Electronic Supplementary Material (ESI) for Dalton Transactions.

Di-pyridyl Organic Cation Directed Hybrid Cuprous Halogenides: Syntheses, Crystal Structures and Photochromism and Photocatalysis

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Supporting Information

Table S1. Comparison of Crystal Data of Compounds **1a** and **1b**.

Compound	**1a**	**1b**
chemical formula	$C_{26}N_4H_{34}OCu_4I_8$	$C_{26}N_4H_{34}OCu_4I_8$
fw	1687.93	1687.93
Space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
a/Å	14.7211(8)	14.713(2)
b/Å	18.6474(11)	18.652(3)
c/Å	29.9786(17)	29.986(4)
β/°	91.4940(10)	91.489(2)
V(Å^3)	8226.6(8)	8226(2)
Z	8	8
D_{calcd} (g·cm^{-3})	2.726	2.719
Temp (K)	293(2)	293(2)
μ (mm^{-1})	8.070	8.070
F(000)	6128	6096
Reflections collected	47342	46601
Unique reflections	9504	9504
Reflections ($I>2\sigma(I)$)	8427	8147
GOF on F^2	1.034	1.067
R_1,wR_2 ($I > 2\sigma(I)$)[a]	0.0281/0.0663	0.0359/0.0831
R_1,wR_2 (all data)	0.0342/0.0688	0.0451/0.0870
$\Delta\rho_{max}$ (e/Å^3)	1.736	1.633
$\Delta\rho_{min}$ (e/Å^3)	-2.039	-2.107

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

Table S2. Selected bond lengths (Å) for compounds **1a** and **1b**.

bonds	**1a**	**1b**	bonds	**1a**	**1b**
Cu(1)-I(1)	2.6180(7)	2.6187(10)	Cu(3)-I(2)	2.5603(7)	2.5590(10)
Cu(1)-I(6)	2.6564(8)	2.6560(10)	Cu(3)-I(5)	2.6416(8)	2.6406(10)
Cu(1)-I(2)	2.6828(7)	2.6820(10)	Cu(3)-I(7)	2.7503(9)	2.7515(12)
Cu(1)-I(3)	2.7213(8)	2.7212(10)	Cu(3)-I(3)	2.7961(10)	2.7967(13)
Cu(2)-I(4)	2.6062(7)	2.6058(10)	Cu(4)-I(8)	2.5104(8)	2.5084(11)
Cu(2)-I(1)	2.6747(8)	2.6757(10)	Cu(4)-I(5)	2.5877(9)	2.5879(12)
Cu(2)-I(7)	2.7370(8)	2.7367(11)	Cu(4)-I(7)	2.7773(10)	2.7785(13)
Cu(2)-I(2)	2.7551(8)	2.7549(10)	Cu(4)-I(3)	3.0300(12)	3.0292(16)
Cu(1)-Cu(3)	2.8454(10)	2.8447(14)	Cu(2)-Cu(3)	2.7382(10)	2.7383(13)
Cu(1)-Cu(2)	2.9480(10)	2.9494(13)	Cu(3)-Cu(4)	2.5121(10)	2.5125(13)

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

Cu(1)-I(1)	2.5951(8)	Cu(2)-I(2)	2.7192(9)
Cu(1)-I(2)	2.7199(8)	Cu(2)-I(2)#1	2.7696(10)
Cu(1)-I(3)	2.6510(8)	Cu(2)-I(3)	2.6204(8)
Cu(1)-I(4)	2.6855(9)	Cu(2)-I(4)#2	2.6649(9)

