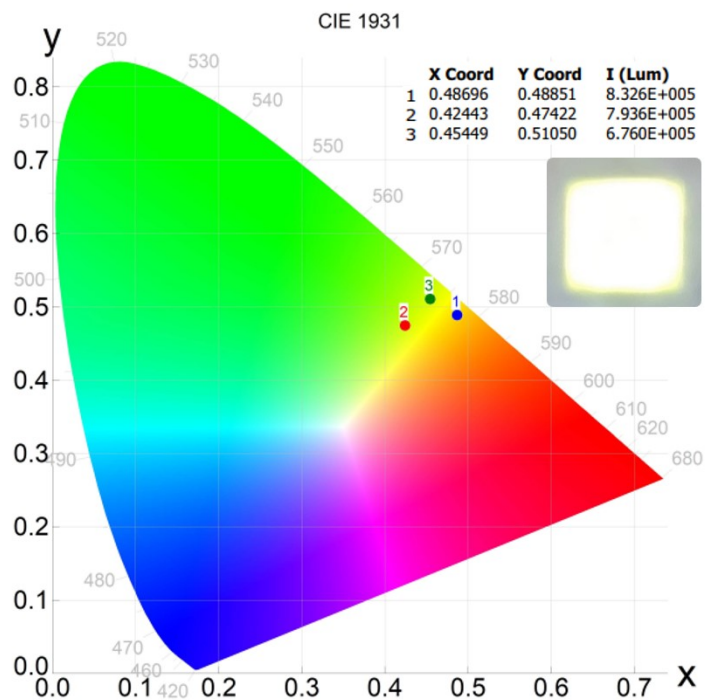


Figure S7. CIE color coordinates of compounds **1-3**. Inset: luminescent coating made by **3**.

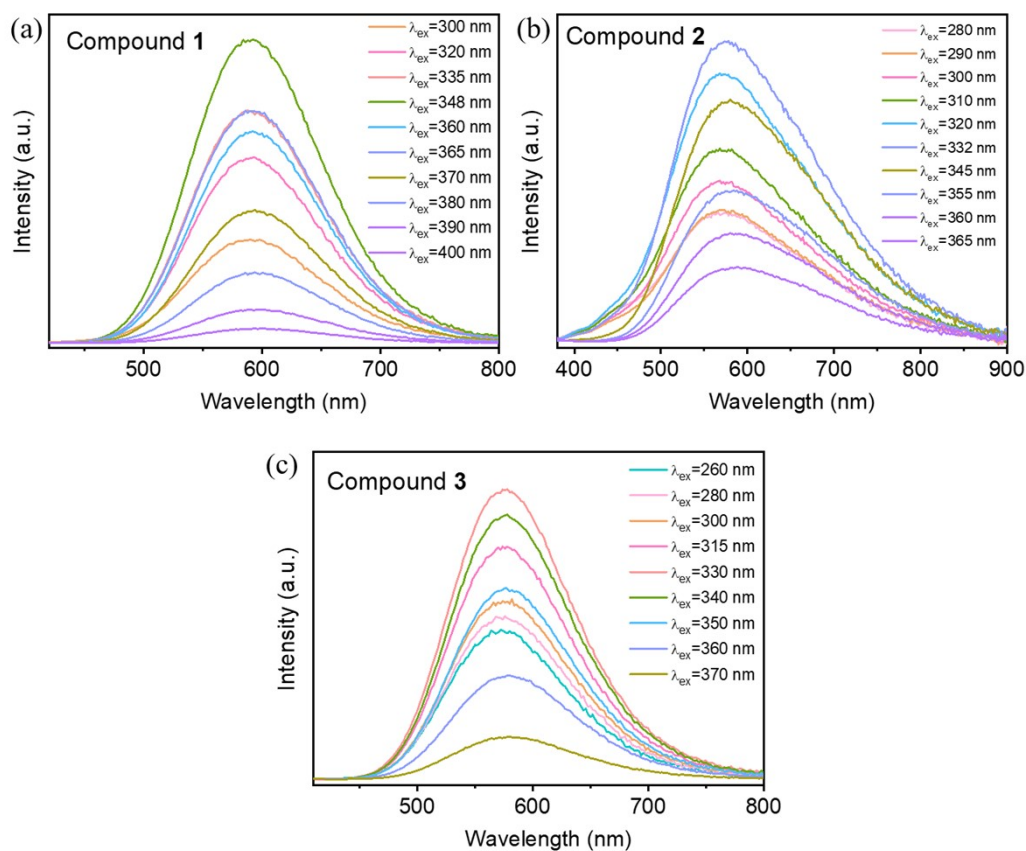


Figure S8. Emission spectra of compounds **1-3** under light excitation of different energies.

