Supporting Information

Organic Cations Directed One-Dimensional Cuprous Halide Compounds: Syntheses, Crystal Structures and Photoluminescent Properties

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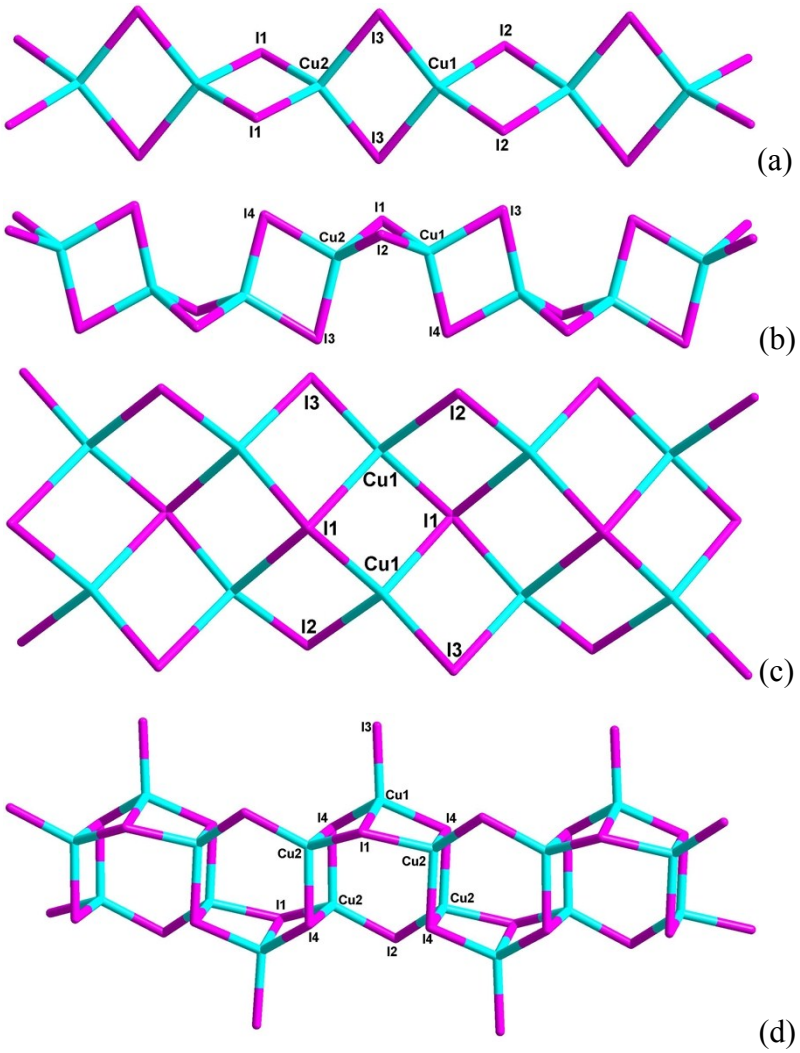

Fig. S1. Detailed view of the 1D $[CuI_2]^-$ chain in compound **1** (a), 1D $[Cu_2I_4]^{2-}$ chain in compound **2** (b), 1D $[Cu_2I_3]^-$ chain in compound **3** (c) and 1D $[Cu_3I_5]^{2-}$ chain in compound **4** (d).