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

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

Cu(1)-I(1)#2	2.5888(12)	Cu(4)-I(8)	2.6387(11)
Cu(1)-I(8)	2.6260(12)	Cu(4)-I(5)	2.6400(11)
Cu(1)-I(4)	2.6490(12)	Cu(4)-I(2)	2.6653(11)
Cu(1)-I(6)	2.8914(14)	Cu(4)-I(7)	2.6662(10)
Cu(2)-I(1)	2.5982(11)	Cu(5)-I(2)#1	2.554(3)
Cu(2)-I(5)	2.6409(11)	Cu(5)-I(3)	2.602(3)
Cu(2)-I(7)	2.6895(11)	Cu(5)-I(2)	2.696(3)
Cu(2)-I(6)#3	2.7638(11)	Cu(5)-I(4)	2.855(3)
Cu(3)-I(5)#2	2.6417(11)	Cu(6A)-I(4)	2.5714(18)
Cu(3)-I(7)	2.6671(11)	Cu(6A)-I(6)	2.711(2)
Cu(3)-I(6)	2.6773(11)	Cu(6A)-I(3)	2.718(2)
Cu(3)-I(8)	2.6896(11)	Cu(6A)-I(2)	2.7361(19)
Cu(3)-Cu(2)#2	2.8493(14)	Cu(1)-Cu(2)#2	2.9622(15)
Cu(3)-Cu(1)	2.9943(16)	Cu(5)-Cu(6A)#1	2.882(3)
Cu(4)-Cu(3)	2.7267(13)	Cu(6A)-Cu(1)	2.986(2)
Cu(4)-Cu(2)	2.7731(14)		

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

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

Cu(1)-Br(1)	2.461(2)	Cu(4)-Br(2)#2	2.432(2)
Cu(1)-Br(5)	2.486(2)	Cu(4)-Br(4)	2.506(2)
Cu(1)-Br(4)	2.502(2)	Cu(4)-Br(8)	2.546(2)
Cu(1)-Br(8)	2.609(2)	Cu(4)-Br(7)#2	2.694(2)
Cu(2)-Br(4)#1	2.484(2)	Cu(5)-Br(6)	2.461(3)
Cu(2)-Br(8)	2.485(3)	Cu(5)-Br(7)	2.578(5)
Cu(2)-Br(7)	2.557(3)	Cu(5)-Br(1)	2.586(4)
Cu(2)-Br(5)	2.619(3)	Cu(5)-Br(3)	2.639(18)
Cu(3)-Br(2)	2.436(2)	Cu(6)-Br(1)	2.513(7)
Cu(3)-Br(5)	2.455(2)	Cu(6)-Br(3)#3	2.567(10)
Cu(3)-Br(6)	2.502(2)	Cu(6)-Br(3)	2.622(10)
Cu(3)-Br(7)	2.913(3)	Cu(6)-Br(6)	2.843(8)
Cu(1)-Cu(2)	2.723(3)	Cu(3)-Cu(5)	2.890(4)
Cu(1)-Cu(4)	2.772(3)	Cu(3)-Cu(4)#1	2.955(3)
Cu(2)-Cu(4)#1	2.798(3)	Cu(5)-Cu(6)#3	2.878(8)

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

Table S6. The hydrogen bonds in compounds **1**-**4**.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
		1		
N(1)-H(1N)···I(4)	0.86	2.77	3.5016	143
N(2)-H(2N)···I(6)	0.86	2.73	3.5045	150
N(3)-H(3)···I(8)	0.86	2.72	3.5271	156
C(6)-H(6)···I(5)	0.93	3.01	3.7357	137
C(14)-H(14)···I(3)	0.93	3.01	3.8911	158
		2		
C(1)-H(1)···I(3)	0.93	2.96	3.7843	149
		3		
N(2)-H(2)···I(8)	0.86	3.00	3.7809	153
C(1)-H(1A)···I(8)	0.93	2.99	3.7985	147
C(6)-H(6)···I(6)	0.93	2.98	3.7318	139
C(12)-H(12A)···I(5)	0.97	3.01	3.9265	158
		4		
N(1)-H(1)···Br(5)	0.86	2.76	3.5346	151
C(1)-H(1A)···Br(5)	0.93	2.76	3.5647	146
C(10)-H(10)···Br(7)	0.93	2.82	3.5609	137
C(12)-H(12A)···Br(4)	0.97	2.85	3.7682	159

