Electronic Supplementary Information

One-dimensional polymeric iodoplumbate hybrids **with lanthanide complex cations: syntheses, crystal structures, photoelectric and photocatalytic properties**

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Table S1. Crystallographic data and refinement of **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{24}H_{56}N_8O_8LaPb_3I_9$	$C_{24}H_{56}N_8O_8SmPb_5I_{13}$	$C_{24}H_{56}N_8O_8GdPb_5I_{13}$
FW	2487.34	3420.76	3427.66
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a [Å]	19.497(4)	18.833(4)	18.777(4)
b [Å]	17.505(4)	20.148(4)	20.133(4)
c [Å]	17.664(4)	20.148(4)	20.095(4)
α [°]	90	90	90
γ [°]	97.67(3)	110.01(3)	109.89(3)
β [°]	90	90	90
V [Å^3]	5975(2)	7183(3)	7143(3)
Z	4	4	4
T[K]	293(2)	293(2)	293(2)
D_c/Mg m^{-3}	2.765	3.163	3.187
F(000)	4400	5924	5932
2*θ* (max) [°]	50.70	50.70	50.70
Measured reflns	26521	31821	67875
Unique reflns	7277	8745	9452
Rint	0.0869	0.1185	0.1526
No. of parameters	393	432	455
R_1 [$I > 2\sigma(I)$]	0.0896	0.1154	0.1211
wR_2 (all data)	0.1613	0.2272	0.2357
GOF on F^2	1.158	1.185	1.282

Table S2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Pb(1)–I(1)	3.3045(16)	Pb(1)–I(2)	3.260(2)
Pb(1)–I(3)	3.031(2)	Pb(1)–I(4)	3.1488(17)
Pb(1)–I(5)	3.2717(19)	Pb(1)–I(9)	3.487(2)
Pb(2)–I(1)	3.615(2)	Pb(2)–I(6)	3.2478(18)
Pb(2)–I(2)	3.2253(19)	Pb(2)–I(8)	3.016(2)
Pb(2)–I(7)	3.2041(17)	Pb(2)–I(9)#2	3.2719(16)
Pb(3)–I(4)#1	3.2190(17)	Pb(3)–I(1)	3.2098(18)
Pb(3)–I(6)	3.250(2)	Pb(3)–I(5)#1	3.189(2)

Pb(3)–I(9)	3.2182(17)	Pb(3)–I(7)	3.2817(17)
La(1)–O(2)	2.463(14)	La(1)–O(1)	2.514(16)
La(1)–O(4)	2.520(2)	La(1)–O(3)	2.442(17)
La(1)–O(6)	2.450(14)	La(1)–O(5)	2.505(14)
La(1)–O(8)	2.485(19)	La(1)–O(7)	2.483(16)
I(1)–Pb(1)–I(2)	86.81(4)	I(1)–Pb(1)–I(3)	98.19(6)
I(1)–Pb(1)–I(4)	168.46(5)	I(1)–Pb(1)–I(5)	92.14(4)
I(2)–Pb(1)–I(3)	93.10(6)	I(2)–Pb(1)–I(4)	92.06(5)
I(2)–Pb(1)–I(5)	164.38(5)	I(3)–Pb(1)– I(4)	93.34(6)
I(3)–Pb(1)–I(5)	102.46(6)	I(4)–Pb(1)–I(5)	85.85(4)
I(1)–Pb(2)–I(2)	82.31(5)	I(1)–Pb(2)–I(6)	84.14(4)
I(1)–Pb(2)–I(7)	82.99(5)	I(1)–Pb(2)–I(8)	175.85(5)
I(1)–Pb(2)–I(9)#2	84.70(5)	I(2)–Pb(2)–I(6)	166.45(6)
I(2)–Pb(2)–I(7)	93.44(5)	I(2)–Pb(2)–I(8)	93.97(6)
I(2)–Pb(2)–I(9)#2	87.05(5)	I(6)–Pb(2)–I(7)	85.16(4)
I(6)–Pb(2)–I(8)	99.56(6)	I(6)–Pb(2)–I(9)#2	91.44(4)
I(7)–Pb(2)–I(8)	99.13(6)	I(7)–Pb(2)–I(9)#2	167.50(5)
I(8)–Pb(2)–I(9)#2	93.29(6)	I(1)–Pb(3)–I(4)#1	91.77(4)
I(1)–Pb(3)–I(5)#1	91.44(5)	I(1)–Pb(3)–I(6)	90.98(5)
I(1)–Pb(3)–I(7)	88.47(4)	I(1)–Pb(3)–I(9)	176.90(5)
I(4)#1–Pb(3)–I(5)#1	86.08(5)	I(4)#1–Pb(3)–I(6)	90.95(5)
I(4)#1–Pb(3)–I(7)	174.83(5)	I(4)#1–Pb(3)–I(9)	85.47(4)
I(5)#1–Pb(3)–I(6)	176.22(5)	I(5)#1–Pb(3)–I(7)	99.08(5)
I(5)#1–Pb(3)–I(9)	86.97(5)	I(6)–Pb(3)–I(7)	83.88(5)
I(6)–Pb(3)–I(9)	90.47(5)	I(7)–Pb(3)–I(9)	94.41(4)
Pb(1)–I(1)–Pb(2)	74.67(4)	Pb(1)–I(1)–Pb(3)	147.72(6)
Pb(2)–I(1)–Pb(3)	73.06(4)	Pb(1)–I(2)–Pb(2)	80.81(4)
Pb(1)–I(4)–Pb(3)#2	79.95(4)	Pb(1)–I(5)–Pb(3)#2	78.58(4)
Pb(2)–I(6)–Pb(3)	77.70(4)	Pb(2)–I(7)–Pb(3)	77.86(4)
Pb(2)#1–I(9)–Pb(3)	151.79(6)	O(1)–La(1)–O(2)	71.8(5)
O(1)–La(1)–O(3)	143.9(5)	O(1)–La(1)–O(4)	131.8(7)
O(1)–La(1)–O(5)	124.7(5)	O(1)–La(1)–O(6)	72.0(5)
O(1)–La(1)–O(7)	77.8(6)	O(1)–La(1)–O(8)	76.3(7)
O(2)–La(1)–O(3)	72.2(5)	O(2)–La(1)–O(4)	130.2(6)
O(2)–La(1)–O(5)	133.2(6)	O(2)–La(1)–O(6)	143.0(5)
O(2)–La(1)–O(7)	75.7(5)	O(2)–La(1)–O(8)	73.6(6)
O(3)–La(1)–O(4)	76.2(8)	O(3)–La(1)–O(5)	79.6(5)
O(3)–La(1)–O(6)	144.1(5)	O(3)–La(1)–O(7)	96.3(6)
O(3)–La(1)–O(8)	90.7(8)	O(4)–La(1)–O(5)	75.0(6)
O(4)–La(1)–O(6)	72.4(7)	O(4)–La(1)–O(7)	70.5(6)
O(4)–La(1)–O(8)	144.4(7)	O(5)–La(1)–O(6)	75.8(5)

