Electronic Supplementary Information

Syntheses, Structures, photoelectric properties and photocatalysis of iodobismuthate hybrids with lanthanide complex cations

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Table S1. Crystallographic data for **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{24}H_{56}O_8N_8LaBi_2I_9$	$C_{24}H_{56}O_8N_8EuBi_2I_9$	$C_{48}H_{112}O_{16}N_{16}Tb_4Bi_2I_{18}$
Formula weight	2283.73	2296.78	4607.49
Cryst syst	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a (Å)	13.3790(10)	9.9686(14)	15.178(13)
b (Å)	14.8016(12)	22.306(4)	22.45(2)
c (Å)	15.5176(17)	26.361(4)	33.98(3)
α (deg)	88.113(7)	90	90
β (deg)	78.328(6)	97.401(5)	95.06(3)
γ (deg)	71.994(6)	90	90
V (Å^3)	2860.6(5)	5812.8(15)	11534(18)
Z	2	4	4
T (K)	223(2)	293(2)	293(2)
2θ(max) (deg)	50.70	50.70	50.00
Total reflections	22966	73659	188114
Unique reflections	10384	10546	20277
R_{int}	0.0557	0.0776	0.0891
Reflections with [I > 2σ(I)]	7957	9882	17049
No. of parameters	486	425	883
R_1 [I > 2σ(I)]	0.0423	0.0407	0.0672

wR_2 [I > 2σ(I)]	0.0758	0.1236	0.1519
$\Delta\rho$ / e Å^{-3}	2.089/ –2.414	1.965/−2.174	3.149/ –2.537
GOF on F^2	0.899	1.099	1.160

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

La(1)–O(1)	2.493(8)	La(1)–O(2)	2.435(6)
La(1)–O(3)	2.505(6)	La(1)–O(4)	2.460(7)
La(1)–O(5)	2.496(6)	La(1)–O(6)	2.502(9)
La(1)–O(7)	2.536(6)	La(1)–O(8)	2.431(6)
Bi(1)–I(1)	3.2289(8)	Bi(1)–I(2)	3.2255(8)
Bi(1)–I(3)	3.2365(7)	Bi(1)–I(4)	2.9628(8)
Bi(1)–I(5)	2.9461(7)	Bi(1)–I(6)	2.9927(8)
Bi(2)–I(1)	3.2134(7)	Bi(2)–I(2)	3.1661(8)
Bi(2)–I(3)	3.2464(9)	Bi(2)–I(7)	2.9418(10)
Bi(2)–I(8)	3.0272(7)	Bi(2)–I(9)	2.9619(7)
O(1)–La(1)–O(2)	75.6(3)	O(1)–La(1)–O(3)	75.5(2)
O(1)–La(1)–O(4)	74.0(3)	O(1)–La(1)–O(5)	143.7(2)
O(1)–La(1)–O(6)	137.3(2)	O(1)–La(1)–O(7)	121.6(3)
O(1)–La(1)–O(8)	70.3(2)	O(2)–La(1)–O(3)	76.8(2)
O(2)–La(1)–O(4)	144.3(3)	O(2)–La(1)–O(5)	115.6(3)
O(2)–La(1)–O(6)	70.7(3)	O(2)–La(1)–O(7)	139.7(3)
O(2)–La(1)–O(8)	85.8(2)	O(3)–La(1)–O(4)	77.8(2)
O(3)–La(1)–O(5)	74.2(2)	O(3)–La(1)–O(6)	119.9(3)
O(3)–La(1)–O(7)	139.9(2)	O(3)–La(1)–O(8)	144.5(2)
O(4)–La(1)–O(5)	80.5(3)	O(4)–La(1)–O(6)	144.7(3)
O(4)–La(1)–O(7)	73.9(3)	O(4)–La(1)–O(8)	100.9(2)
O(5)–La(1)–O(6)	76.4(3)	O(5)–La(1)–O(7)	73.6(2)
O(5)–La(1)–O(8)	141.2(2)	O(6)–La(1)–O(7)	74.2(3)
O(6)–La(1)–O(8)	81.6(3)	O(7)–La(1)–O(8)	69.8(2)
I(1)–Bi(1)–I(2)	81.00(2)	I(1)–Bi(1)–I(3)	83.44(2)
I(1)–Bi(1)–I(4)	171.70(2)	I(1)–Bi(1)–I(5)	91.26(2)
I(1)–Bi(1)–I(6)	90.92(2)	I(2)–Bi(1)–I(3)	80.711(19)
I(2)–Bi(1)–I(4)	91.25(2)	I(2)–Bi(1)–I(5)	93.34(2)
I(2)–Bi(1)–I(6)	170.43(2)	I(3)–Bi(1)–I(4)	92.44(2)
I(3)–Bi(1)–I(5)	172.56(3)	I(3)–Bi(1)–I(6)	93.35(2)
I(4)–Bi(1)–I(5)	92.14(2)	I(4)–Bi(1)–I(6)	96.52(3)
I(5)–Bi(1)–I(6)	91.94(2)	I(1)–Bi(2)–I(2)	82.145(19)
I(1)–Bi(2)–I(3)	83.53(2)	I(1)–Bi(2)–I(7)	90.92(2)
I(1)–Bi(2)–I(8)	87.787(19)	I(1)–Bi(2)–I(9)	175.38(2)
I(2)–Bi(2)–I(3)	81.45(2)	I(2)–Bi(2)–I(7)	93.43(2)
I(2)–Bi(2)–I(8)	166.75(2)	I(2)–Bi(2)–I(9)	94.29(2)

I(3)–Bi(2)–I(7)	172.90(2)	I(3)–Bi(2)–I(8)	88.90(2)
I(3)–Bi(2)–I(9)	93.06(2)	I(7)–Bi(2)–I(8)	95.34(3)
I(7)–Bi(2)–I(9)	92.23(3)	I(8)–Bi(2)–I(9)	95.28(2)
Bi(1)–I(1)–Bi(2)	81.381(18)	Bi(1)–I(2)–Bi(2)	82.158(18)
Bi(1)–I(3)–Bi(2)	80.765(19)		