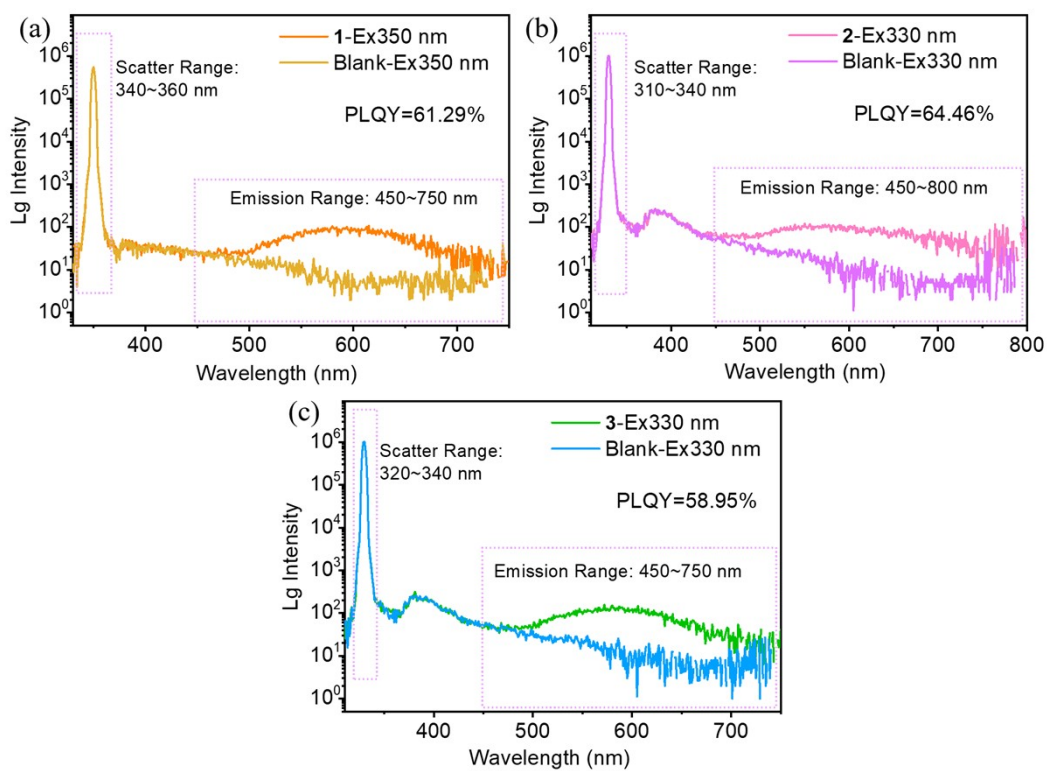


Figure S9. Photoluminescent quantum yield analysis curves of compounds 1-3.