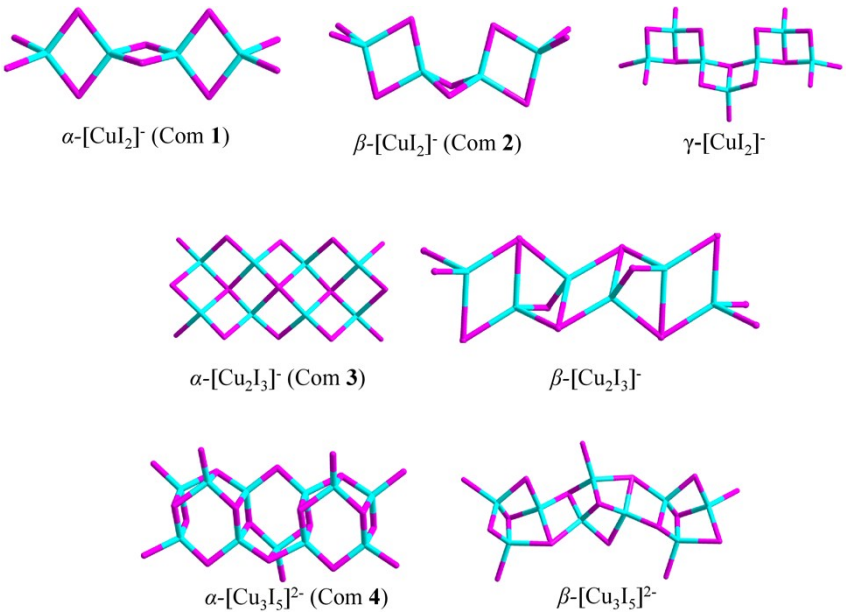

Fig. S2. Variation of the partial structural motifs of 1D $[CuI_2]^-$, $[Cu_2I_3]^-$ and $[Cu_3I_5]^{2-}$ chains based on $[CuI_4]$ tetrahedrons.

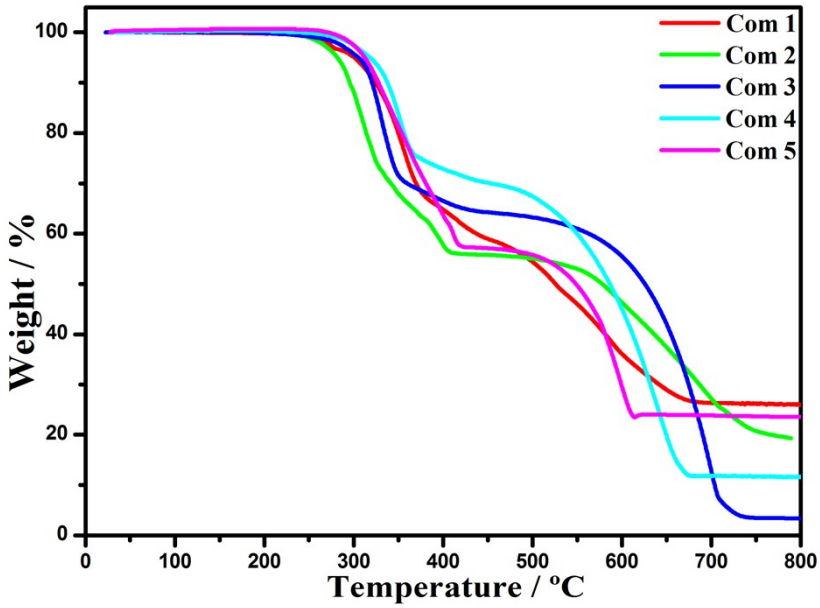

Fig. S3. The thermogravimetric analysis curves for compounds **1**−**5** under nitrogen atmosphere.