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

Eu(1)–O(1)	2.423(7)	Eu(1)–O(2)	2.384(7)
Eu(1)–O(3)	2.382(7)	Eu(1)–O(4)	2.414(9)
Eu(1)–O(5)	2.422(7)	Eu(1)–O(6)	2.344(7)
Eu(1)–O(7)	2.378(9)	Eu(1)–O(8)	2.448(7)
Bi(1)–I(1)	3.2069(8)	Bi(1)–I(2)	3.3046(8)
Bi(1)–I(3)	3.2348(8)	Bi(1)–I(4)	2.9792(8)
Bi(1)–I(5)	2.9405(9)	Bi(1)–I(6)	2.9760(9)
Bi(2)–I(1)	3.1664(7)	Bi(2)–I(2)	3.2374(8)
Bi(2)–I(3)	3.2565(8)	Bi(2)–I(7)	2.9676(8)
Bi(2)–I(8)	2.9596(8)	Bi(2)–I(9)	3.0025(8)
O(1)–Eu(1)–O(2)	75.5(3)	O(1)–Eu(1)–O(3)	72.6(2)
O(1)–Eu(1)–O(4)	130.2(4)	O(1)–Eu(1)–O(5)	130.8(3)
O(1)–Eu(1)–O(6)	142.4(2)	O(1)–Eu(1)–O(7)	76.2(3)
O(1)–Eu(1)–O(8)	72.5(2)	O(2)–Eu(1)–O(3)	95.7(3)
O(2)–Eu(1)–O(4)	72.9(3)	O(2)–Eu(1)–O(5)	145.0(3)
O(2)–Eu(1)–O(6)	90.4(3)	O(2)–Eu(1)–O(7)	141.4(3)
O(2)–Eu(1)–O(8)	74.9(3)	O(3)–Eu(1)–O(4)	73.4(3)
O(3)–Eu(1)–O(5)	76.1(3)	O(3)–Eu(1)–O(6)	144.5(2)
O(3)–Eu(1)–O(7)	100.4(3)	O(3)–Eu(1)–O(8)	145.1(2)
O(4)–Eu(1)–O(5)	72.2(3)	O(4)–Eu(1)–O(6)	75.1(3)
O(4)–Eu(1)–O(7)	145.5(3)	O(4)–Eu(1)–O(8)	131.8(3)
O(5)–Eu(1)–O(6)	79.0(2)	O(5)–Eu(1)–O(7)	73.4(3)
O(5)–Eu(1)–O(8)	129.8(3)	O(6)–Eu(1)–O(7)	96.2(3)
O(6)–Eu(1)–O(8)	70.1(2)	O(7)–Eu(1)–O(8)	71.8(3)
Bi(1)–I(1)–Bi(2)	83.23(2)	Bi(1)–I(2)–Bi(2)	80.63(2)
Bi(1)–I(3)–Bi(2)	81.39(2)	I(1)–Bi(1)–I(3)	80.71(2)
I(1)–Bi(1)–I(2)	83.45(2)	I(1)–Bi(1)–I(5)	88.39(2)
I(1)–Bi(1)–I(4)	91.42(2)	I(2)–Bi(1)–I(3)	79.77(2)
I(1)–Bi(1)–I(6)	171.74(2)	I(2)–Bi(1)–I(5)	171.84(2)
I(2)–Bi(1)–I(4)	85.89(2)	I(3)–Bi(1)–I(4)	164.31(2)
I(2)–Bi(1)–I(6)	97.54(3)	I(3)–Bi(1)–I(6)	91.38(3)
I(3)–Bi(1)–I(5)	99.35(3)	I(4)–Bi(1)–I(6)	96.83(2)
I(4)–Bi(1)–I(5)	93.94(3)	I(1)–Bi(2)–I(2)	85.19(2)
I(5)–Bi(1)–I(6)	90.59(3)	I(1)–Bi(2)–I(7)	85.03(2)

I(1)–Bi(2)–I(3)	80.98(2)	I(1)–Bi(2)–I(9)	174.63(2)
I(1)–Bi(2)–I(8)	92.28(2)	I(2)–Bi(2)–I(7)	92.09(2)
I(2)–Bi(2)–I(3)	80.45(2)	I(2)–Bi(2)–I(9)	89.68(2)
I(2)–Bi(2)–I(8)	171.82(2)	I(3)–Bi(2)–I(8)	91.48(2)
I(3)–Bi(2)–I(7)	164.62(2)	I(7)–Bi(2)–I(8)	95.45(2)
I(3)–Bi(2)–I(9)	99.77(2)	I(8)–Bi(2)–I(9)	93.02(3)
I(7)–Bi(2)–I(9)	93.58(2)		

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

Bi(1)–I(1)	3.224(2)	Bi(1)–I(2)	3.279(2)
Bi(1)–I(3)	3.221(3)	Bi(1)–I(4A)	2.993(3)
Bi(1)–I(4B)	2.952(16)	Bi(1)–I(5A)	2.949(3)
Bi(1)–I(5B)	3.118(16)	Bi(1)–I(6)	2.951(2)
Bi(2)–I(1)	3.167(2)	Bi(2)–I(2)	3.177(2)
Bi(2)–I(3)	3.288(3)	Bi(2)–I(7)	3.009(2)
Bi(2)–I(8)	2.998(2)	Bi(2)–I(9)	2.963(2)
Bi(3)–I(10)	3.208(2)	Bi(3)–I(11)	3.253(2)
Bi(3)–I(12)	3.205(3)	Bi(3)–I(13)	2.976(2)
Bi(3)–I(14)	2.997(2)	Bi(3)–I(15)	2.980(3)
Bi(4A)–I(10)	3.265(2)	Bi(4A)–I(11)	3.247(3)
Bi(4A)–I(12)	3.199(3)	Bi(4A)–I(16)	2.951(3)
Bi(4A)–I(17)	2.975(2)	Bi(4A)–I(18)	2.983(3)
Bi(4B)–I(10)	3.252(13)	Bi(4B)–I(11)	2.867(11)
Bi(4B)–I(12)	3.023(13)	Bi(4B)–I(16)	3.316(11)
Bi(4B)–I(17)	3.003(13)	Bi(4B)–I(18)	3.148(12)
Tb(1)–O(1)	2.387(12)	Tb(1)–O(2)	2.361(14)
Tb(1)–O(3)	2.349(14)	Tb(1)–O(4)	2.367(13)
Tb(1)–O(5)	2.437(13)	Tb(1)–O(6)	2.343(11)
Tb(1)–O(7)	2.333(13)	Tb(1)–O(8)	2.331(16)
Tb(2)–O(9)	2.355(13)	Tb(2)–O(10)	2.362(14)
Tb(2)–O(11)	2.456(13)	Tb(2)–O(12)	2.345(13)
Tb(2)–O(13)	2.333(13)	Tb(2)–O(14)	2.425(13)
Tb(2)–O(15)	2.331(12)	Tb(2)–O(16)	2.417(14)
I(1)–Bi(1)–I(2)	81.02(7)	I(1)–Bi(1)–I(3)	84.01(6)
I(1)–Bi(1)–I(4A)	89.71(7)	I(1)–Bi(1)–I(4B)	105.9(4)
I(1)–Bi(1)–I(5A)	172.60(6)	I(1)–Bi(1)–I(5B)	161.7(4)
I(1)–Bi(1)–I(6)	87.37(8)	I(2)–Bi(1)–I(3)	78.73(7)
I(2)–Bi(1)–I(4A)	95.09(7)	I(2)–Bi(1)–I(4B)	106.7(4)
I(2)–Bi(1)–I(5A)	93.18(9)	I(2)–Bi(1)–I(5B)	106.1(4)
I(2)–Bi(1)–I(6)	165.47(4)	I(3)–Bi(1)–I(4A)	171.78(5)