O(5)–La(1)–O(7)	145.3(5)	O(5)–La(1)–O(8)	70.1(6)
O(6)–La(1)–O(7)	89.4(5)	O(6)–La(1)–O(8)	104.8(7)
O(7)–La(1)–O(8)	144.6(6)	La(1)–O(1)–C(1)	140.7(16)
La(1)–O(2)–C(4A)	148(2)	La(1)–O(2)–C(4B)	145(2)
La(1)–O(3)–C(7)	144.3(19)	La(1)–O(4)–C(10)	136(2)
La(1)–O(5)–C(13)	150.2(16)	La(1)–O(6)–C(16)	134.7(16)
La(1)–O(7)–C(19)	150.5(14)	La(1)–O(8)–C(22A)	149(3)
La(1)–O(8)–C(22B)	128(4)		

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

Table S3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Pb(1)–I(1)	3.259(3)	Pb(1)–I(2)	3.348(2)
Pb(1)–I(2)#1	3.391(2)	Pb(1)–I(3)	3.160(3)
Pb(1)–I(4)	3.132(3)	Pb(1)–I(5)	3.172(3)
Pb(2)–I(1)	3.205(3)	Pb(2)–I(2)	3.461(3)
Pb(2)–I(3)	3.207(3)	Pb(2)–I(6)	3.320(2)
Pb(2)–I(7)	3.103(3)	Pb(2)–I(8)	3.224(3)
Pb(3)–I(2)	3.310(2)	Pb(3)–I(4)#1	3.231(3)
Pb(3)–I(5)#1	3.202(3)	Pb(3)–I(6)	3.271(2)
Pb(3)–I(9)	3.207(3)	Pb(3)–I(10)	3.121(2)
Pb(4)–I(6)	3.741(3)	Pb(4)–I(9)	3.152(3)
Pb(4)–I(10)	3.187(2)	Pb(4)–I(11)	3.410(3)
Pb(4)–I(12)	2.943(3)	Pb(4)–I(13)#2	3.296(3)
Pb(5)–I(6)	3.385(2)	Pb(5)–I(7)	3.311(3)
Pb(5)–I(8)	3.146(3)	Pb(5)–I(11)	3.246(3)
Pb(5)–I(11)#2	3.346(3)	Pb(5)–I(13)	3.084(3)
Sm(1)–O(1)	2.31(2)	Sm(1)–O(2)	2.38(2)
Sm(1)–O(3)	2.34(2)	Sm(1)–O(4)	2.43(2)
Sm(1)–O(5)	2.377(19)	Sm(1)–O(6)	2.28(2)
Sm(1)–O(7)	2.39(3)	Sm(1)–O(8)	2.36(3)
I(1)–Pb(1)–I(2)	88.65(7)	I(1)–Pb(1)–I(2)#1	92.39(7)
I(1)–Pb(1)–I(3)	85.66(7)	I(1)–Pb(1)–I(4)	94.95(7)
I(1)–Pb(1)–I(5)	174.51(8)	I(2)–Pb(1)–I(2)#1	91.45(6)
I(2)–Pb(1)–I(3)	86.68(7)	I(2)#1–Pb(1)–I(3)	177.32(7)
I(2)–Pb(1)–I(4)	175.94(7)	I(2)#1–Pb(1)–I(4)	86.55(7)
I(2)–Pb(1)–I(5)	87.76(6)	I(2)#1–Pb(1)–I(5)	83.55(7)
I(3)–Pb(1)–I(4)	95.44(8)	I(3)–Pb(1)–I(5)	98.28(7)
I(4)–Pb(1)–I(5)	88.51(7)	I(1)–Pb(2)–I(2)	87.59(6)
I(1)–Pb(2)–I(3)	85.78(7)	I(1)–Pb(2)–I(6)	95.22(7)
I(1)–Pb(2)–I(7)	98.57(7)	I(1)–Pb(2)–I(8)	174.75(8)

I(2)–Pb(2)–I(3)	84.06(7)	I(2)–Pb(2)–I(6)	91.07(6)
I(2)–Pb(2)–I(7)	173.72(7)	I(2)–Pb(2)–I(8)	87.49(7)
I(3)–Pb(2)–I(6)	174.98(7)	I(3)–Pb(2)–I(7)	97.55(8)
I(3)–Pb(2)–I(8)	95.51(7)	I(6)–Pb(2)–I(7)	87.17(7)
I(6)–Pb(2)–I(8)	83.06(6)	I(7)–Pb(2)–I(8)	86.32(7)
I(2)–Pb(3)–I(4)#1	86.32(7)	I(2)–Pb(3)–I(5)#1	84.40(6)
I(2)–Pb(3)–I(6)	94.69(6)	I(2)–Pb(3)–I(9)	93.49(7)
I(2)–Pb(3)–I(10)	177.36(7)	I(4)#1–Pb(3)–I(5)#1	86.29(7)
I(4)#1–Pb(3)–I(6)	178.94(7)	I(4)#1–Pb(3)–I(9)	92.56(7)
I(4)#1–Pb(3)–I(10)	94.81(7)	I(5)#1–Pb(3)–I(6)	93.48(7)
I(5)#1–Pb(3)–I(9)	177.66(8)	I(5)#1–Pb(3)–I(10)	93.28(7)
I(6)–Pb(3)–I(9)	87.70(7)	I(6)–Pb(3)–I(10)	84.17(6)
I(9)–Pb(3)–I(10)	88.84(7)	I(6)–Pb(4)–I(9)	80.75(7)
I(6)–Pb(4)–I(10)	75.95(6)	I(6)–Pb(4)–I(11)	83.84(6)
I(6)–Pb(4)–I(12)	167.27(8)	I(6)–Pb(4)–I(13)#2	96.17(7)
I(9)–Pb(4)–I(10)	88.65(7)	I(9)–Pb(4)–I(11)	89.57(7)
I(9)–Pb(4)–I(12)	94.54(10)	I(9)–Pb(4)–I(13)#2	175.83(8)
I(10)–Pb(4)–I(11)	159.74(7)	I(10)–Pb(4)–I(12)	92.20(8)
I(10)–Pb(4)–I(13)#2	93.36(7)	I(11)–Pb(4)–I(12)	108.06(8)
I(11)–Pb(4)–I(13)#2	87.29(7)	I(12)–Pb(4)–I(13)#2	89.04(10)
I(6)–Pb(5)–I(7)	82.84(6)	I(6)–Pb(5)–I(8)	83.19(7)
I(6)–Pb(5)–I(11)	92.33(7)	I(6)–Pb(5)–I(11)#2	87.97(6)
I(6)–Pb(5)–I(13)	171.75(8)	I(7)–Pb(5)–I(8)	84.16(7)
I(7)–Pb(5)–I(11)	174.97(7)	I(7)–Pb(5)–I(11)#2	98.12(7)
I(7)–Pb(5)–I(13)	88.99(8)	I(8)–Pb(5)–I(11)	93.90(7)
I(8)–Pb(5)–I(11)#2	170.54(7)	I(8)–Pb(5)–I(13)	97.23(7)
I(11)–Pb(5)–I(11)#2	83.06(7)	I(11)–Pb(5)–I(13)	95.86(8)
I(11)#2–Pb(5)–I(13)	92.00(7)	Pb(1)–I(1)–Pb(2)	76.59(6)
Pb(1)–I(2)–Pb(1)#1	88.55(6)	Pb(1)–I(2)–Pb(2)	72.05(5)
Pb(1)#1–I(2)–Pb(2)	130.71(7)	Pb(1)–I(2)–Pb(3)	130.19(7)
Pb(1)#1–I(2)–Pb(3)	73.09(5)	Pb(2)–I(2)–Pb(3)	85.57(6)
Pb(1)–I(3)–Pb(2)	77.97(6)	Pb(1)–I(4)–Pb(3)#1	77.66(6)
Pb(1)–I(5)–Pb(3)#1	77.53(6)	Pb(2)–I(6)–Pb(3)	88.54(6)
Pb(2)–I(6)–Pb(4)	134.92(7)	Pb(2)–I(6)–Pb(5)	75.26(5)
Pb(3)–I(6)–Pb(4)	71.46(5)	Pb(3)–I(6)–Pb(5)	130.84(7)
Pb(4)–I(6)–Pb(5)	87.80(6)	Pb(2)–I(7)–Pb(5)	79.25(6)
Pb(2)–I(8)–Pb(5)	79.97(6)	Pb(3)–I(9)–Pb(4)	80.59(6)
Pb(3)–I(10)–Pb(4)	81.38(6)	Pb(4)–I(11)–Pb(5)	96.02(7)
Pb(4)–I(11)–Pb(5)#2	87.09(7)	Pb(4)–I(11)–Pb(5)#2	96.93(7)
Pb(4)#2–I(13)–Pb(5)	93.62(7)	O(1)–Sm(1)–O(2)	70.2(8)
O(1)–Sm(1)–O(3)	115.4(10)	O(1)–Sm(1)–O(4)	137.5(8)
O(1)–Sm(1)–O(5)	82.3(9)	O(1)–Sm(1)–O(6)	142.8(9)