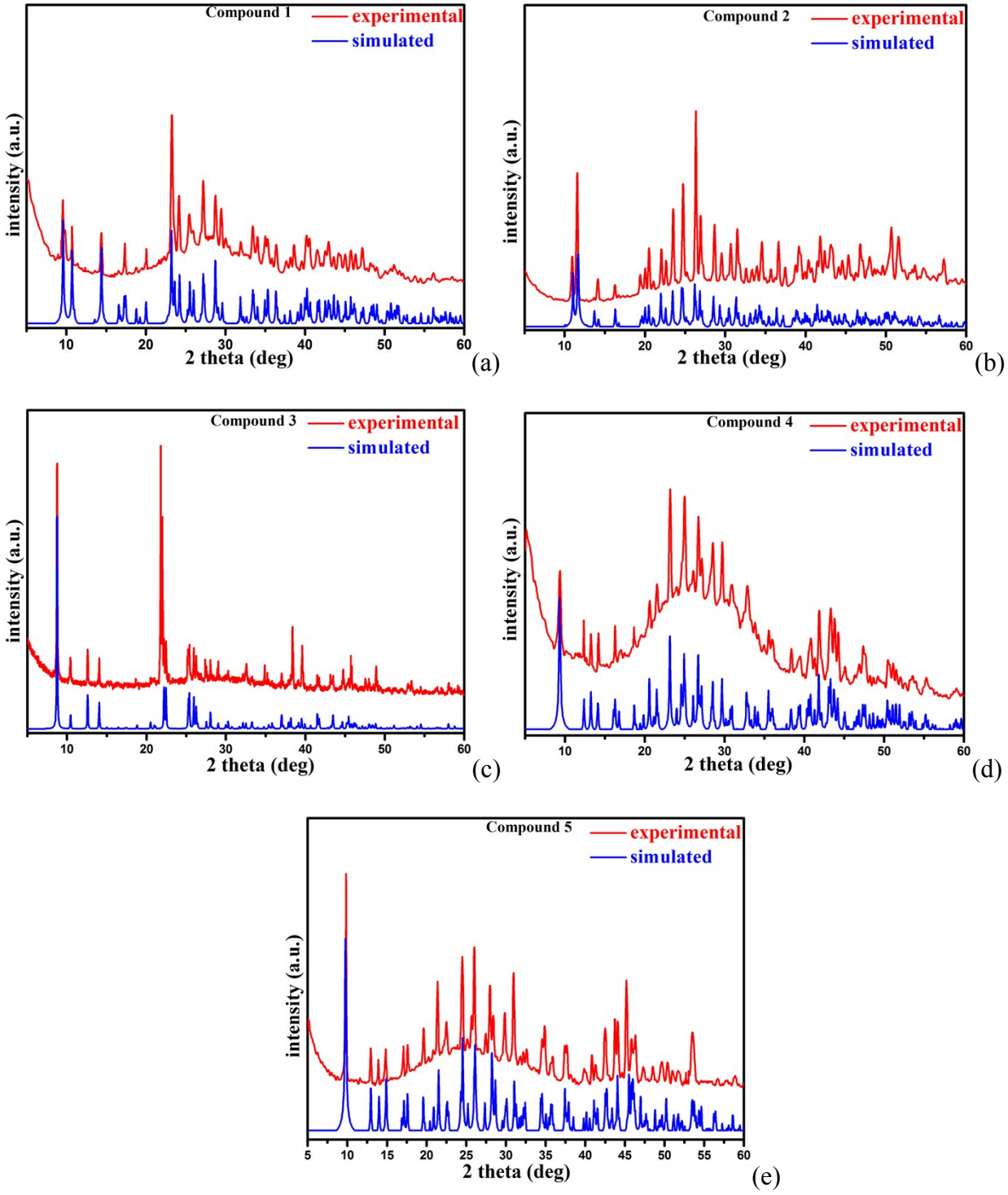

Fig. S4. Experimental and simulated XRD patterns of compounds **1-5**.