I(3)–Bi(1)–I(4B)	169.2(5)	I(3)–Bi(1)–I(5A)	90.37(7)
I(3)–Bi(1)–I(5B)	81.0(4)	I(3)–Bi(1)–I(6)	91.45(7)
I(4A)–Bi(1)–I(4B)	18.8(5)	I(4A)–Bi(1)–I(5A)	95.42(7)
I(4A)–Bi(1)–I(5B)	106.1(4)	I(4A)–Bi(1)–I(6)	93.56(7)
I(4B)–Bi(1)–I(5A)	80.1(4)	I(4B)–Bi(1)–I(5B)	88.4(6)
I(4B)–Bi(1)–I(6)	84.8(3)	I(5A)–Bi(1)–I(5B)	17.9(4)
I(5A)–Bi(1)–I(6)	97.61(9)	I(5B)–Bi(1)–I(6)	82.6(4)
I(1)–Bi(2)–I(2)	83.52(7)	I(1)–Bi(2)–I(3)	83.85(7)
I(1)–Bi(2)–I(7)	174.55(4)	I(1)–Bi(2)–I(8)	84.70(7)
I(1)–Bi(2)–I(9)	93.20(7)	I(2)–Bi(2)–I(3)	79.23(7)
I(2)–Bi(2)–I(7)	93.77(8)	I(2)–Bi(2)–I(8)	167.56(4)
I(2)–Bi(2)–I(9)	91.19(7)	I(3)–Bi(2)–I(7)	91.01(7)
I(3)–Bi(2)–I(8)	95.56(6)	I(3)–Bi(2)–I(9)	170.22(4)
I(7)–Bi(2)–I(8)	97.63(8)	I(7)–Bi(2)–I(9)	91.58(7)
I(8)–Bi(2)–I(9)	93.43(6)	I(10)–Bi(3)–I(11)	80.80(7)
I(10)–Bi(3)–I(12)	82.84(6)	I(10)–Bi(3)–I(13)	91.68(8)
I(10)–Bi(3)–I(14)	169.78(4)	I(10)–Bi(3)–I(15)	87.31(6)
I(11)–Bi(3)–I(12)	81.41(7)	I(11)–Bi(3)–I(13)	165.23(4)
I(11)–Bi(3)–I(14)	88.99(8)	I(11)–Bi(3)–I(15)	99.14(7)
I(12)–Bi(3)–I(13)	85.06(7)	I(12)–Bi(3)–I(14)	95.53(6)
I(12)–Bi(3)–I(15)	169.93(5)	I(13)–Bi(3)–I(14)	98.23(8)
I(13)–Bi(3)–I(15)	93.15(7)	I(14)–Bi(3)–I(15)	94.54(6)
I(10)–Bi(4A)–I(11)	80.03(7)	I(10)–Bi(4A)–I(12)	82.04(7)
I(10)–Bi(4A)–I(16)	87.97(7)	I(10)–Bi(4A)–I(17)	173.57(6)
I(10)–Bi(4A)–I(18)	93.72(8)	I(11)–Bi(4A)–I(12)	81.58(7)
I(11)–Bi(4A)–I(16)	165.70(5)	I(11)–Bi(4A)–I(17)	96.01(8)
I(11)–Bi(4A)–I(18)	89.55(7)	I(12)–Bi(4A)–I(16)	89.12(7)
I(12)–Bi(4A)–I(17)	92.40(8)	I(12)–Bi(4A)–I(18)	170.70(6)
I(16)–Bi(4A)–I(17)	95.21(8)	I(16)–Bi(4A)–I(18)	99.03(7)
I(17)–Bi(4A)–I(18)	91.30(8)	I(10)–Bi(4B)–I(11)	86.1(3)
I(10)–Bi(4B)–I(12)	85.0(3)	I(10)–Bi(4B)–I(16)	82.3(3)
I(10)–Bi(4B)–I(17)	169.8(4)	I(10)–Bi(4B)–I(18)	90.9(3)
I(11)–Bi(4B)–I(12)	91.3(3)	I(11)–Bi(4B)–I(16)	168.3(5)
I(11)–Bi(4B)–I(17)	104.1(4)	I(11)–Bi(4B)–I(18)	93.7(4)
I(12)–Bi(4B)–I(16)	85.7(3)	I(12)–Bi(4B)–I(17)	95.4(4)
I(12)–Bi(4B)–I(18)	173.4(4)	I(16)–Bi(4B)–I(17)	87.5(3)
I(16)–Bi(4B)–I(18)	88.5(3)	I(17)–Bi(4B)–I(18)	87.6(3)
Bi(1)–I(1)–Bi(2)	82.74(8)	Bi(1)–I(2)–Bi(2)	81.70(7)
Bi(1)–I(3)–Bi(2)	80.92(8)	Bi(1)–I(4A)–Bi(4B)	78.2(10)
Bi(1)–I(4B)–Bi(4A)	83.0(10)	Bi(1)–I(5A)–Bi(5B)	91.0(9)
Bi(1)–I(5B)–Bi(5A)	71.1(9)	Bi(3)–I(10)–Bi(4A)	82.00(8)
Bi(3)–I(10)–Bi(4B)	75.3(2)	Bi(4A)–I(10)–Bi(4B)	7.26(18)

Bi(4A)–I(11)–Bi(4B)	3.0(3)	Bi(3)–I(11)–Bi(4A)	81.57(7)
Bi(3)–I(11)–Bi(4B)	80.0(3)	Bi(4A)–I(12)–Bi(4B)	6.9(2)
Bi(3)–I(12)–Bi(4A)	83.07(8)	Bi(3)–I(12)–Bi(4B)	78.5(2)
Bi(4A)–I(16)–Bi(4B)	3.5(2)	Bi(4A)–I(17)–Bi(4B)	7.9(2)
Bi(4A)–I(18)–Bi(4B)	7.1(2)	O(1)–Tb(1)–O(2)	75.1(5)
O(1)–Tb(1)–O(3)	77.1(5)	O(1)–Tb(1)–O(4)	72.7(4)
O(1)–Tb(1)–O(5)	116.9(5)	O(1)–Tb(1)–O(6)	72.7(4)
O(1)–Tb(1)–O(7)	144.2(5)	O(1)–Tb(1)–O(8)	141.9(5)
O(2)–Tb(1)–O(3)	71.4(5)	O(2)–Tb(1)–O(4)	78.7(5)
O(2)–Tb(1)–O(5)	140.9(5)	O(2)–Tb(1)–O(6)	141.5(5)
O(2)–Tb(1)–O(7)	119.0(5)	O(2)–Tb(1)–O(8)	75.2(6)
O(3)–Tb(1)–O(4)	141.9(5)	O(3)–Tb(1)–O(5)	145.4(5)
O(3)–Tb(1)–O(6)	81.4(5)	O(3)–Tb(1)–O(7)	77.2(5)
O(3)–Tb(1)–O(8)	114.7(6)	O(4)–Tb(1)–O(5)	71.1(5)
O(4)–Tb(1)–O(6)	110.4(5)	O(4)–Tb(1)–O(7)	139.5(5)
O(4)–Tb (1)–O(8)	78.6(5)	O(5)–Tb(1)–O(6)	74.1(5)
O(5)–Tb(1)–O(7)	74.4(5)	O(5)–Tb(1)–O(8)	75.0(6)
O(6)–Tb(1)–O(7)	79.1(4)	O(6)–Tb(1)–O(8)	142.4(5)
O(7)–Tb(1)–O(8)	72.5(5)	O(9)–Tb(2)–O(10)	72.5(5)
O(9)–Tb(2)–O(11)	74.4(5)	O(9)–Tb(2)–O(12)	80.7(5)
O(9)–Tb(2)–O(13)	141.5(5)	O(9)–Tb(2)–O(14)	142.3(5)
O(9)–Tb(2)–O(15)	116.2(5)	O(9)–Tb(2)–O(16)	74.3(5)
O(10)–Tb(2)–O(11)	74.9(5)	O(10)–Tb(2)–O(12)	142.0(4)
O(10)–Tb(2)–O(13)	82.2(5)	O(10)–Tb(2)–O(14)	142.2(5)
O(10)–Tb(2)–O(15)	74.2(4)	O(10)–Tb(2)–O(16)	115.0(5)
O(11)–Tb(2)–O(12)	72.3(4)	O(11)–Tb(2)–O(13)	71.3(4)
O(11)–Tb(2)–O(14)	120.5(5)	O(11)–Tb(2)–O(15)	141.7(4)
O(11)–Tb(2)–O(16)	141.8(4)	O(12)–Tb(2)–O(13)	104.4(5)
O(12)–Tb(2)–O(14)	73.0(5)	O(12)–Tb(2)–O(15)	143.2(4)
O(12)–Tb(2)–O(16)	81.7(5)	O(13)–Tb(2)–O(14)	72.6(4)
O(13)–Tb(2)–O(15)	82.7(5)	O(13)–Tb(2)–O(16)	143.9(4)
O(14)–Tb(2)–O(15)	75.1(4)	O(14)–Tb(2)–O(16)	75.6(5)
O(15)–Tb(2)–O(16)	73.1(5)		