O(1)–Sm(1)–O(7)	73.7(10)	O(1)–Sm(1)–O(8)	74.7(10)
O(2)–Sm(1)–O(3)	73.9(8)	O(2)–Sm(1)–O(4)	75.6(8)
O(2)–Sm(1)–O(5)	83.5(8)	O(2)–Sm(1)–O(6)	147.0(8)
O(2)–Sm(1)–O(7)	138.8(9)	O(2)–Sm(1)–O(8)	111.5(10)
O(3)–Sm(1)–O(4)	76.9(9)	O(3)–Sm(1)–O(5)	143.1(9)
O(3)–Sm(1)–O(6)	85.6(9)	O(3)–Sm(1)–O(7)	141.7(8)
O(3)–Sm(1)–O(8)	71.2(10)	O(4)–Sm(1)–O(5)	69.3(8)
O(4)–Sm(1)–O(6)	74.8(8)	O(4)–Sm(1)–O(7)	123.1(10)
O(4)–Sm(1)–O(8)	143.1(10)	O(5)–Sm(1)–O(6)	99.1(8)
O(5)–Sm(1)–O(7)	72.6(8)	O(5)–Sm(1)–O(8)	145.5(10)
O(6)–Sm(1)–O(7)	71.4(9)	O(6)–Sm(1)–O(8)	84.9(9)
O(7)–Sm(1)–O(8)	76.5(10)	Sm(1)–O(1)–C(1)	131(2)
Sm(1)–O(2)–C(4)	136(2)	Sm(1)–O(3)–C(7)	139(2)
Sm(1)–O(4)–C(10)	133(2)	Sm(1)–O(5)–C(13)	136(2)
Sm(1)–O(6)–C(16)	144(3)	Sm(1)–O(7)–C(19)	136(3)
Sm(1)–O(8)–C(22)	140(3)		

Symmetry transformations used to generate equivalent atoms: #1 –x, –y+1, –z; #2 –x, –y+1, –z+1.

Table S4. Selected Bond Lengths (Å) and Angles (deg) for **3**

Pb(1)–I(1)#1	3.388(2)	Pb(1)–I(1)	3.341(2)
Pb(1)–I(2)	3.249(3)	Pb(1)–I(3)	3.162(3)
Pb(1)–I(4)	3.132(3)	Pb(1)–I(5)	3.160(3)
Pb(2)–I(1)	3.310(2)	Pb(2)–I(4)#1	3.221(3)
Pb(2)–I(5)#1	3.200(3)	Pb(2)–I(6)	3.266(2)
Pb(2)–I(7)	3.200(3)	Pb(2)–I(8)	3.113(2)
Pb(3)–I(1)	3.453(3)	Pb(3)–I(2)	3.203(3)
Pb(3)–I(3)	3.208(3)	Pb(3)–I(6)	3.313(2)
Pb(3)–I(9)	3.220(3)	Pb(3)–I(10)	3.094(3)
Pb(4)–I(6)	3.385(2)	Pb(4)–I(9)	3.139(3)
Pb(4)–I(10)	3.311(3)	Pb(4)–I(11)	3.239(3)
Pb(4)–I(11)#2	3.333(3)	Pb(4)–I(12)	3.083(3)
Pb(5)–I(6)	3.743(3)	Pb(5)–I(7)	3.139(3)
Pb(5)–I(8)	3.182(3)	Pb(5)–I(11)	3.411(3)
Pb(5)–I(12)#2	3.287(3)	Pb(5)–I(13)	2.946(3)
Gd(1)–O(1)	2.31(2)	Gd(1)–O(2)	2.32(2)
Gd(1)–O(3)	2.44(2)	Gd(1)–O(4)	2.37(2)
Gd(1)–O(5)	2.36(2)	Gd(1)–O(6)	2.30(3)
Gd(1)–O(7)	2.35(3)	Gd(1)–O(8)	2.37(2)
I(1)–Pb(1)–I(1)#1	91.49(6)	I(1)#1–Pb(1)–I(2)	92.28(7)
I(1)–Pb(1)–I(2)	88.87(7)	I(1)–Pb(1)–I(3)	86.79(7)
I(1)#1–Pb(1)–I(3)	177.45(7)	I(1)–Pb(1)–I(4)	175.83(7)