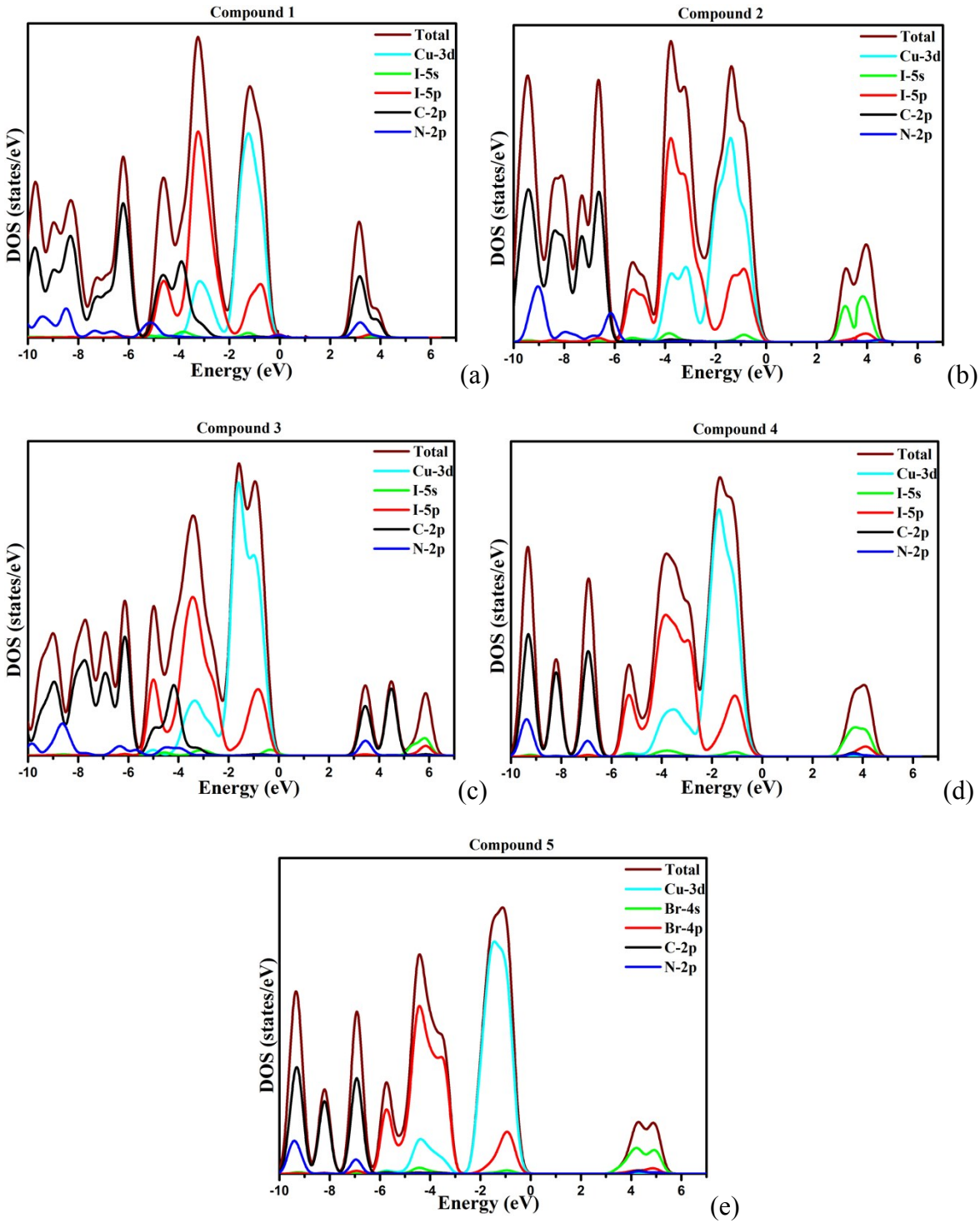

Fig. S5. The calculated total and partial density of states for compounds **1**-**5**.