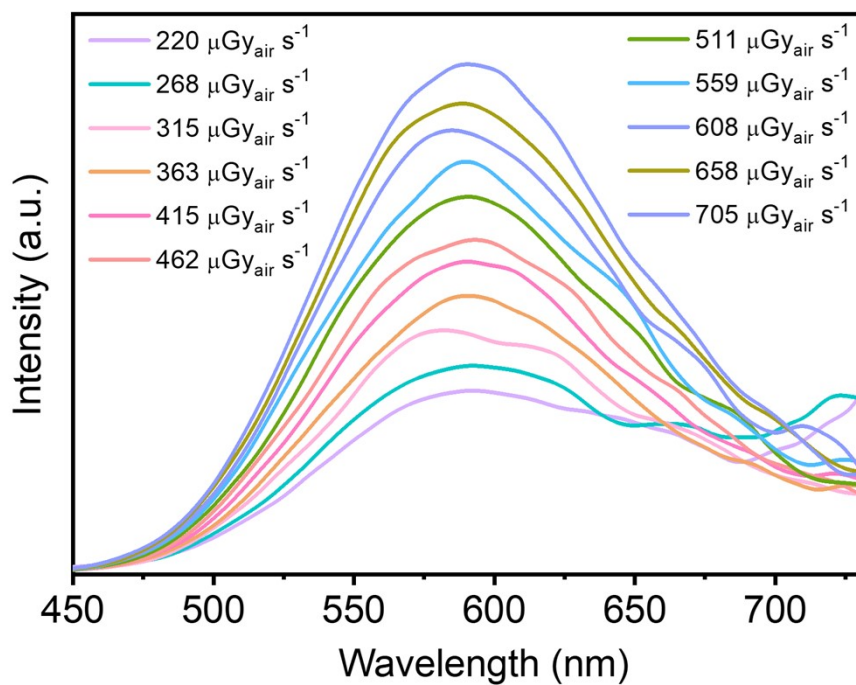


Figure S10. Radioluminescence (RL) spectra of compound 3 in the dose rate range of 220 to 705 $\mu\text{Gy}_{\text{air}} \text{s}^{-1}$.

Table S1. Preparation information of three R-ted-R organic ligands.

Ligand number	Systematic name	Abbreviation	Corresponding bromoalkane and its dosage	Yield
L ₁	1,4-dipropyl-1,4-diazabicyclo [2.2.2]octan-1,4-dium bromide	Pr-ted-Pr	1-bromopropane, 4.92 g	63%
L ₂	1,4-dibutyl-1,4-diazabicyclo [2.2.2]octan-1,4-dium bromide	Bu-ted-Bu	1-bromobutane, 5.48 g	55%
L ₃	1,4-dipentyl-1,4-diazabicyclo [2.2.2]octan-1,4-dium bromide	Pen-ted-Pen	1-bromopentane, 6.04 g	49%

Table S2. Summary of single crystal analysis data of compounds **1-3**.

Hybrid	Compound 1 (Cu ₄ I ₈)(CuI ₄) ₃ (C ₁₂ H ₂₆ N ₂) ₆ ^[a]	Compound 2 (Cu ₃ I ₆)(C ₁₄ H ₃₀ N ₂) ^[b]	Compound 3 (Cu ₃ I ₆) ₄ (C ₁₆ H ₃₄ N ₂) ₆
Ligand abbreviation	Pr-ted-Pr	Bu-ted-Bu	Pen-ted-Pen
Empirical formula	C ₇₂ H ₁₅₉ Cu ₇ I ₂₀ N ₁₂ O	C ₁₇ H ₄₂ Cu ₃ I ₆ N ₂ KO ₃	C ₄₈ H ₁₀₂ Cu ₆ I ₁₂ N ₆
Formula weight	4191.96	1314.91	2667.07
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁ 2	<i>Cc</i>
<i>a</i> (Å)	8.1488(5)	13.2569(3)	16.9436(2)
<i>b</i> (Å)	28.0082(18)	31.2788(9)	28.3740(3)
<i>c</i> (Å)	30.0270(19)	8.5120(2)	32.0723(3)
α (deg)	62.316(2)	90	90
β (deg)	83.563(2)	90	102.407(1)
γ (deg)	83.272(2)	90	90
<i>V</i> (Å ³)	6013.9(7)	3529.59(15)	15058.9(3)
<i>Z</i>	2	4	4
Test temperature(K)	100	100	100
λ (Å)	0.71073	0.71073	0.71073
<i>R</i> ₁	0.0728	0.0294	0.0485
<i>wR</i> ₂	0.2237	0.0697	0.1088

^[a] One H₃O⁺ in compound **1**, ^[b] one K⁺ and three CH₃OH in compound **2** are omitted for consistency of the structural formula.

Table S3. Comparison of some optical properties of compounds **1-3**.

Compound	Band gap (eV)	PLE _{max} (nm)	PL _{max} (nm)	Stokes shift (nm)	fwhm (nm)	PLQY (%)
1	3.32	348	592	244	132	61.29
2	3.36	332	578	246	180	64.46
3	3.32	330	578	248	130	58.95

Table S4. The WLED performance of compound **3** [(Cu₃I₆)₄(C₁₆H₃₄N₂)₆] compared with other similar materials.