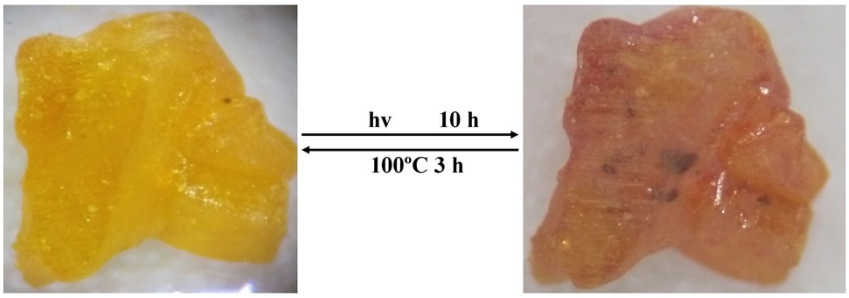

Fig. **S1**. The photochromic behavior of compound **1**.

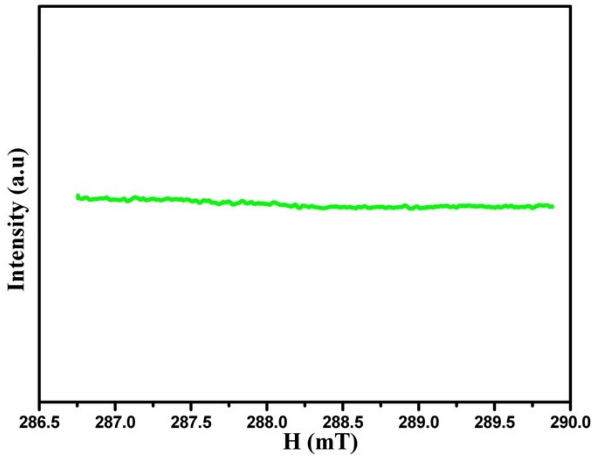

Fig. **S2**. EPR spectra for compound **1** after visible light irradiation.

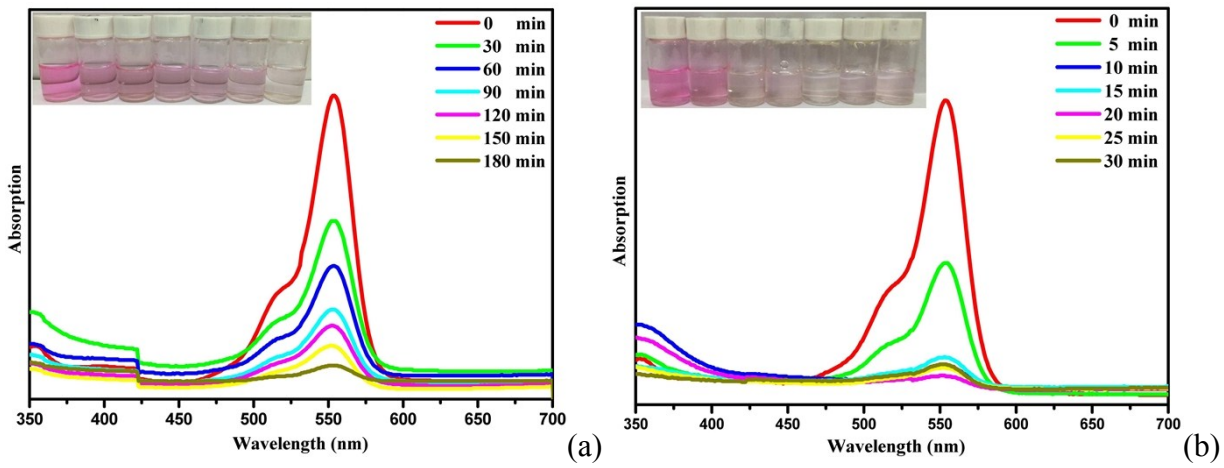

Fig. **S3** The absorption spectra of the RhB solution in the presence of compound **2** (a) and **3** (b) under the visible light irradiation.