I(1)#1–Pb(1)–I(4)	86.56(7)	I(1)–Pb(1)–I(5)	87.63(7)
I(1)#1–Pb(1)–I(5)	83.72(7)	I(2)–Pb(1)–I(3)	85.82(7)
I(2)–Pb(1)–I(4)	94.89(7)	I(2)–Pb(1)–I(5)	174.60(7)
I(3)–Pb(1)–I(4)	95.28(7)	I(3)–Pb(1)–I(5)	98.08(8)
I(4)–Pb(1)–I(5)	88.50(7)	I(1)–Pb(2)–I(4)#1	86.48(6)
I(1)–Pb(2)–I(5)#1	84.38(6)	I(1)–Pb(2)–I(6)	94.51(6)
I(1)–Pb(2)–I(7)	93.38(7)	I(1)–Pb(2)–I(8)	177.42(7)
I(4)#1–Pb(2)–I(5)#1	86.29(7)	I(4)–Pb(2)–I(6)	178.94(7)
I(4)#1–Pb(2)–I(7)	92.62(7)	I(4)#1–Pb(2)–I(8)	94.68(7)
I(5)#1–Pb(2)–I(6)	93.44(7)	I(5)#1–Pb(2)–I(7)	177.57(8)
I(5)#1–Pb(2)–I(8)	93.38(7)	I(6)–Pb(2)–I(7)	87.69(7)
I(6)–Pb(2)–I(8)	84.32(6)	I(7)–Pb(2)–I(8)	88.88(7)
I(1)–Pb(3)–I(2)	87.68(6)	I(1)–Pb(3)–I(3)	84.22(7)
I(1)–Pb(3)–I(6)	91.06(6)	I(1)–Pb(3)–I(9)	87.49(7)
I(1)–Pb(3)–I(10)	173.65(7)	I(2)–Pb(3)–I(3)	85.84(7)
I(2)–Pb(3)–I(6)	95.17(7)	I(2)–Pb(3)–I(9)	174.87(8)
I(2)–Pb(3)–I(10)	98.56(7)	I(3)–Pb(3)–I(6)	175.13(7)
I(3)–Pb(3)–I(9)	95.39(7)	I(3)–Pb(3)–I(10)	97.30(7)
I(6)–Pb(3)–I(9)	83.19(7)	I(6)–Pb(3)–I(10)	87.27(7)
I(9)–Pb(3)–I(10)	86.23(7)	I(6)–Pb(4)–I(9)	83.25(7)
I(6)–Pb(4)–I(10)	82.69(6)	I(6)–Pb(4)–I(11)	92.47(7)
I(6)–Pb(4)–I(11)#2	87.80(7)	I(6)–Pb(4)–I(12)	171.45(8)
I(9)–Pb(4)–I(10)	83.95(7)	I(9)–Pb(4)–I(11)	93.98(7)
I(9)–Pb(4)–I(11)#2	170.51(7)	I(9)–Pb(4)–I(12)	97.12(7)
I(10)–Pb(4)–I(11)	174.92(7)	I(10)–Pb(4)–I(11)#2	98.09(7)
I(10)–Pb(4)–I(12)	88.84(8)	I(11)–Pb(4)–I(11)#2	83.21(7)
I(11)–Pb(4)–I(12)	96.02(8)	I(11)#2–Pb(4)–I(12)	92.20(7)
I(6)–Pb(5)–I(7)	80.70(7)	I(6)–Pb(5)–I(8)	75.94(6)
I(6)–Pb(5)–I(11)	83.82(6)	I(6)–Pb(5)–I(12)#2	96.13(7)
I(6)–Pb(5)–I(13)	167.15(8)	I(7)–Pb(5)–I(8)	88.75(7)
I(7)–Pb(5)–I(11)	89.47(7)	I(7)–Pb(5)–I(12)#2	175.73(8)
I(7)–Pb(5)–I(13)	94.73(10)	I(8)–Pb(5)–I(11)	159.70(7)
I(8)–Pb(5)–I(12)#2	93.26(7)	I(8)–Pb(5)–I(13)	92.04(8)
I(11)–Pb(5)–I(12)#2	87.34(7)	I(11)–Pb(5)–I(13)	108.26(9)
I(12)#2–Pb(5)–I(13)	88.96(10)	Pb(1)–I(1)–Pb(1)#1	88.52(6)
Pb(1)–I(1)–Pb(2)	130.07(7)	Pb(1)#1–I(1)–Pb(2)	72.95(5)
Pb(1)–I(1)–Pb(3)	71.97(5)	Pb(1)#1–I(1)–Pb(3)	130.59(7)
Pb(2)–I(1)–Pb(3)	85.64(6)	Pb(1)–I(2)–Pb(3)	76.47(6)
Pb(1)–I(3)–Pb(3)	77.63(6)	Pb(1)–I(4)–Pb(2)#1	77.62(6)
Pb(1)–I(5)–Pb(2)#1	77.52(6)	Pb(2)–I(6)–Pb(3)	88.65(6)
Pb(2)–I(6)–Pb(4)	130.72(8)	Pb(2)–I(6)–Pb(5)	71.27(5)
Pb(3)–I(6)–Pb(4)	75.25(5)	Pb(3)–I(6)–Pb(5)	134.79(7)

Pb(4)–I(6)–Pb(5)	87.69(6)	Pb(2)–I(7)–Pb(5)	80.64(7)
Pb(2)–I(8)–Pb(5)	81.33(6)	Pb(3)–I(9)–Pb(4)	80.04(7)
Pb(3)–I(10)–Pb(4)	79.29(6)	Pb(4)–I(11)–Pb(4)#2	96.79(7)
Pb(4)–I(11)–Pb(5)	96.02(7)	Pb(4)#2–I(11)–Pb(5)	86.96(7)
Pb(4)–I(12)–Pb(5)#2	93.49(7)	O(1)–Gd(1)–O(2)	84.6(9)
O(1)–Gd(1)–O(3)	73.6(8)	O(1)–Gd(1)–O(4)	145.5(9)
O(1)–Gd(1)–O(5)	98.2(8)	O(1)–Gd(1)–O(6)	143.4(10)
O(1)–Gd(1)–O(7)	71.4(10)	O(1)–Gd(1)–O(8)	84.9(8)
O(2)–Gd(1)–O(3)	75.4(10)	O(2)–Gd(1)–O(4)	74.3(8)
O(2)–Gd(1)–O(5)	143.3(9)	O(2)–Gd(1)–O(6)	116.9(12)
O(2)–Gd(1)–O(7)	139.9(9)	O(2)–Gd(1)–O(8)	70.7(10)
O(3)–Gd(1)–O(4)	74.9(9)	O(3)–Gd(1)–O(5)	70.5(8)
O(3)–Gd(1)–O(6)	138.0(9)	O(3)–Gd(1)–O(7)	124.4(9)
O(3)–Gd(1)–O(8)	141.2(9)	O(4)–Gd(1)–O(5)	84.0(8)
O(4)–Gd(1)–O(6)	71.1(10)	O(4)–Gd(1)–O(7)	140.3(9)
O(4)–Gd(1)–O(8)	112.3(9)	O(5)–Gd(1)–O(6)	82.0(11)
O(5)–Gd(1)–O(7)	73.5(9)	O(5)–Gd(1)–O(8)	146.0(9)
O(6)–Gd(1)–O(7)	73.7(11)	O(6)–Gd(1)–O(8)	76.1(10)
O(7)–Gd(1)–O(8)	75.5(10)	Gd(1)–O(1)–C(1)	145(3)
Gd(1)–O(2)–C(4)	145(2)	Gd(1)–O(3)–C(7)	134(2)
Gd (1)–O(4)–C(10)	140(3)	Gd(1)–O(5)–C(13)	138(2)
Gd (1)–O(6)–C(16)	133(3)	Gd(1)–O(7)–C(19)	133(3)
Gd (1)–O(8)–C(22A)	142(2)	Gd(1)–O(8)–C(22B)	155(2)