Number	Compound	CRI	CIE coordinates	CCT (K)	Reference
1	BAM, (Cu ₃ I ₆) ₄ (C ₁₆ H ₃₄ N ₂) ₆	85	(0.33, 0.39)	5220	This work
2	YAG: Ce, CuX ₂ (tpp) ₂ (i-bu- <i>ted</i>)	/	(0.329, 0.406)	5652	[1]
3	Cu ₂ I ₂ (tpp) ₂ (bpp), Cu ₂ I ₂ (tpp) ₂ (4,4'-bpy)	73.8	(0.31, 0.36)	4512	[2]
4	1D-CuBr(py) _{0.9995} (pz) _{0.0005}	68.4	(0.34, 0.41)	5792	[3]
5	1D-CuBr(py) _{0.9993} (pz) _{0.0007}	67.0	(0.35, 0.42)	5024	[3]
6	1D-CuBr(py) _{0.9988} (pz) _{0.0012}	67.2	(0.39, 0.43)	3888	[3]
7	1D-CuBr(py) _{0.9968} (pz) _{0.0032}	58.0	(0.42, 0.46)	3658	[3]
8	1D-CuBr(py) _{0.9988} (2- <i>ct-pz</i>) _{0.0012}	65.4	(0.26, 0.36)	4259	[3]
9	1D-CuBr(py) _{0.9988} (2- <i>me-pz</i>) _{0.0012}	65.5	(0.28, 0.37)	3940	[3]
10	1D-CuBr(py) _{0.9988} (2- <i>Cl-pz</i>) _{0.0012}	77.2	(0.43, 0.42)	3697	[3]
11	1D-CuBr(py) _{0.9988} (2- <i>Br-pz</i>) _{0.0012}	75.6	(0.44, 0.40)	3360	[3]
12	(Sr, Ca)AlSiN ₃ :Eu, (BPTA) ₂ MnBr ₄	93.2	(0.34, 0.39)	5301	[4]
13	BAM, [M ₂ ImH] ₃ ⁺ [SbCl ₆] ₃ ⁻	~80.5	(0.306, 0.323)	~7000	[5]
14	Cu ₂ X ₃ (tpp) ₂ (<i>n-pr-<i>ted</i></i>), Cu ₄ I ₆ (<i>ted-oct-<i>ted</i></i>)	90	(0.406, 0.422)	3800	[6]

Table S5. The performance of compound **3** [(Cu₃I₆)₄(C₁₆H₃₄N₂)₆] compared with other similar X-ray scintillators.

Compound	Light yield (photons/MeV)	Detection limit	Reference
(Cu ₃ I ₆) ₄ (C ₁₆ H ₃₄ N ₂) ₆	17508	1.14 μGy _{air} /s	This work
(4-bzpy) ₄ Cu ₄ I ₄	60948	/	[7]
(4-bzpy) ₂ Cu ₆ I ₈	5353	/	[7]
(4-bzpy) ₃ Cu ₃ I ₆	7011	/	[7]
Cu ₂ Au ₂ (R-BTT) ₄	13600-17000	111.7 nGy _{air} /s	[8]
PPh ₄ CuBr ₂	5000	6.37 μGy _{air} /s	[9]
(Bmpip) ₂ Cu ₂ Br ₄	1600	0.71 μGy _{air} /s	[9]
Cu ₄ I ₄ py ₄	9277±850	/	[10]
CuCl(PPh ₃) ₂ (3-mepy)	5951±135	338.8 nGy _{air} /s	[11]

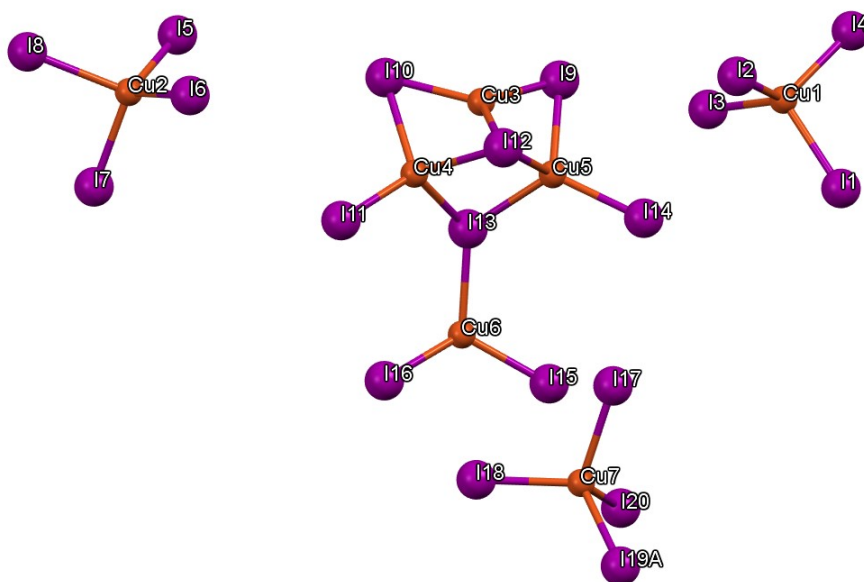


Figure S11. Schematic diagrams of inorganic module of compound **1**.