Table S5. Hydrogen Bond Lengths (Å) and Angles (deg) for **1**.

D–H···A	d(H···A)	d(D···A)	<(DHA)
C(2)-H(2C)···I(8)#1	3.296	3.891	121.43
C(6)–H(6A)···I(1)	3.326	4.203	151.20
C(6)–H(6A)···I(2)	3.181	3.784	121.90
C(10)–H(10)···I(8)#2	3.036	3.970	172.65
C(12)–H(12C)···I(6)#2	3.023	3.953	160.94
C(14)–H(14A)···I(7)#3	3.206	3.991	139.12
C(14)–H(14C)···I(8)#2	3.260	4.152	153.68
C(16)–H(16)···I(5)	3.284	4.179	159.89
C(18)–H(18C)··· I(5)	3.185	4.119	162.24
C(20)–H(20A)···I(8)#2	3.213	4.156	164.44
C(21)–H(21C)···I(6)#4	3.214	3.808	121.19
C(23)–H(23A)···I(9)#5	3.196	4.052	147.99
C(23)–H(23B)···I(4)#6	3.329	3.893	119.00
Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+1; #2 -x, -y+1, -z+1; #3 x-1, y, z; #4 -x, -y, -z+1; #5 -x+1, -y, -z+1; #6 x, y, z-1.			

Table S6. Hydrogen Bond Lengths (Å) and Angles (deg) for **2**.

D–H···A	d(H···A)	d(D···A)	<(DHA)
C(1)–H(1)···I(1)#1	3.284	4.153	156.37
C(4)–H(4)···I(3)	3.276	4.102	149.09
C(6)–H(6A)···I(3)	3.282	4.176	155.76
C(8)–H(8A)···I(3)	3.283	4.009	133.88
C(9)–H(9A)···I(5)#2	3.280	3.997	132.98
C(9)–H(9B)···I(7)#1	3.236	4.146	158.85
C(12A)–H(12C)···I(6)#2	3.280	3.986	131.89
C(15)–H(15A)···I(4)#3	3.203	4.148	168.46
C(16)–H(16)···I(2)#3	3.313	3.976	130.12
C(17)–H(17B)···I(2)#4	3.196	4.133	165.89
C(19)–H(19)···I(2)#3	3.307	4.153	152.31
C(21B)–H(21A)···I(9)#5	3.326	4.719	146.59
C(21A)–H(21B)···I(7)#5	3.179	4.000	144.50
C(21B)–H(21B)···I(7)#5	3.179	3.994	169.12
C(21A)–H(21C)···I(7)#3	3.180	3.889	132.00
C(21B)–H(21C)···I(7)#3	3.180	4.174	166.99
C(24)–H(24B)···I(9)#4	3.222	4.158	165.41

C(24)–H(24C)···I(9)#5	3.240	4.150	158.98
Symmetry transformations used to generate equivalent atoms: #1 x+1, y, z; #2 -x+1, y-1/2, -z+1/2; #3 x+1, -y+3/2, z+1/2; #4 x, -y+3/2, z+1/2; #5 -x+1, y+1/2, -z+1/2.			

Table S7. Hydrogen Bond Lengths (Å) and Angles (deg) for **3**.

D–H···A	d(H···A)	d(D···A)	<(DHA)
C(5)–H(5C)···I(5B)#2	2.712	3.635	161.33
C(8)–H(8C)···I(15)#3	3.302	4.024	133.61
C(11)–H(11B)···O(9)#1	2.624	3.504	152.61
C(12)–H(12B)···I(12)#1	3.043	3.799	136.65
C(15)–H(15A)···I(15)#4	3.193	4.041	148.25
C(15)–H(15C)···I(16)#3	3.258	4.217	176.70
C(16)–H(16)··I(10)#3	3.188	3.946	139.96
C(17A)–H(17A)···I(4A)#4	3.165	4.093	163.00
C(17B)–H(17B)··· I(2)#4	3.328	4.002	145.12
C(17A)–H(17C)··· I(12)#3	3.068	3.979	158.85
C(17A)–H(17D)··· I(2)#4	3.142	3.729	137.16
C(17B)–H(17D)··· I(2)#4	3.142	4.002	149.98
C(17B)–H(17F)··· I(12)#3	3.271	4.167	156.05
C(19)–H(19)···I(10)#3	3.157	4.056	163.12
C(20)–H(20B)···I(13)#4	3.160	3.940	139.48
C(22)–H(22)···I(3)#2	3.229	4.137	165.86
C(23B)–H(23A)···I(8)#2	3.268	3.784	151.17
C(23A)–H(23C)···I(7)#2	3.108	3.958	148.37
C(23B)–H(23D)···I(11)#1	3.044	3.815	138.33
C(25)–H(25)···I(1)#5	3.130	3.970	151.15
C(26)–H(26C)···I(8)#6	3.329	4.076	136.16
C(27)–H(27B)···I(7)#6	3.283	3.854	119.99
C(32A)–H(32A)···I(7)#2	3.326	4.019	130.78
C(32A)–H(32D)···N(13)	2.566	3.868	174.90
C(32B)–H(32D)···N(13)	2.566	3.421	135.67
C(33)–H(33B)···I(13)#4	3.182	3.994	143.40
C(35)–H(35B)···I(10)#3	3.165	4.016	148.72
C(35)–H(35C)···I(8)#5	3.258	4.012	136.76
C(39)–H(39A)···I(3)#2	3.292	4.024	134.50
C(39)–H(39A)···I(7)#2	3.148	3.900	136.41
C(41)–H(41B)···I(4B)	3.103	4.010	158.07
C(44)–H(44C)···I(2)#2	3.257	4.071	143.75
C(47)–H(47B)···I(4A)#5	3.329	4.274	168.45
C(48)–H(48A)···I(4B)	2.905	3.681	138.67

Symmetry transformations used to generate equivalent atoms: #1 x-1/2, -y+1/2, z+1/2; #2 -x+1, -y+1, -z+1; #3 x+1/2, -y+1/2, z+1/2; #4 -x+3/2, y-1/2, -z+3/2; #5 -x+2, -y+1, -z+1; #6 x, y-1, z.