Table S5. Hydrogen Bond Lengths (Å) and Angles (deg) for **1-3**

D–H···A	d(H···A)	d(D···A)	<(DHA)
1			
C(3)–H(3C)···I(3)#1	3.014	3.917	157.32
C(7)–H(7)···I(4)#2	3.019	3.759	137.67
C(9)–H(9A)···I(9)#3	3.241	3.892	126.72
C(11)–H(11A)···O(6)#4	2.605	3.432	144.55
C(16)–H(16)···O(5)	2.622	3.139	115.69
2			
C(3)–H(3B)···I(13)#1	2.996	3.953	175.51
C(5)–H(5B)···I(6)#2	3.251	4.197	169.02
C(6)–H(6A)···I(12)#3	3.152	4.023	151.67
C(6)–H(6C)···I(10)#2	3.286	4.084	141.90
C(7)–H(7)···I(10)#4	3.212	3.890	131.40
C(9)–H(9A)···I(10)#4	3.086	3.951	150.72
C(9)–H(9B)···I(7)#2	3.219	4.139	161.13
C(14)–H(14B)···I(8)#5	3.219	3.955	134.80
C(15)–H(15B)···I(4)#6	3.289	4.146	149.57

C(16)–H(16)···I(10)#4	3.222	4.004	142.97
C(17)–H(17B)···I(2)#7	3.125	3.840	132.58
C(20)–H(20C)···I(9)#7	3.187	4.020	146.17
C(24)–H(24C)···I(11)#1	2.911	3.722	142.90
3			
C(1)–H(1)···I(8)#1	3.159	3.991	149.93
C(2)–H(2B)···I(1)#2	3.121	3.918	141.57
C(3)–H(3A)···I(7)#1	3.037	3.906	151.32
C(3)–H(3B)···I(3)#2	3.266	4.035	138.41
C(4)–H(4)···I(8)#1	3.298	3.910	125.39
C(6)–H(6A)···I(8)#1	3.206	3.966	137.46
C(6)–H(7)···O(1)	2.476	2.984	114.51
C(11)–H(11B)···I(6)#3	3.307	4.235	163.17
C(12)–H(12A)···I(13)#4	3.046	3.938	155.08
C(17)–H(17B)···I(12)#5	3.104	4.033	163.30
C(18)–H(18C)···I(2)#6	3.250	3.831	120.79
C(19)–H(19)···O(5)	2.539	3.007	111.49
C(21)–H(21A)···I(9)#2	3.144	4.081	165.71

Symmetry transformations used to generate equivalent atoms: For **1:** #1–x, –y+1, –z+1; #2 x, y–1, z; #3 x, –y+1/2, z+1/2; #4 x, –y+1/2, z–1/2. For **2:** #1 x+1/2, –y+1/2, z–1/2; #2 –x+1/2, y–1/2, –z+1/2; #3 –x+1, –y+1, –z+1; #4 x+1, y–1, z; #5 x+1, y, z; #6 x+3/2, –y+1/2, z+1/2; #7 –x+3/2, y–1/2, –z+1/2. For **3:** #1 x+1, y –1, z; #2 –x+3/2, y –1/2, –z+1/2; #3 –x+1/2, y –1/2, –z+1/2; #4 –x+1, –y+1, –z+1; #5 x+1/2, –y+1/2, z –1/2; #6 x+1, y, z.

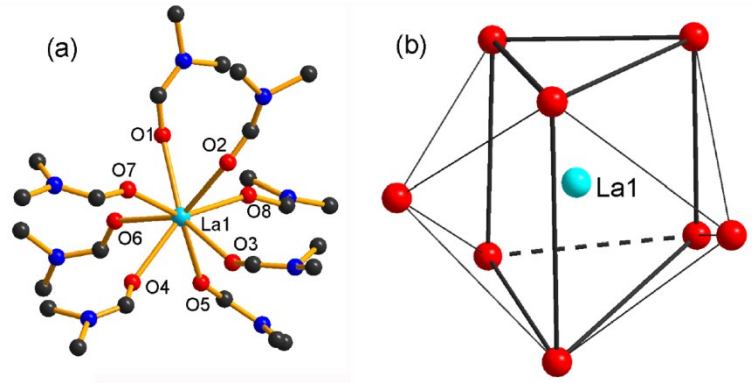

Fig. S1 (a) Crystal structure of the $[La(DMF)_8]^{3+}$ with the labelling scheme in **1.** (b) The dicapped trigonal prism LaO_8 of in the $[La(DMF)_8]^{3+}$ complex cation.

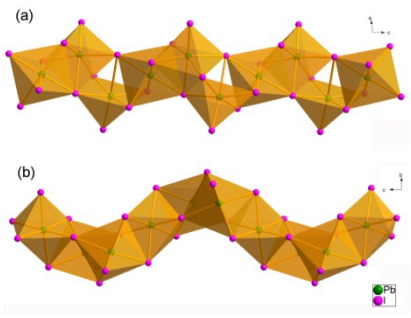

Fig. S2 (a) Crystal structure of the1-D $[Pb_3I_9]_n^{3n-}$ chain in **1** viewed along the *b* (a) and *a* (b) axis**.**

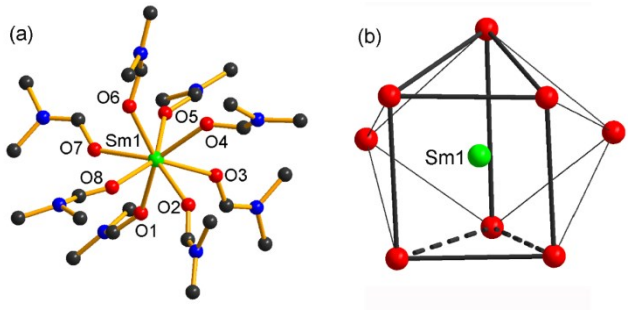

Fig. S3 (a) Crystal structure of the $[Sm(DMF)_8]^{3+}$ with the labelling scheme in **2.** (b) The dicapped trigonal prism SmO_8 of in the $[Sm(DMF)_8]^{3+}$ complex cation.

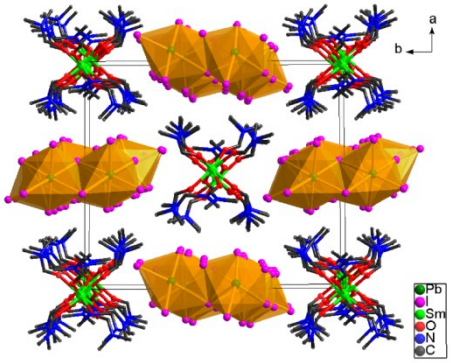

Fig. S4 Packing diagram of **2** viewed along the c axis. Yellow octahedron: PbI_6.