Table S6. Bond angles of inorganic module of compound **1**.

Number	Atom1	Atom2	Atom3	Angle(°)
1	Cu3	I9	Cu5	58.01(9)
2	Cu3	I10	Cu4	58.37(9)
3	Cu3	I12	Cu4	56.56(9)
4	Cu3	I12	Cu5	55.89(8)
5	Cu3	I12	Cu6	164.01(9)
6	Cu4	I12	Cu5	79.81(7)
7	Cu4	I12	Cu6	132.98(7)
8	Cu5	I12	Cu6	132.71(7)
9	Cu4	I13	Cu5	82.36(7)
10	Cu4	I13	Cu6	125.62(8)

Number	Atom1	Atom2	Atom3	Angle(°)
11	Cu5	I13	Cu6	126.67(8)
12	I9	Cu3	I10	128.3(1)
13	I9	Cu3	I12	116.0(1)
14	I10	Cu3	I12	115.3(1)
15	I10	Cu4	I11	114.89(9)
16	I10	Cu4	I12	103.64(8)
17	I10	Cu4	I13	106.95(8)
18	I11	Cu4	I12	114.03(9)
19	I11	Cu4	I13	118.67(9)
20	I12	Cu4	I13	96.21(7)
21	I9	Cu5	I12	104.95(7)
22	I9	Cu5	I13	106.94(7)
23	I9	Cu5	I14	110.03(8)
24	I12	Cu5	I13	95.66(7)
25	I12	Cu5	I14	117.28(8)
26	I13	Cu5	I14	120.20(8)
27	I13	Cu5	Cu3	79.6(1)
28	I14	Cu5	Cu3	159.9(1)
29	I13	Cu6	I15	116.7(1)
30	I13	Cu6	I16	115.0(1)
31	I13	Cu6	I12	89.59(7)
32	I15	Cu6	I16	120.2(1)
33	I15	Cu6	I12	98.80(8)
34	I16	Cu6	I12	109.42(9)
35	I1	Cu1	I2	103.34(8)
36	I1	Cu1	I3	116.96(9)
37	I1	Cu1	I4	106.16(8)
38	I2	Cu1	I3	108.25(8)
39	I2	Cu1	I4	120.08(9)
40	I3	Cu1	I4	102.80(8)
41	I5	Cu2	I6	108.3(1)
42	I5	Cu2	I7	116.0(1)
43	I5	Cu2	I8	110.6(1)
44	I6	Cu2	I7	113.5(1)
45	I6	Cu2	I8	113.7(1)
46	I7	Cu2	I8	94.4(1)
47	I17	Cu7	I18	104.9(1)
48	I17	Cu7	I20	111.4(1)
49	I17	Cu7	I19A	115.8(1)
50	I18	Cu7	I20	114.8(1)
51	I18	Cu7	I19A	111.4(1)
52	I20	Cu7	I19A	98.8(1)

Table S7. Bond length of inorganic module of compound **1**.

Number	Atom1	Atom2	Length(Å)
1	I9	Cu3	2.500(3)
2	I9	Cu5	2.734(3)
3	I10	Cu3	2.504(3)
4	I10	Cu4	2.760(4)
5	I11	Cu4	2.528(2)
6	I12	Cu3	2.652(4)
7	I12	Cu4	2.782(2)
8	I12	Cu5	2.776(2)
9	I12	Cu6	3.088(3)
10	I13	Cu4	2.692(2)
11	I13	Cu5	2.723(2)
12	I13	Cu6	2.680(3)
13	I14	Cu5	2.536(2)
14	I15	Cu6	2.535(3)
15	I16	Cu6	2.539(2)
16	Cu6	I12	3.088(3)
17	I1	Cu1	2.708(3)
18	I2	Cu1	2.643(2)
19	I3	Cu1	2.637(2)
20	I4	Cu1	2.675(3)
21	I5	Cu2	2.625(4)
22	I6	Cu2	2.622(4)
23	I7	Cu2	2.639(3)
24	I8	Cu2	2.776(4)
25	I17	Cu7	2.676(3)
26	I18	Cu7	2.626(3)
27	I20	Cu7	2.670(3)
28	Cu7	I19A	2.702(5)