Table S8. Summary of Catalytic Activities of Some Iodobismuthate Hybrids with Different Cations in Photodegradation of Organic

Compounds	organic dyes	light source	irradiation time	band gaps of hybrids	degradation ratio	Ref.
$(CH_3NH_3)_3Bi_2I_9$	[c]MB	halogen lamp	120 min	1.94 eV	83%	1
	[d]RhB	halogen lamp	120 min	1.94 eV	97%	
[a] $[Me_3TPT]_2[Bi_6I_{24}]$	[e]MO	Xe lamp	50 min	2.07 eV	93%	2
$(MePh_3P)_3[Bi_3I_{12}]$	MB	UV light	60 min	1.97 eV	62%	3
$(Ph_4P)_3[Bi_3I_{12}]$	MB	UV light	60 min	2.08 eV	55%	
[b] $\{[did](Bi_2I_8)(BiI_5)\}$	MB	Xe lamp	150 min	2.82 eV	51%	4
$\{[(BiI_6)I_{13}]\cdot 2I_3\cdot(H\text{-}BPA)_4\}_n$	RhB	Xe lamp	120 min	2.64 eV	92%	5
$[NH_4][Ni(phen)_3]BiI_6$	[f]CV	visible-light	25 min	2.09 eV	100%	6
$[Ti_{12}O_{15}(O^iPr)_{17}]_3[Bi_3I_{12}]$	RhB	Xe lamp	30 min	2.15 eV	90%	7
$[Ti_{12}O_{14}(O^iPr)_{18}][Bi_4I_{14}(THF)_2]$	RhB	Xe lamp	30 min	2.03 eV	97%	
$[Ti_{12}O_{14}(O^iPr)_{18}][Ti_{11}BO_{14}(O^iPr)_{17}]$ - $[Bi_6I_{22}]$	RhB	Xe lamp	30 min	1.95 eV	94%	

[a] TPT = 2,4,6-tri(4-pyridyl)-1,3,5-triazine, [b] did = did^{2+} = (1^2z, 5^2z)-1^1H, 5^1H-1, 5(1, 3)-diimidazol-3-iuma-3, 7(1,2)-dibenzenacyclooctaphane-1^3, 5^3-diium, [c]MB= methylene blue, [d] RhB = rhodamine B, [e]MO=methyl orange, [f]CV= crystal violet.

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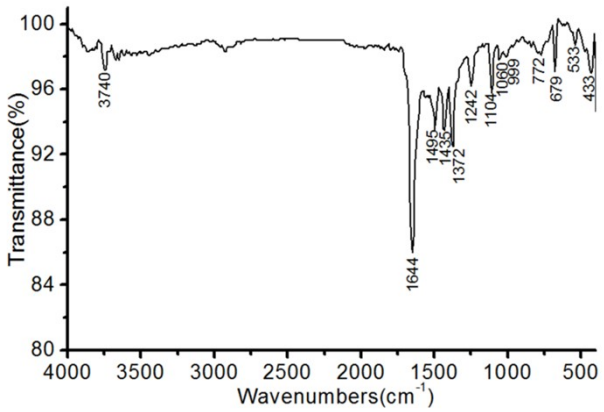


Fig. S1 IR spectrum of **1**.

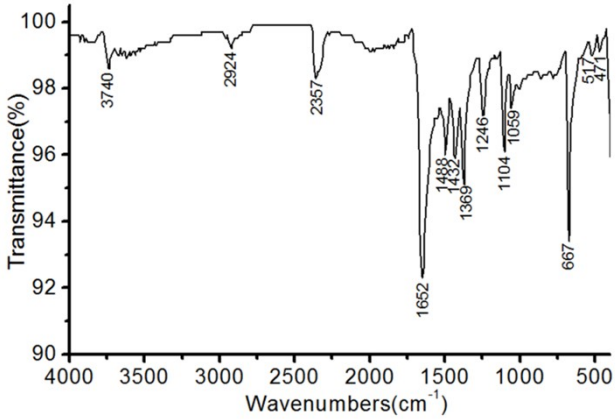


Fig. S2 IR spectrum of **2**.

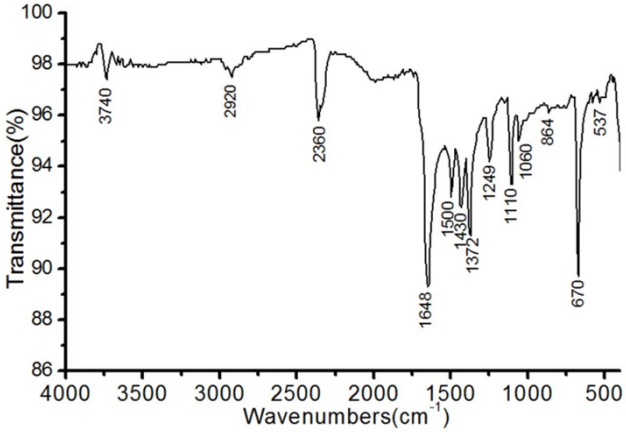


Fig. S3 IR spectrum of **3**.

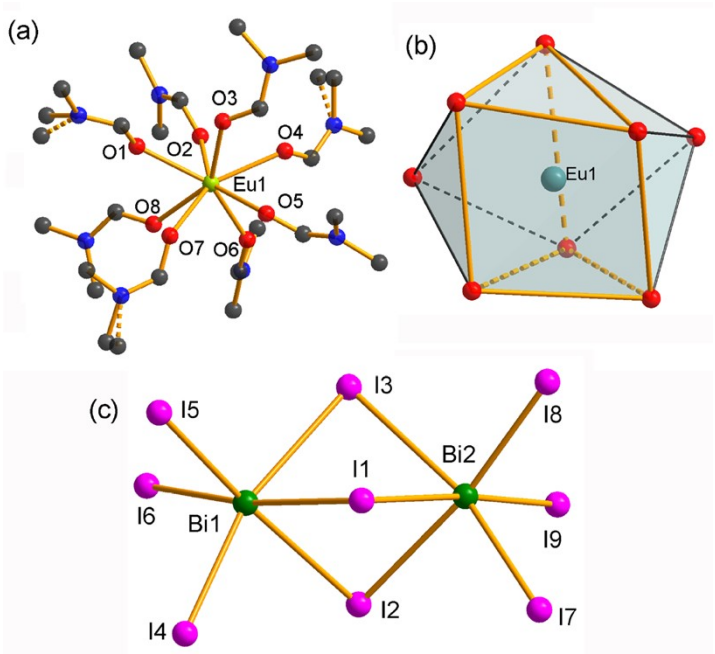


Fig. S4 Structural diagrams for **2**: (a) $[Eu(DMF)_8]^{3+}$ cation, (b) distorted bicapped triangular prism EuO_8 of $[Eu(DMF)_8]^{3+}$, and (c) $[Bi_2I_9]^{3-}$ anion.