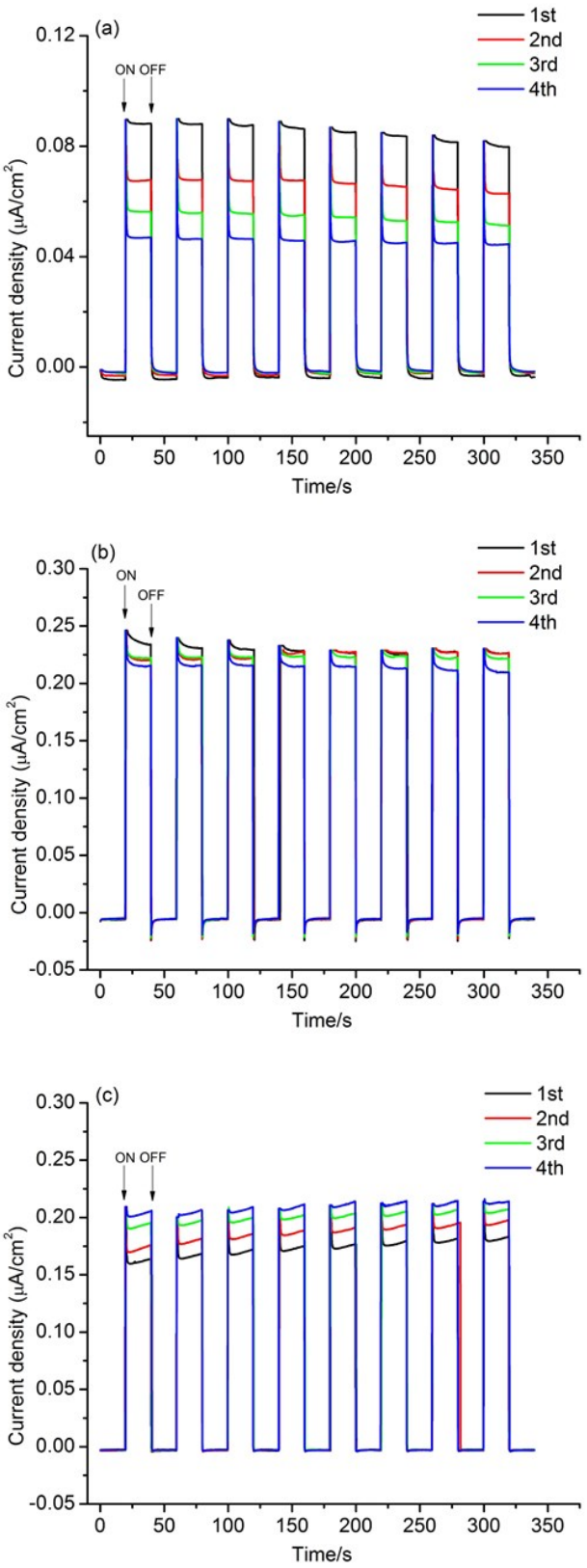

Fig. S5. The photocurrent response behaviours of **1** (a), **2** (b) and **3** (c).

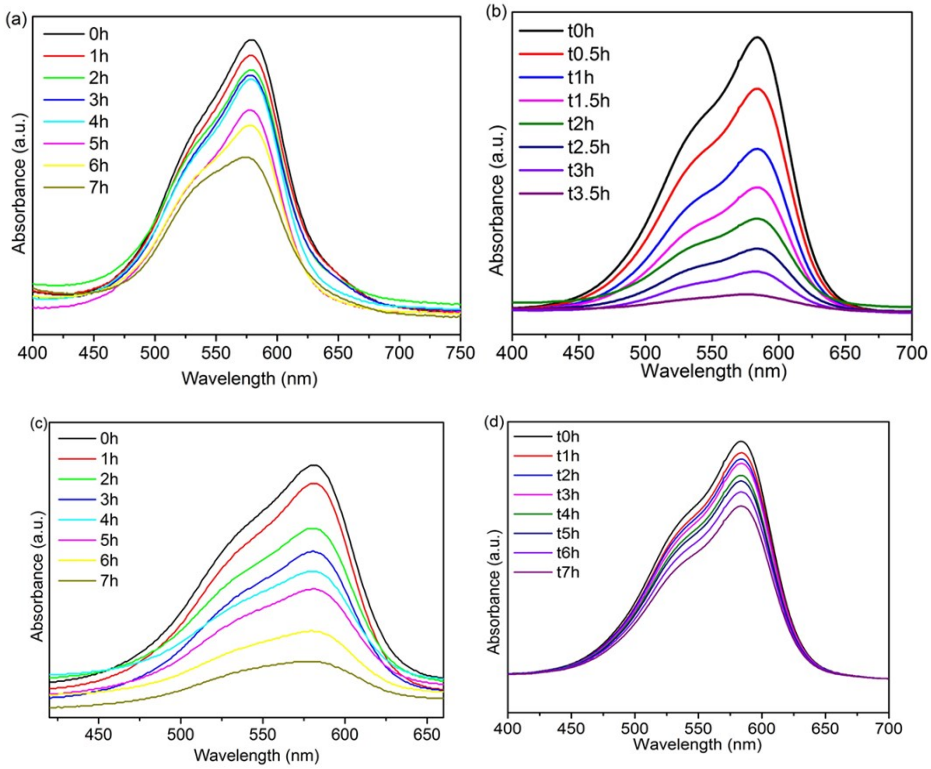

Fig. S6. Time dependent absorption spectra of CV solution with photodegradation catalyzed by compounds **1** (a), **2** (b), **3** (c) and PbI_2 (d).

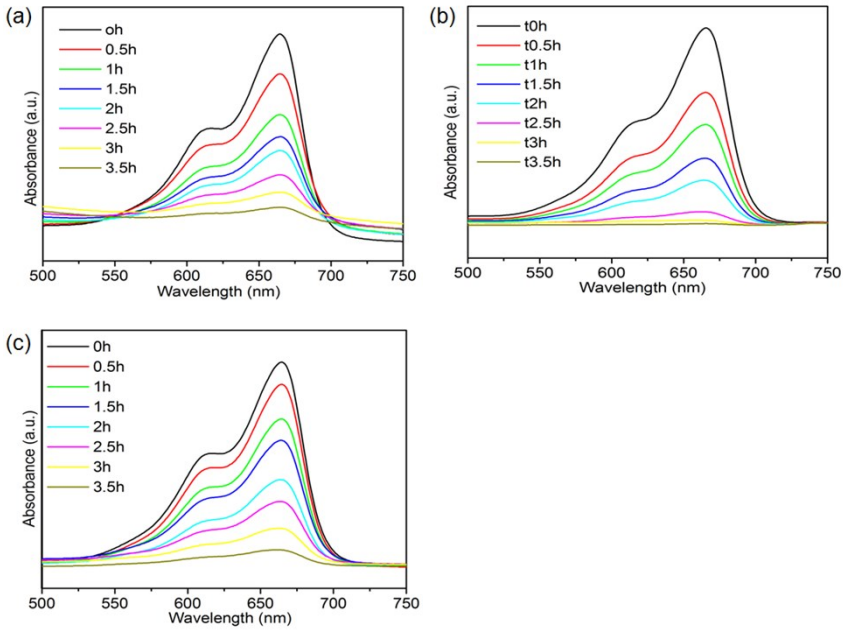

Fig. S7. Time dependent absorption spectra of MB solution with photodegradation catalyzed by compounds **1** (a), **2** (b), and **3** (c).