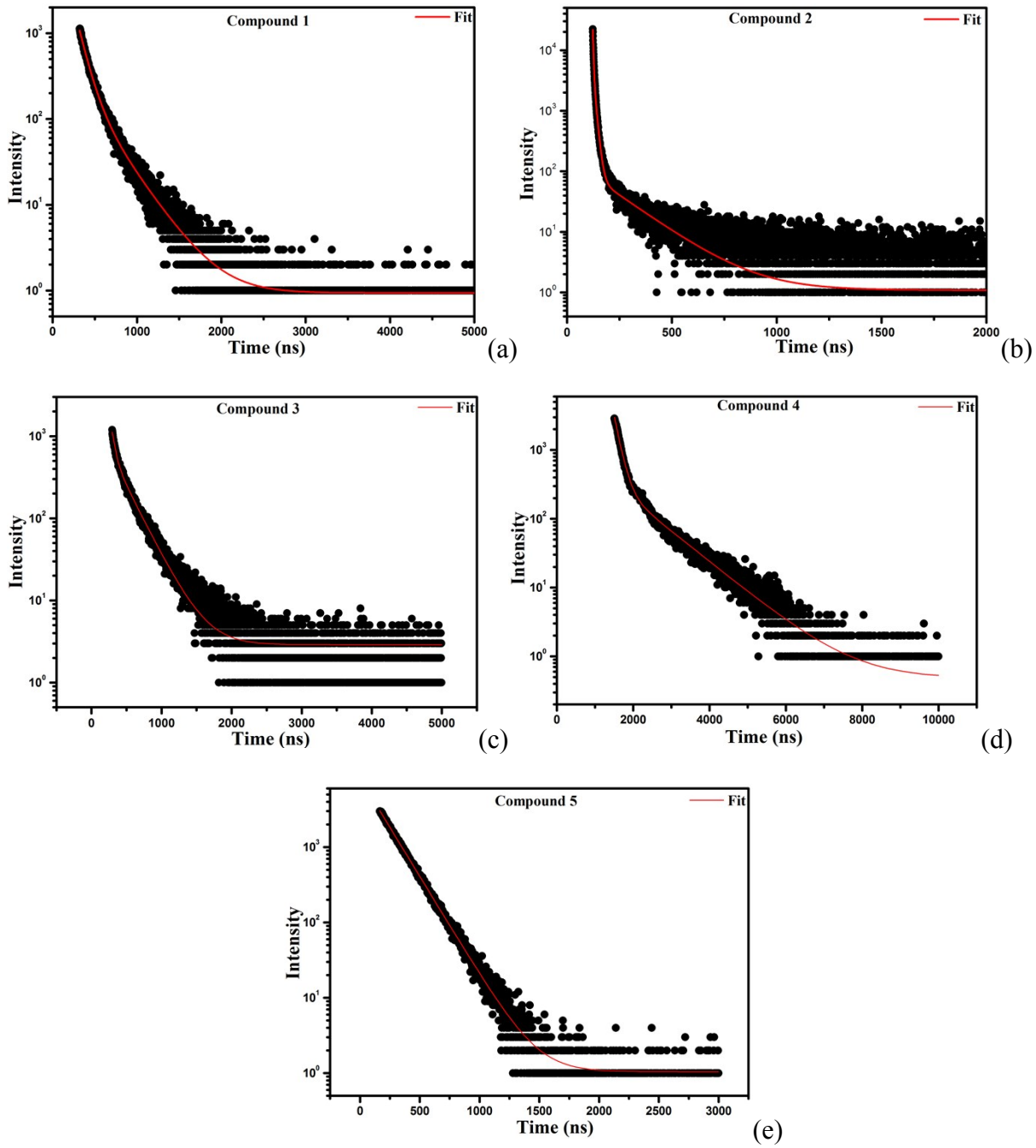

Fig. **S6**. The time-resolved PL emissions of compounds **1**-**5**.