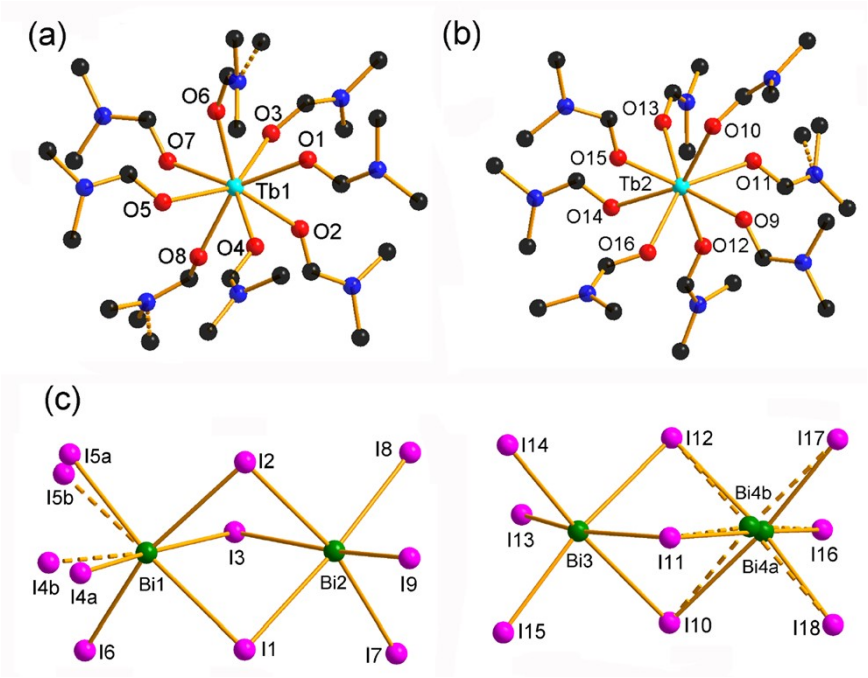


Fig. S5 Structural diagrams of $[Tb(DMF)_8]^{3+}$ cations (a, b), and $[Bi_2I_9]^{3-}$ anions (c) for **3**.

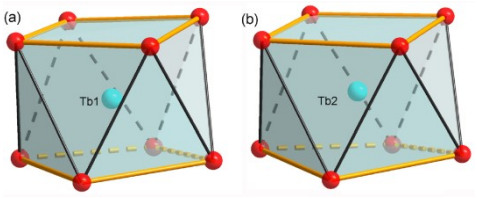


Fig. S6 Distorted square antiprisms TbO_8 of $[Tb(1)(DMF)_8]^{3+}$ (a), and $[Tb(2)(DMF)_8]^{3+}$ (b) in compound **3**.

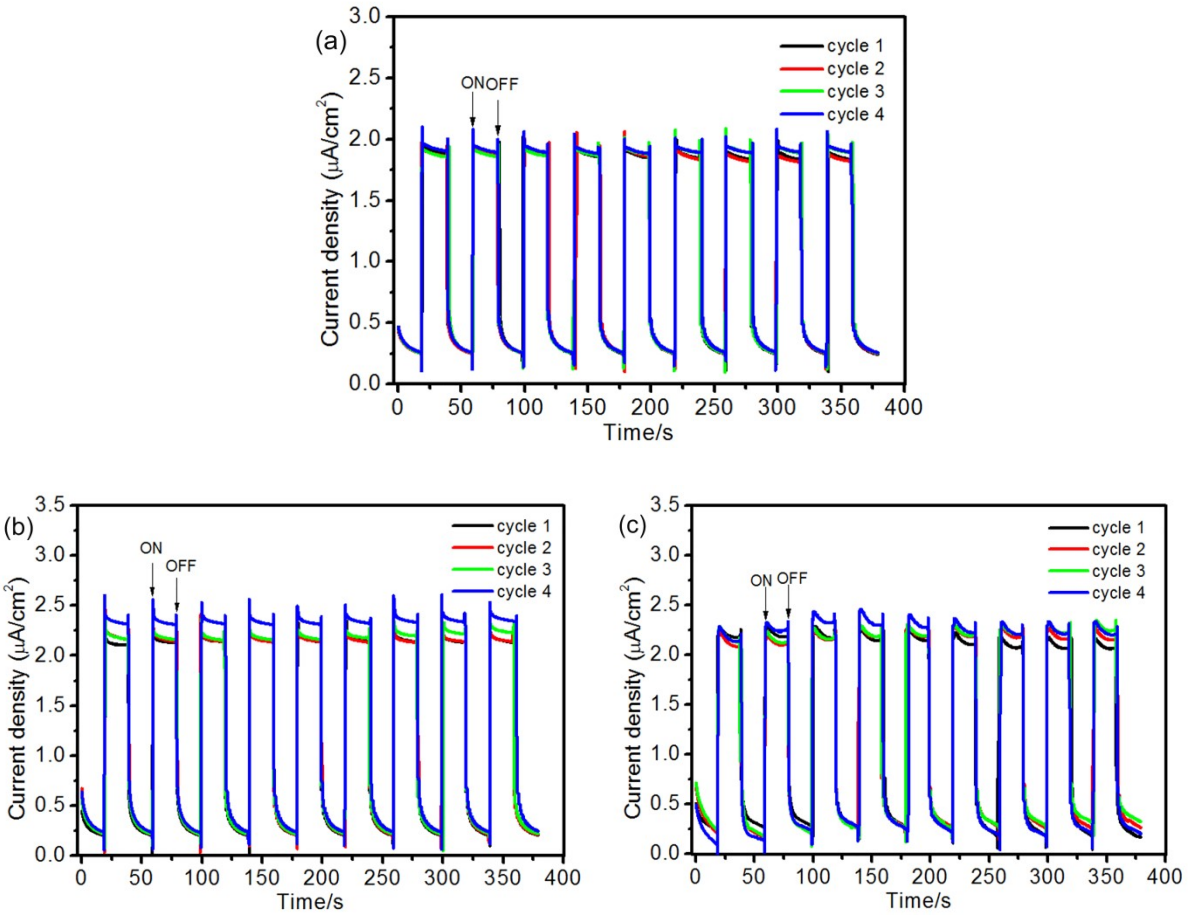


Fig. S7 Photocurrent responses of four successive measurements on compounds **1** (a), **2** (b), and **3** (c).

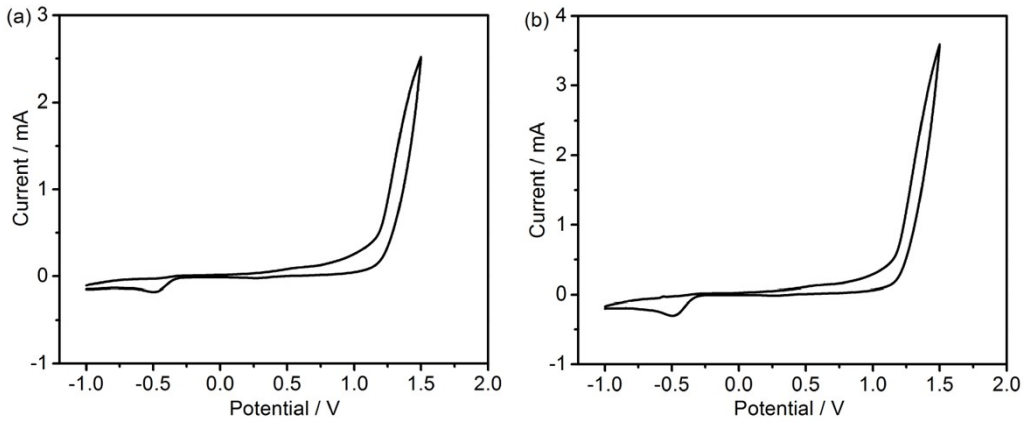


Fig. S8 Cyclic voltammograms of blank (a), and compound **1** (b) in DMF solution with a scan rate of 50 mV/s