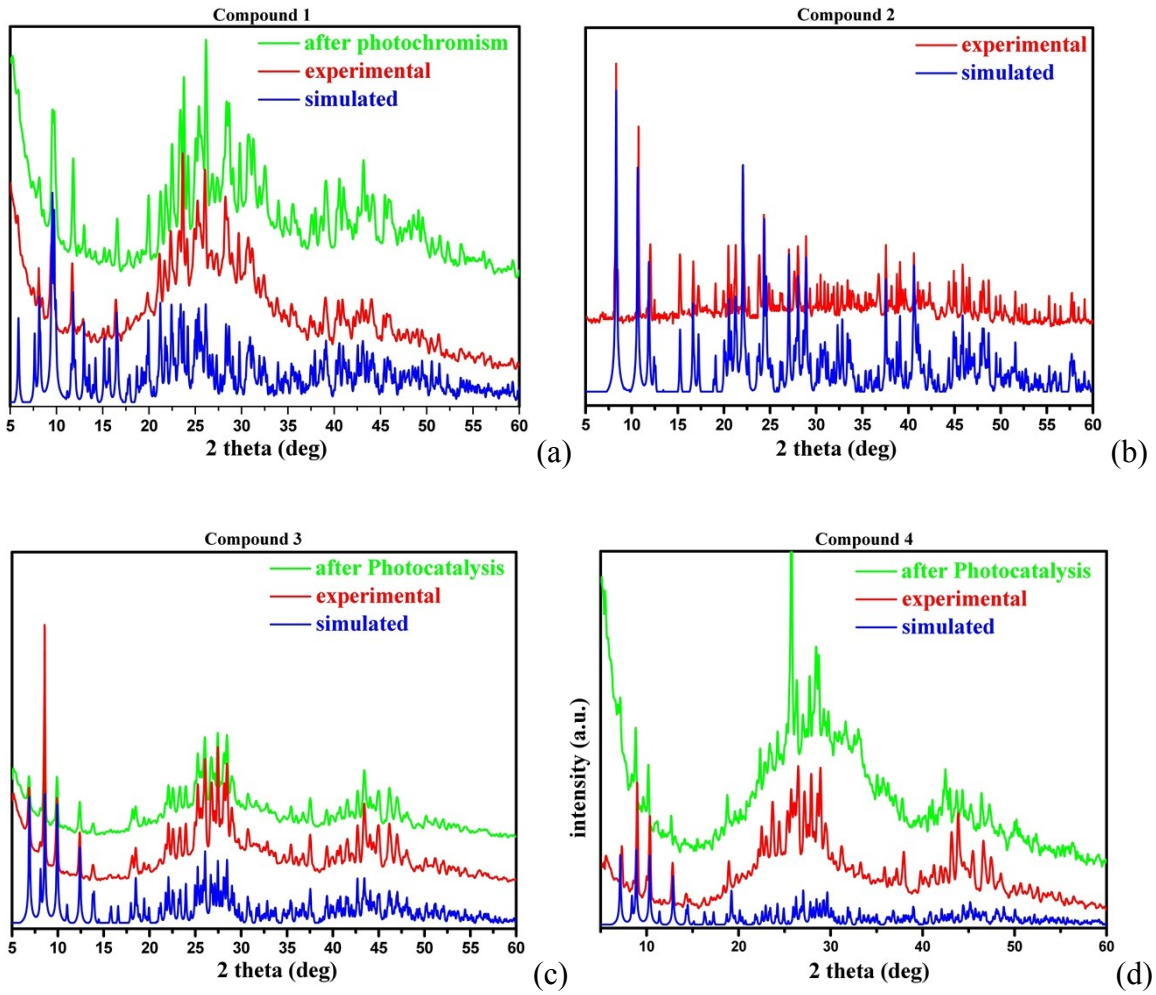

Fig. **S4**. Experimental and simulated XRD powder patterns for compounds **1** (a), **2** (b), **3** (c) and **4** (d).