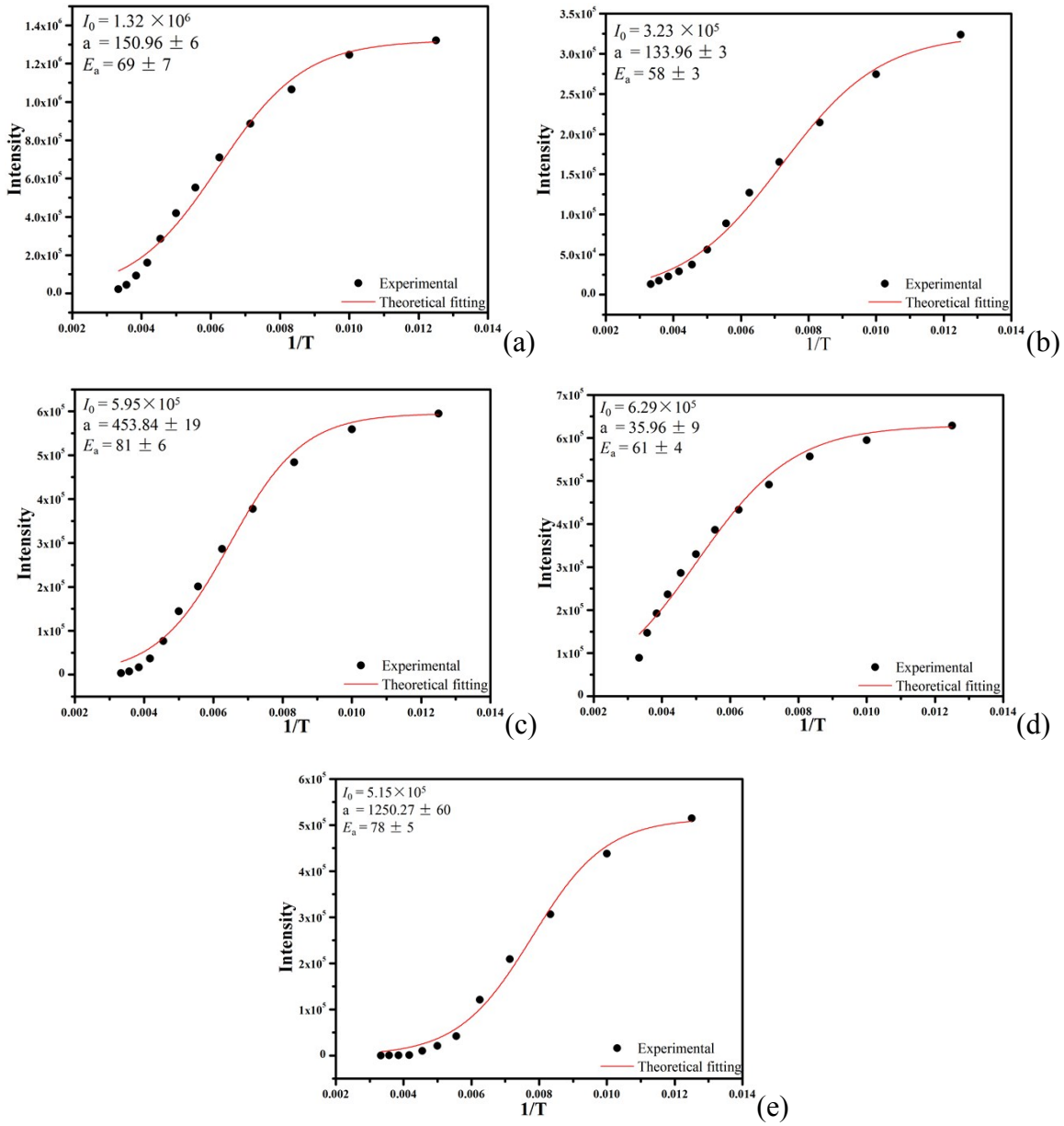

Fig. **S7**. Temperature dependence of the PL intensity and theoretical fitting data from Arrhenius-type model for compounds **1** (a), **2** (b), **3** (c), **4** (d) and **5** (e).

Table S1. Crystal Data and Structure Refinements for compounds **1-5**.

Compound	**1**	**2**	**3**	**4**	**5**
chemical	$C_6NH_8CuI_2$	$C_8N_2H_{18}Cu_2I_4$	$C_7NH_{10}Cu_2I_3$	$C_6N_2H_{14}Cu_3I_5$	$C_6N_2H_{14}Cu_3Br_5$
fw	411.47	776.92	615.94	939.31	704.36
Space group	*Cmca*	$P2_1/c$	*Pnma*	*Pnma*	*Pnma*
a/Å	13.102(10)	9.2225(9)	16.9103(11)	18.748(3)	17.951(2)
b/Å	18.403(14)	10.9983(11)	6.3543(4)	8.3956(12)	7.9123(10)
c/Å	16.480(13)	15.5063(16)	12.5868(8)	11.0005(16)	10.4907(14)
β/°	90	93.8620(10)	90	90	90
V(Å^3)	3974(5)	1569.3(3)	1352.49(15)	1731.5(4)	1490.0(3)
Z	16	4	4	4	4
D_{calcd} (g·cm^{-3})	2.751	3.289	3.025	3.603	3.140
Temp (*K*)	298(2)	298(2)	298(2)	298(2)	298(2)
μ (mm^{-1})	8.348	10.558	9.954	12.545	17.626
F(000)	2976	1400	1104	1664	1304
Reflections	16376	17756	15117	19071	16396
Unique	2383	3595	1701	2155	1828
Reflections	2223	2825	1519	2042	1538
GOF on F^2	1.067	1.058	1.067	1.018	1.033
R_1,wR_2 ($I > 2\sigma(I)$)[a]	0.0333/0.0958	0.0648/0.2193	0.0217/0.0495	0.0208/0.0495	0.0443/0.1105
R_1,wR_2 (all	0.0382/0.0998	0.0806/0.2323	0.0258/0.0513	0.0226/0.0504	0.0537/0.1176
$\Delta\rho_{max}$ (e/Å^3)	0.693	4.148	1.161	1.164	1.719
$\Delta\rho_{min}$ (e/Å^3)	-0.847	-3.495	-0.618	-0.777	-1.721