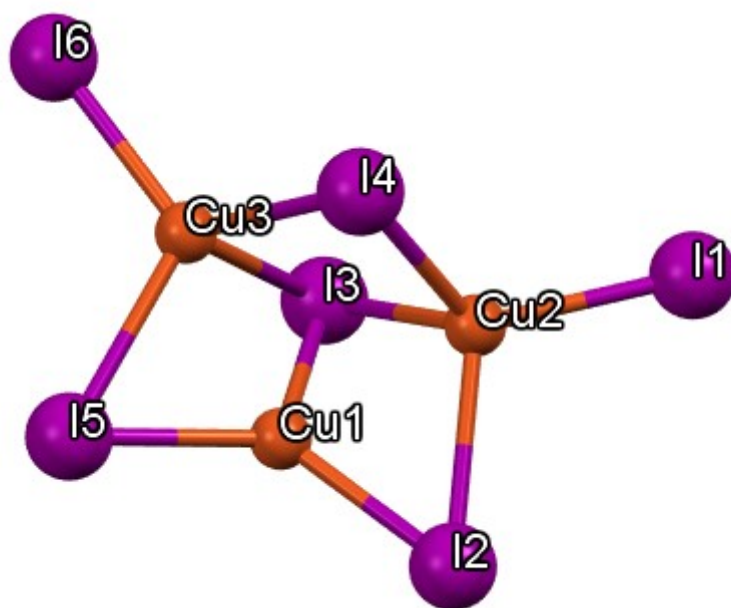


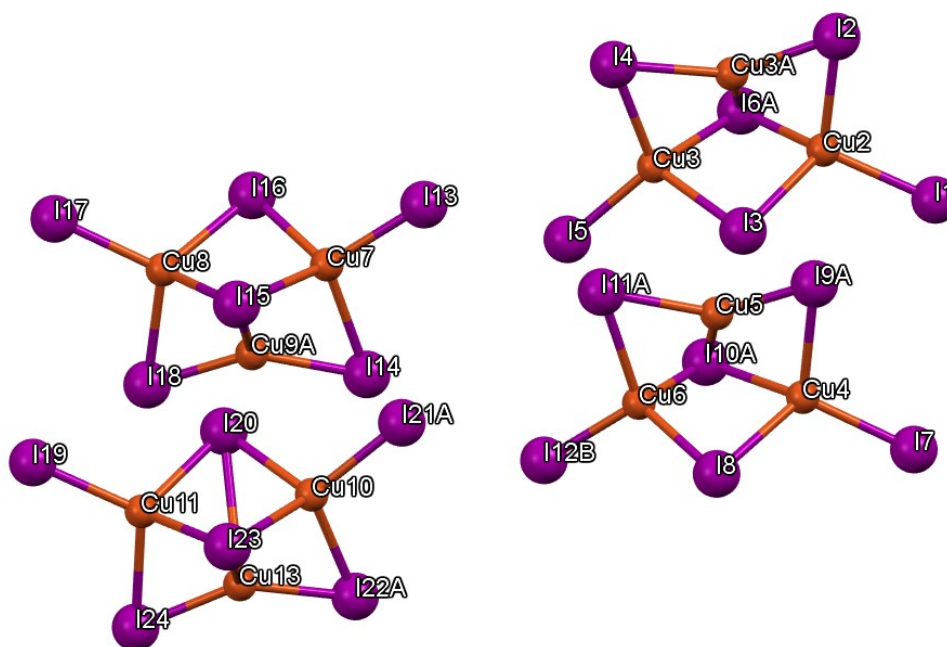
Figure S12. Schematic diagram of inorganic module of compound **2**.

Table S8. Bond angles of inorganic module of compound **2**.