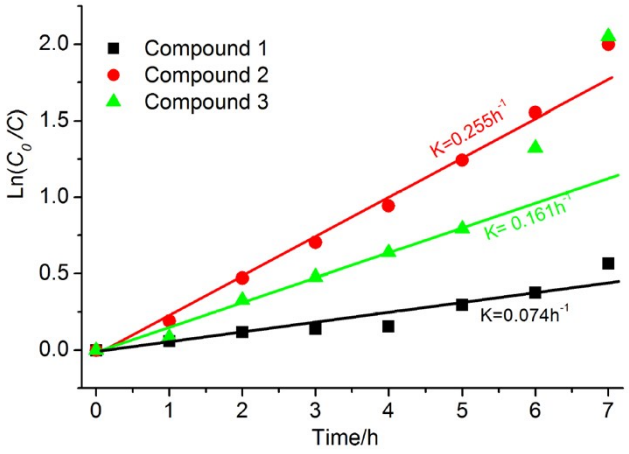

Fig. S8. The linear relationship of ln(C_0/C) via reaction time over compounds **1**(a), **2**(b), **3**(c) in the photodegradation of CV.

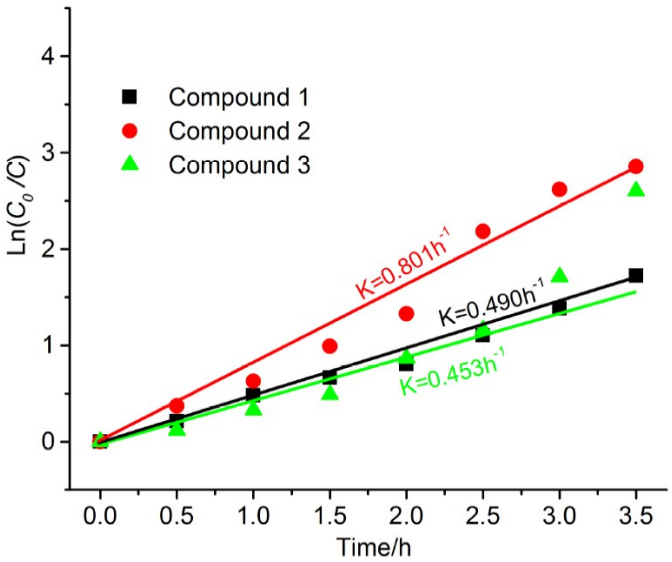

Fig. S9. The linear relationship of ln(C_0/C) over reaction time over compounds **1**, **2** and **3** in the photodegradation of MB.

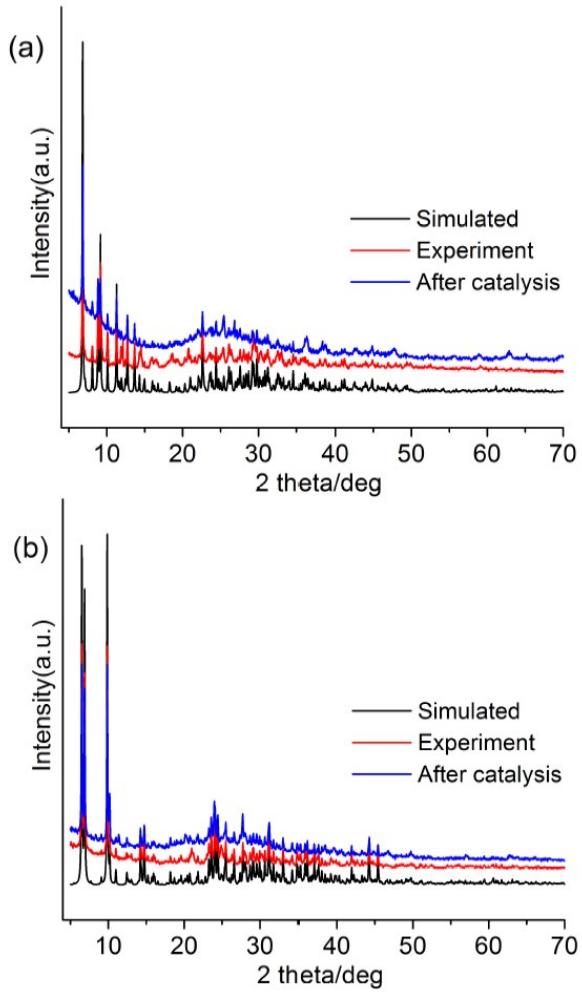

Fig. S10. Simulated and experimental powder XRD patterns of compounds **1** (a), and **2** (b).

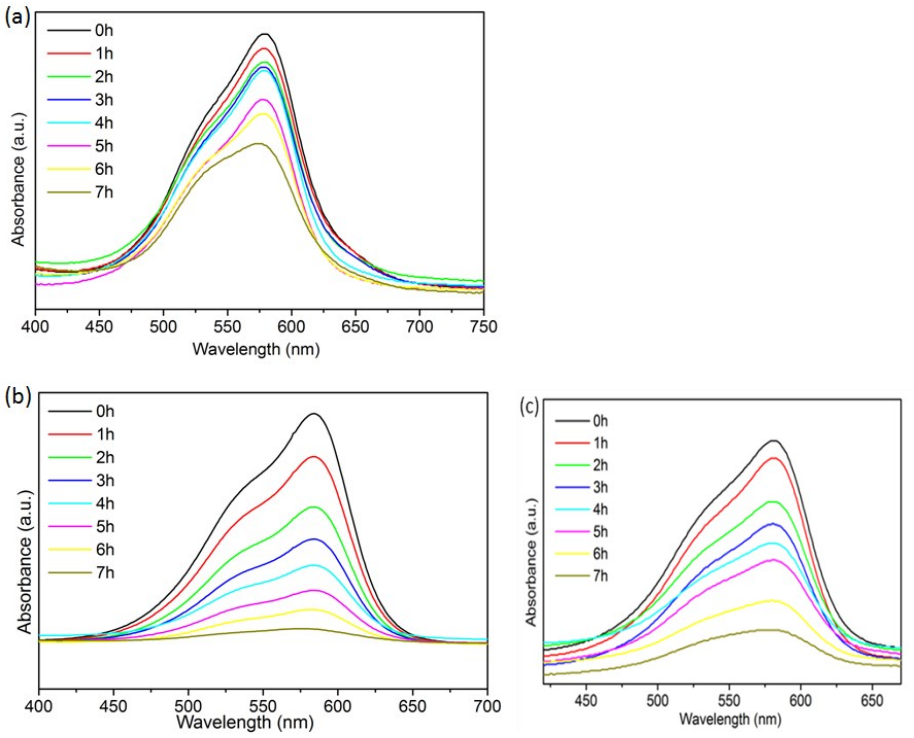

Fig. S11. Time dependent absorption spectra of CV solution with photodegradation catalyzed by compound **2** in the presence of BQ (a), AO (b), and TBA (c).