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma w[(F_o)^2 - (F_c)^2]^2/\Sigma w[(F_o)^2]^2\}^{1/2}$

Table S2. Selected bond lengths (Å) and angle (°) for compound **1**.

Cu(1)-I(3)	2.6750(15)	Cu(2)-I(1)	2.6583(15)
Cu(1)-I(3)#1	2.6751(15)	Cu(2)-I(1)#3	2.6583(15)
Cu(1)-I(2)	2.7015(15)	Cu(2)-I(3)	2.6740(15)
Cu(1)-I(2)#2	2.7015(15)	Cu(2)-I(3)#1	2.6740(15)
I(3)-Cu(1)-I(3)#1	106.68(7)	I(1)-Cu(2)-I(1)#3	104.78(7)
I(3)-Cu(1)-I(2)	118.58(5)	I(1)-Cu(2)-I(3)	111.34(5)
I(3)#1-Cu(1)-I(2)	106.80(5)	I(1)#3-Cu(2)-I(3)	111.37(4)
I(3)-Cu(1)-I(2)#2	106.80(5)	I(1)-Cu(2)-I(3)#1	111.37(4)
I(3)#1-Cu(1)-I(2)#2	118.58(5)	I(1)#3-Cu(2)-I(3)#1	111.34(5)
I(2)-Cu(1)-I(2)#2	100.02(6)	I(3)-Cu(2)-I(3)#1	106.74(7)

Symmetry transformations used to generate equivalent atoms: #1 *x*, -*y*-1, -*z*+1, #2 -*x*-1, -*y*-1, -*z*+1, #3 -*x*, -*y*-1, *z*+1.

Table S3. Selected bond lengths (Å) and angle (°) for compound **2**.

Cu(1)-I(2)	2.573(2)	Cu(2)-I(1)	2.642(2)
Cu(1)-I(3)#1	2.557(2)	Cu(2)-I(2)	2.579(2
Cu(1)-I(4)#1	2.495(2)	Cu(2)-I(3)	2.556(2)
Cu(1)-I(1)	2.619(2)	Cu(2)-I(4)	2.501(2)
Cu(2)-Cu(1)	2.737(2)	Cu(2)-Cu(1)#1	3.015(2)
I(4)#2-Cu(1)-I(3)#2	106.81(7)	I(4)-Cu(2)-I(3)	106.64(8)
I(4)#2-Cu(1)-I(2)	111.51(8)	I(4)-Cu(2)-I(2)	106.31(8)
I(3)#2-Cu(1)-I(2)	108.66(8)	I(3)-Cu(2)-I(2)	116.51(8)
I(4)#2-Cu(1)-I(1)	115.50(8)	I(4)-Cu(2)-I(1)	105.27(8)
I(3)#2-Cu(1)-I(1)	109.24(7)	I(3)-Cu(2)-I(1)	117.01(8)
I(2)-Cu(1)-I(1)	104.98(7)	I(2)-Cu(2)-I(1)	104.13(7)

Symmetry transformations used to generate equivalent atoms: #1 -*x*+3/2, *y*-1/2, -*z*+1/2, #2 -*x*+3/2, *y*+1/2, -*z*+1/2.