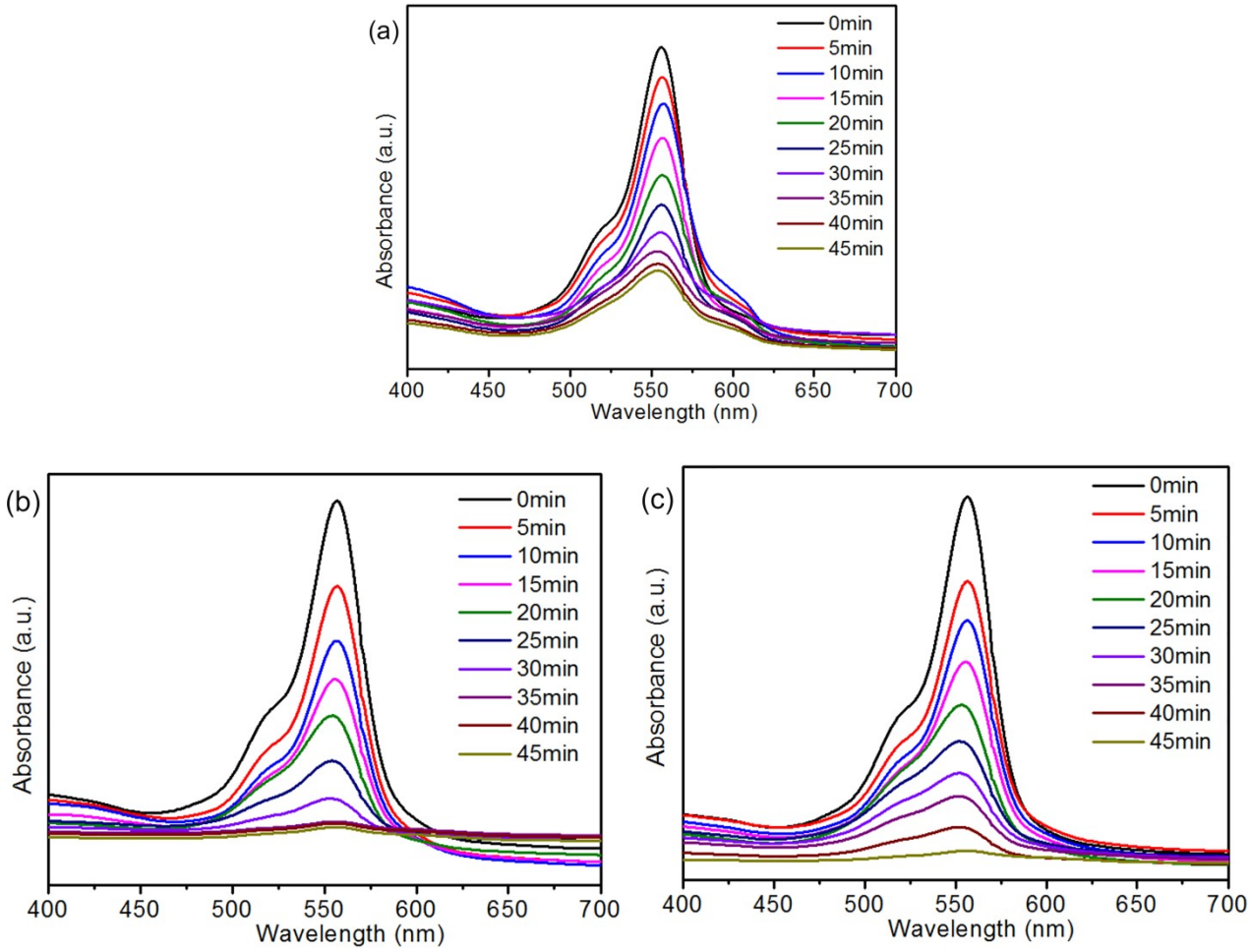


Fig. S9 Time dependent absorption spectra of RhB solutions in photodegradation reactions over compounds **1** (a), **2** (b) and **3** (c).

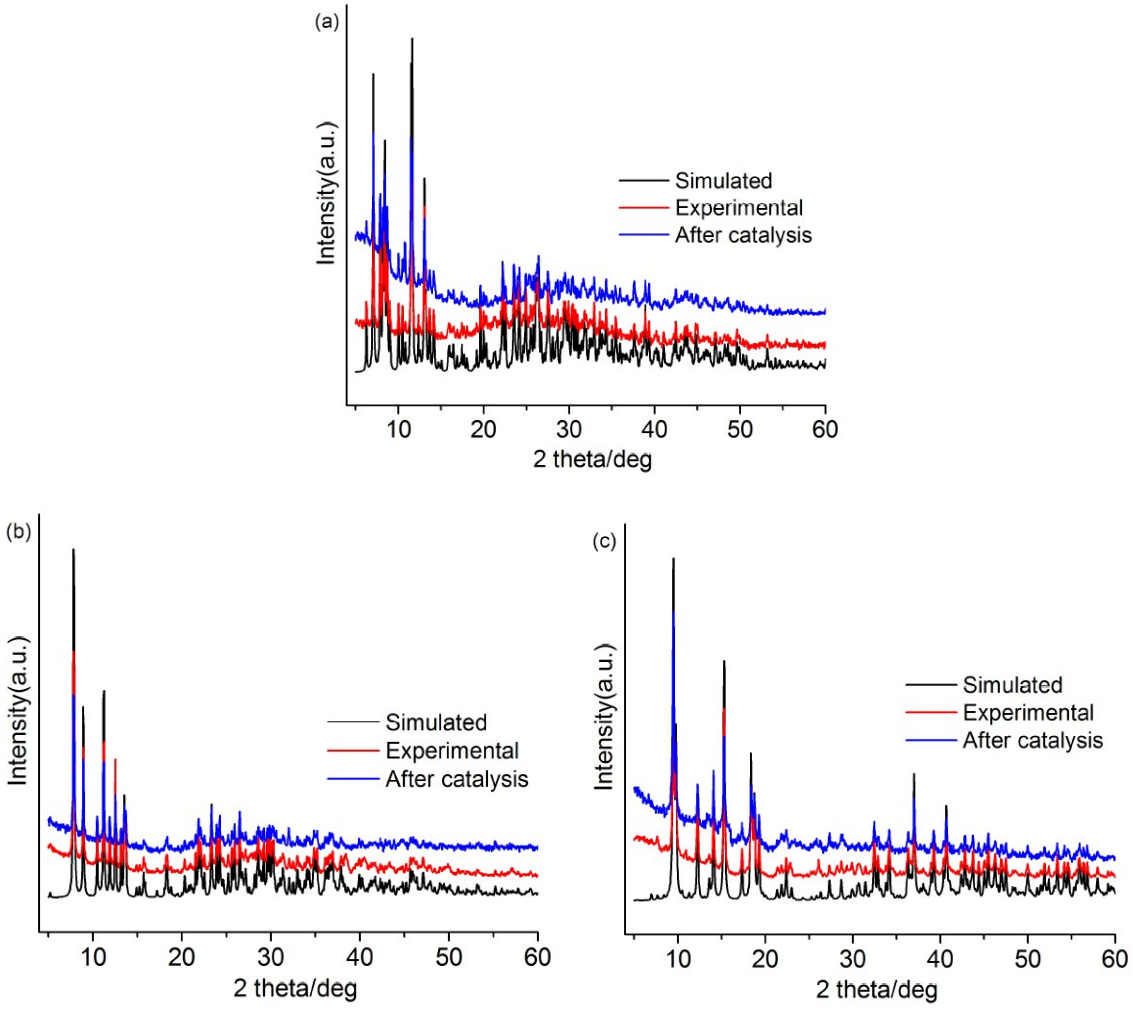
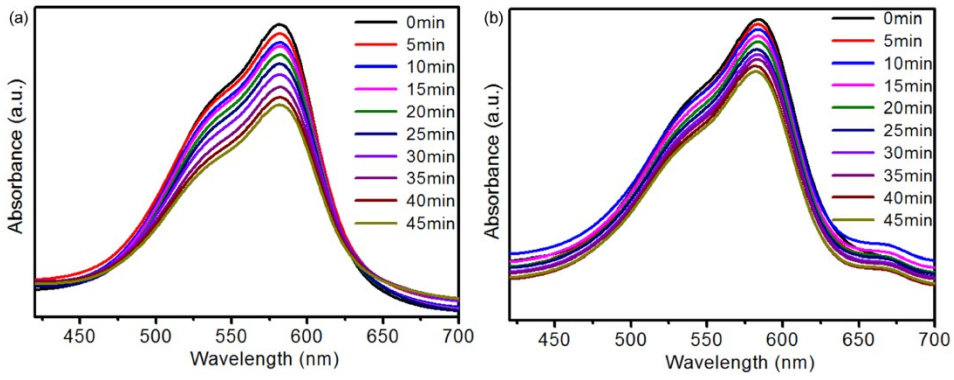