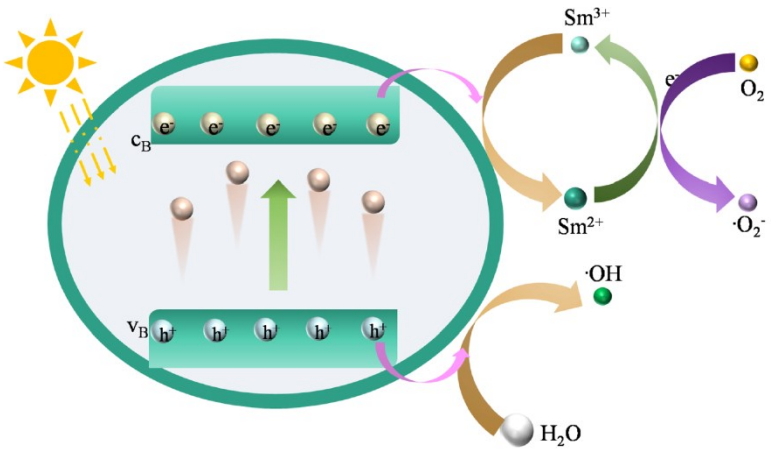

Fig. S12. Propsoed reaction mechanism for photocatalytic degradation of CV over catalyst **2** under visible light irradiation.

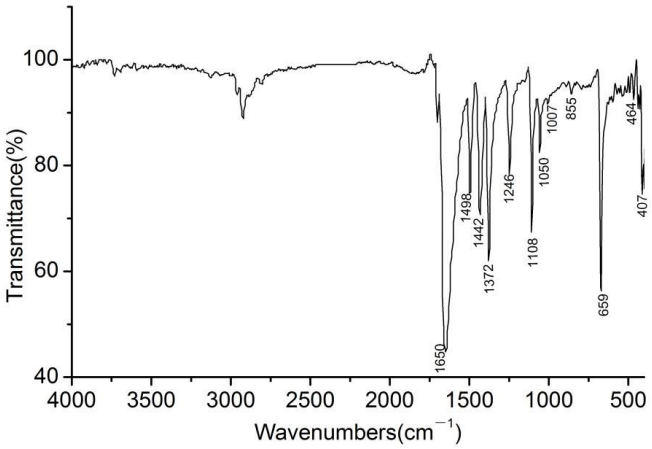

Fig. S13. IR spectrum of complex **1.**

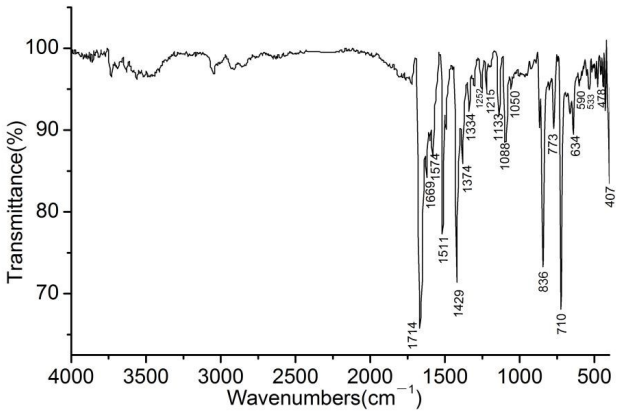

Fig. S14. IR spectrum of complex **2.**

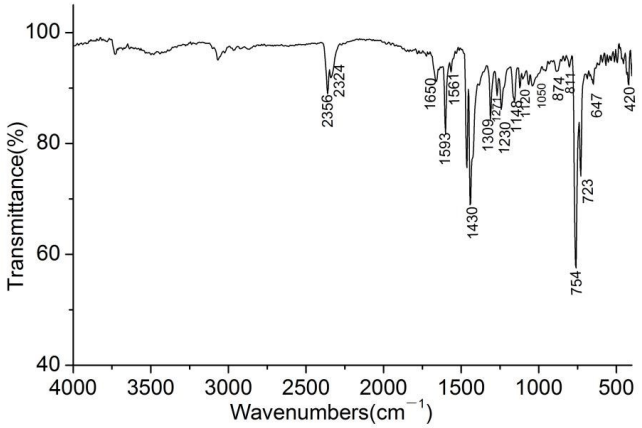

Fig. S15. IR spectrum of complex **3.**

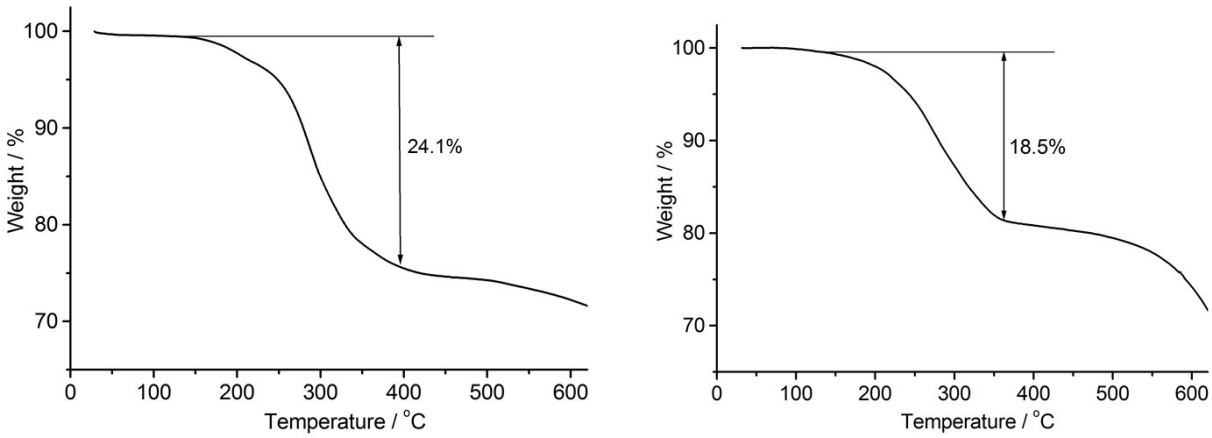

Fig. S16. TGA curves of compounds **1** (left), and **2** (right).

The thermal properties of the compounds **1** and **2** were investigated by thermogravimetric analysis (TGA), and the test were carried out under nitrogen atmosphere in the temperature from 25°C to 620°C (Fig. S16). Compound **1** displayed a weight loss of about 24.1% in one step between 150°C and 395 °C, which is in good accordance with the theoretical mass loss of 23.5% for the DMF ligands. Compound **2** exhibits a similar thermo decomposition with a weight loss of 18.5% in the temperature range of 140–360 °C, which corresponds the removal of DMF ligands (theoretical value of 17.1%).