Number	Atom1	Atom2	Atom3	Angle(°)
1	Cu1	I2	Cu2	56.96(5)
2	Cu1	I3	Cu2	54.82(4)
3	Cu1	I3	Cu3	55.15(5)
4	Cu2	I3	Cu3	74.56(4)
5	Cu2	I4	Cu3	79.75(4)
6	Cu1	I5	Cu3	57.26(7)
7	I2	Cu1	I3	114.09(6)
8	I2	Cu1	I5	128.92(9)
9	I3	Cu1	I5	116.76(8)
10	I1	Cu2	I12	110.09(5)
11	I1	Cu2	I13	112.98(5)
12	I1	Cu2	I14	118.44(5)
13	I2	Cu2	I13	102.06(4)
14	I2	Cu2	I14	111.54(5)
15	I3	Cu2	I14	100.20(4)
16	I3	Cu3	I14	99.33(5)
17	I3	Cu3	I15	105.65(7)
18	I3	Cu3	I16	109.92(5)
19	I4	Cu3	I15	107.24(7)
20	I4	Cu3	I16	117.16(5)
21	I5	Cu3	I16	115.75(7)

Table S9. Bound lengths of inorganic module of compound **2**.

Number	Atom1	Atom2	Length(Å)
1	I1	Cu2	2.561(1)
2	I2	Cu1	2.502(2)
3	I2	Cu2	2.776(1)
4	I3	Cu1	2.675(2)
5	I3	Cu2	2.811(1)
6	I3	Cu3	2.820(2)
7	I4	Cu2	2.646(1)
8	I4	Cu3	2.673(1)
9	I5	Cu1	2.543(3)
10	I5	Cu3	2.757(3)
11	I6	Cu3	2.535(1)

Figure S13. Schematic diagram of inorganic module of compound **3**.Table S10. Bound angles of inorganic module of compound **3**.

Number	Atom1	Atom2	Atom3	Angle(°)
1	Cu2	I2	Cu3A	56.4(2)
2	Cu2	I3	Cu3	81.8(1)
3	Cu3	I4	Cu3A	58.3(2)
4	Cu2	I6A	Cu3	77.2(6)
5	Cu2	I6A	Cu3A	55.0(5)
6	Cu3	I6A	Cu3A	56.4(5)
7	I1	Cu2	I2	110.2(1)
8	I1	Cu2	I3	113.3(1)
9	I1	Cu2	I6A	121.2(5)

Number	Atom1	Atom2	Atom3	Angle(°)
10	I2	Cu2	I3	111.6(1)
11	I2	Cu2	I6A	100.6(5)
12	I3	Cu2	I6A	98.9(5)
13	I3	Cu3	I4	108.4(1)
14	I3	Cu3	I5	112.6(1)
15	I3	Cu3	I6A	97.3(5)
16	I4	Cu3	I5	116.3(1)
17	I4	Cu3	I6A	103.1(5)
18	I5	Cu3	I6A	117.0(5)
19	I2	Cu3A	I4	130.7(2)
20	I2	Cu3A	I6A	114.6(5)
21	I4	Cu3A	I6A	114.0(5)
22	Cu4	I8	Cu6	78.8(1)
23	Cu4	I9A	Cu5	57.4(2)
24	Cu4	I10A	Cu5	52.8(5)
25	Cu4	I10A	Cu6	78.8(7)
26	Cu5	I10A	Cu6	62.3(6)
27	Cu5	I11A	Cu6	58.0(1)
28	I7	Cu4	I8	115.0(1)
29	I7	Cu4	I9A	111.6(2)
30	I7	Cu4	I10A	125.5(5)
31	I7	Cu4	Cu5	160.8(2)
32	I8	Cu4	I9A	109.2(2)
33	I8	Cu4	I10A	90.7(5)
34	I9A	Cu4	I10A	102.3(5)
35	I9A	Cu5	I10A	128.2(6)
36	I9A	Cu5	I11A	129.6(3)
37	I10A	Cu5	I11A	101.9(6)
38	I8	Cu6	I10A	105.9(6)
39	I8	Cu6	I11A	110.5(1)
40	I8	Cu6	I12B	116.4(2)
41	I10A	Cu6	I11A	101.2(6)
42	I10A	Cu6	I12B	110.7(6)
43	I11A	Cu6	I12B	110.9(2)
44	Cu10	I20	Cu11	83.8(1)
45	Cu10	I20	Cu13	47.5(1)
46	Cu11	I20	Cu13	49.9(1)
47	Cu10	I22A	Cu13	56.0(2)
48	Cu10	I23	Cu11	76.9(2)
49	Cu10	I23	Cu13	53.1(2)
50	Cu11	I23	Cu13	54.7(2)
51	Cu11	I24	Cu13	58.3(2)
52	I20	Cu10	I21A	113.6(2)