Fig. S10 Simulated and experimental powder XRD patterns, and experimental powder XRD pattern after photocatalysis for compound **1** (a), **2** (b) and **3**(c).



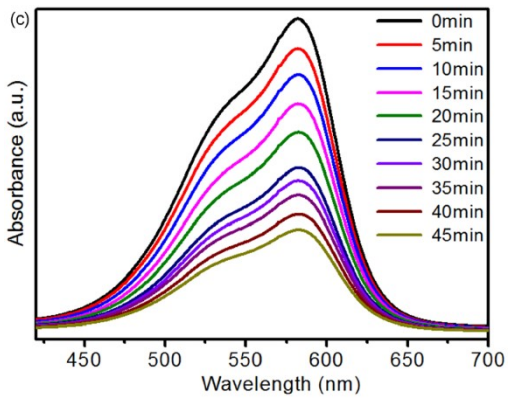


Fig. S11 Time dependent absorption spectra of CV solution with photodegradation catalyzed by compound **2** in the presence of radical quenching agents BQ (a), AO (b), and TBA (c).

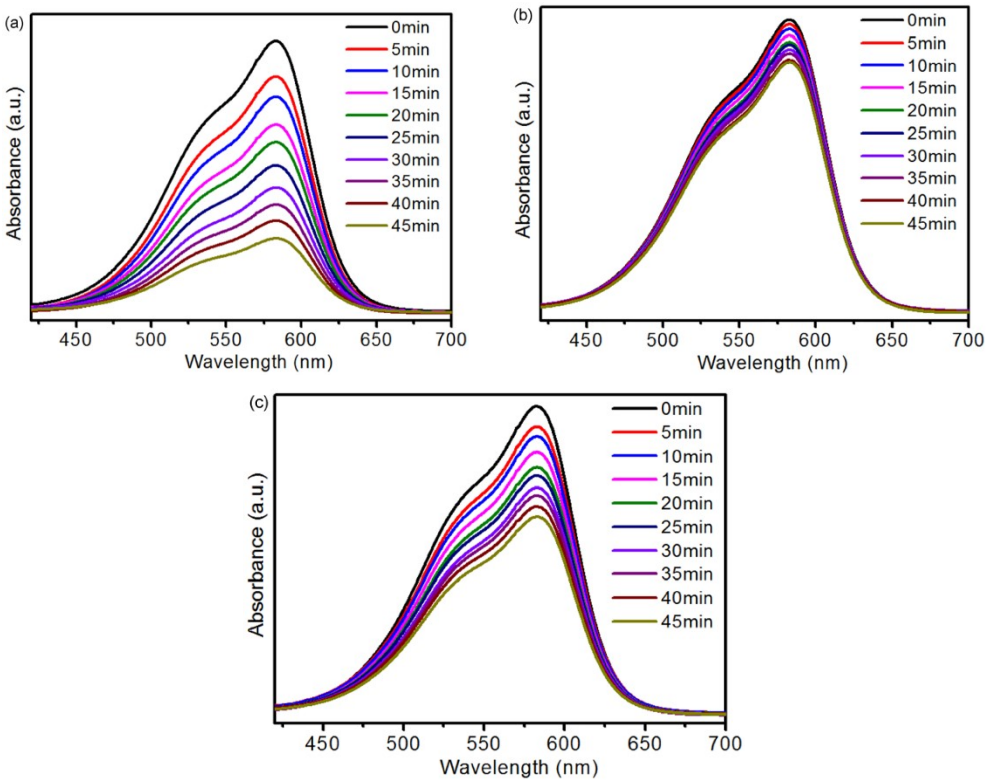


Fig. S12 Time dependent absorption spectra of CV solution with photodegradation catalyzed by compound **3** in the presence of radical quenching agents BQ (a), AO (b), and TBA (c).

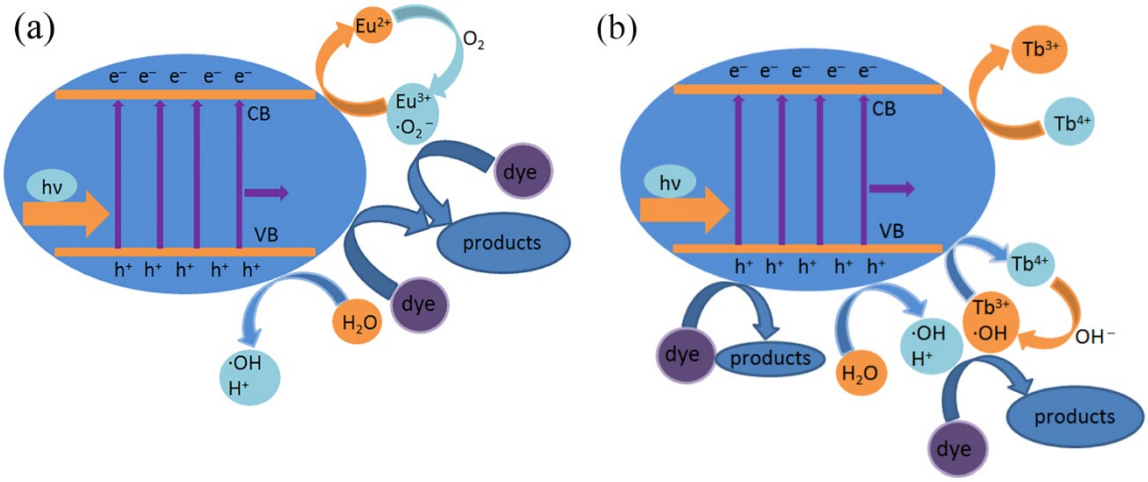


Fig. S13. Schematic diagrams illustrating the photocatalytic mechanism for CV degradation over **2** (a) and **3** (b) under visible light irradiation.