Table S4. Selected bond lengths (Å) and angle (°) for compound **3**.

Cu(1)-I(3)	2.6084(6)	Cu(1)-I(1)#1	2.7142(6)
Cu(1)-I(2)	2.6272(6)	Cu(1)-I(1)	2.7305(6)
I(3)-Cu(1)-I(2)	114.02(2)	I(3)-Cu(1)-I(1)	111.03(2)
I(3)-Cu(1)-I(1)#1	109.36(2)	I(2)-Cu(1)-I(1)	104.41(2)
I(2)-Cu(1)-I(1)#1	108.23(2)	I(1)#1-Cu(1)-I(1)	109.626(19)

Symmetry transformations used to generate equivalent atoms: #1 -*x*, -*y*, -*z*+1.

Table S5. Selected bond lengths (Å) and angle (°) for compound **4**.

Cu(1)-I(3)	2.6210(9)	Cu(2)-I(2)	2.6186(7)
Cu(1)-I(4)	2.6915(6)	Cu(2)-I(1)	2.6481(6)
Cu(1)-I(4)#1	2.6916(6)	Cu(2)-I(4)	2.6488(7)
Cu(1)-I(1)	2.7161(9)	Cu(2)-I(4)#2	2.7067(7)
Cu(1)-Cu(2)#1	2.8049(8)	Cu(1)-Cu(2)	2.8049(8)
I(3)-Cu(1)-I(4)	108.04(2)	I(2)-Cu(2)-I(1)	107.73(2)
I(3)-Cu(1)-I(4)#1	108.04(2)	I(2)-Cu(2)-I(4)	112.45(2)
I(4)-Cu(1)-I(4)#1	100.31(3)	I(1)-Cu(2)-I(4)	118.09(2)
I(3)-Cu(1)-I(1)	111.17(3)	I(2)-Cu(2)-I(4)#2	116.42(2)
I(4)-Cu(1)-I(1)	114.28(2)	I(1)-Cu(2)-I(4)#2	100.84(2)
I(4)#1-Cu(1)-I(1)	114.28(2)	I(4)-Cu(2)-I(4)#2	101.03(2)

Symmetry transformations used to generate equivalent atoms: #1 *x*, -*y*-1/2, *z*, #2 -*x*+1, -*y*, -*z*+1.

Table S6. Selected bond lengths (Å) and angle (°) for compound **5**.

Cu(1)-Br(2)	2.4112(14)	Cu(2)-Br(1)	2.4360(10)
Cu(1)-Br(3)	2.5841(15)	Cu(2)-Br(3)	2.5102(11)
Cu(1)-Br(4)	2.5264(10)	Cu(2)-Br(4)	2.4993(10)
Cu(1)-Br(4)#2	2.5264(10)	Cu(2)-Br(4)#3	2.5259(11)
Cu(1)-Cu(2)	2.7994(13)	Cu(1)-Cu(2)#2	2.7995(13)
Br(2)-Cu(1)-Br(4)#2	111.77(4)	Br(1)-Cu(2)-Br(4)	114.17(4)
Br(2)-Cu(1)-Br(4)	111.78(4)	Br(1)-Cu(2)-Br(3)	107.85(4)
Br(4)#2-Cu(1)-Br(4)	100.02(5)	Br(4)-Cu(2)-Br(3)	113.56(4)
Br(2)-Cu(1)-Br(3)	112.28(5)	Br(1)-Cu(2)-Br(4)#3	117.07(4)
Br(4)#2-Cu(1)-Br(3)	110.18(4)	Br(4)-Cu(2)-Br(4)#3	103.59(4)
Br(4)-Cu(1)-Br(3)	110.18(4)	Br(3)-Cu(2)-Br(4)#3	99.89(4)

Symmetry transformations used to generate equivalent atoms: #1 *x*, -*y*+1/2, *z*, #2 *x*, -*y*-1/2, *z*, #3 -*x*+1, -*y*, -*z*+2.