Number	Atom1	Atom2	Atom3	Angle(°)
53	I20	Cu10	I22A	109.4(2)
54	I20	Cu10	I23	97.5(2)
55	I21A	Cu10	I22A	113.5(2)
56	I21A	Cu10	I23	115.7(2)
57	I22A	Cu10	I23	105.8(2)
58	I19	Cu11	I20	114.6(2)
59	I19	Cu11	I23	119.5(2)
60	I19	Cu11	I24	114.4(2)
61	I20	Cu11	I23	95.4(2)
62	I20	Cu11	I24	111.0(2)
63	I23	Cu11	I24	99.6(2)
64	I20	Cu13	I22A	96.5(2)
65	I20	Cu13	I23	86.5(2)
66	I20	Cu13	I24	99.5(2)
67	I22A	Cu13	I23	114.9(2)
68	I22A	Cu13	I24	131.1(3)
69	I23	Cu13	I24	112.0(2)
70	Cu7	I14	Cu9A	57.1(1)
71	Cu7	I15	Cu8	76.9(1)
72	Cu7	I15	Cu9A	55.1(1)
73	Cu8	I15	Cu9A	54.7(1)
74	Cu7	I16	Cu8	79.9(1)
75	Cu8	I18	Cu9A	57.7(1)
76	I13	Cu7	I14	110.1(1)
77	I13	Cu7	I15	116.7(1)
78	I13	Cu7	I16	115.1(1)
79	I14	Cu7	I15	105.7(1)
80	I14	Cu7	I16	108.7(1)
81	I15	Cu7	I16	99.7(1)
82	I15	Cu8	I16	96.7(1)
83	I15	Cu8	I17	115.9(1)
84	I15	Cu8	I18	103.6(1)
85	I16	Cu8	I17	117.3(1)
86	I16	Cu8	I18	111.2(1)
87	I17	Cu8	I18	110.7(1)
88	I14	Cu9A	I15	113.1(2)
89	I14	Cu9A	I18	132.7(2)
90	I15	Cu9A	I18	113.4(2)

Table S11. Bond lengths of inorganic module of compound **3**.

Number	Atom1	Atom2	Length(Å)
1	I1	Cu2	2.594(4)
2	I2	Cu2	2.731(4)

Number	Atom1	Atom2	Length(Å)
3	I2	Cu3A	2.531(6)
4	I3	Cu2	2.684(4)
5	I3	Cu3	2.724(3)
6	I4	Cu3	2.665(3)
7	I4	Cu3A	2.609(6)
8	I5	Cu3	2.522(4)
9	I6A	Cu2	2.82(2)
10	I6A	Cu3	2.85(2)
11	I6A	Cu3A	2.55(3)
12	I7	Cu4	2.588(4)
13	I8	Cu4	2.687(4)
14	I8	Cu6	2.720(4)
15	I9A	Cu4	2.755(9)
16	I9A	Cu5	2.425(9)
17	I10A	Cu4	3.00(2)
18	I10A	Cu5	2.56(2)
19	I10A	Cu6	2.35(3)
20	I11A	Cu5	2.507(4)
21	I11A	Cu6	2.733(4)
22	I12B	Cu6	2.505(4)
23	I19	Cu11	2.531(4)
24	I20	Cu10	2.662(5)
25	I20	Cu11	2.666(5)
26	I20	Cu13	3.293(5)
27	I21A	Cu10	2.559(5)
28	I22A	Cu10	2.704(5)
29	I22A	Cu13	2.535(5)
30	I23	Cu10	2.820(7)
31	I23	Cu11	2.902(6)
32	I23	Cu13	2.690(7)
33	I24	Cu11	2.752(7)
34	I24	Cu13	2.521(7)
35	I13	Cu7	2.553(4)
36	I14	Cu7	2.755(3)
37	I14	Cu9A	2.490(5)
38	I15	Cu7	2.712(4)
39	I15	Cu8	2.835(4)
40	I15	Cu9A	2.731(5)
41	I16	Cu7	2.689(3)
42	I16	Cu8	2.687(4)
43	I17	Cu8	2.527(4)
44	I18	Cu8	2.756(4)
45	I18	Cu9A	2.525(5)

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