Supporting Information (SI)

Charge Transfer Stimulated Visible-Light Photochromism of Naphthalenediimide-Based Zinc Halide Coordination Polymers for Detecting/Filtrating Harmful Blue Rays

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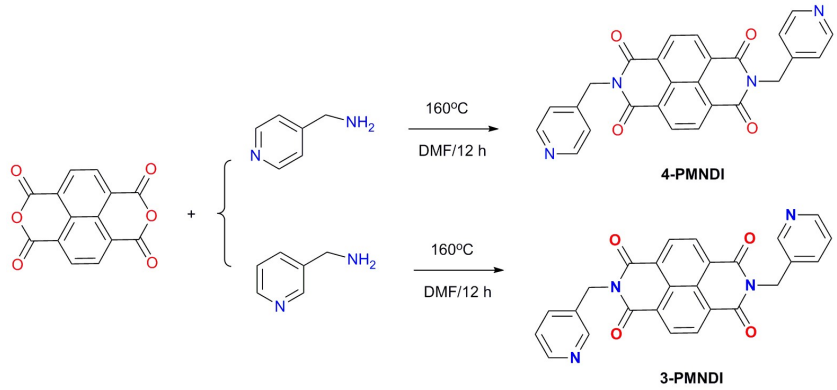
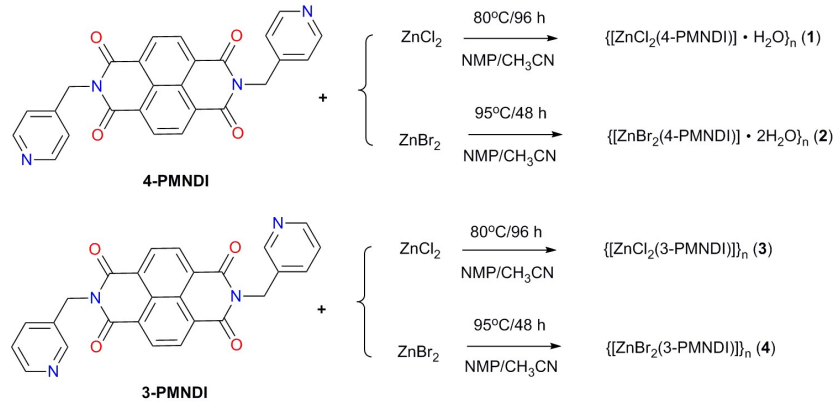
Content

1. Scheme



Scheme S1. Synthetic procedures for the Ligand 4/3-PMNDI.



Scheme S2. Synthetic procedures for the complexes **1**–**4**.

2. Figures

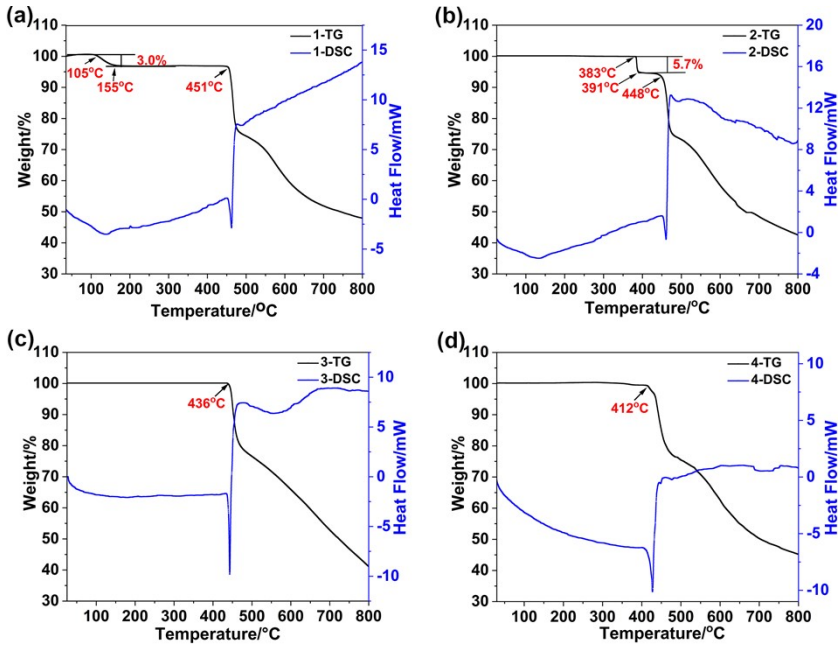


Fig. S1 Thermo-gravimetric (TG) and Differential scanning calorimetry (DSC) curves of **1**–**4**.

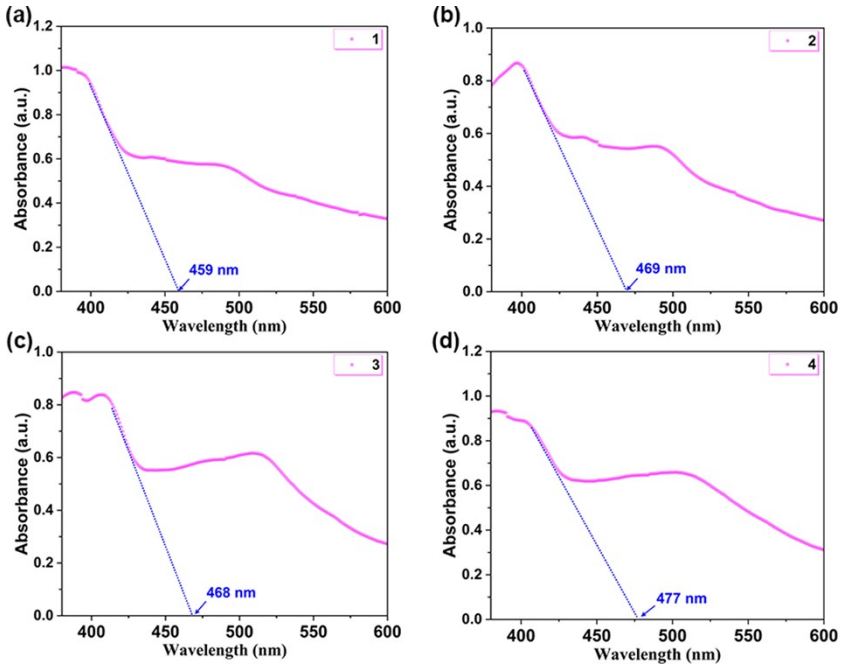


Fig. S2 The original absorption bands in the UV-vis absorption spectra of complexes **1**–**4**.

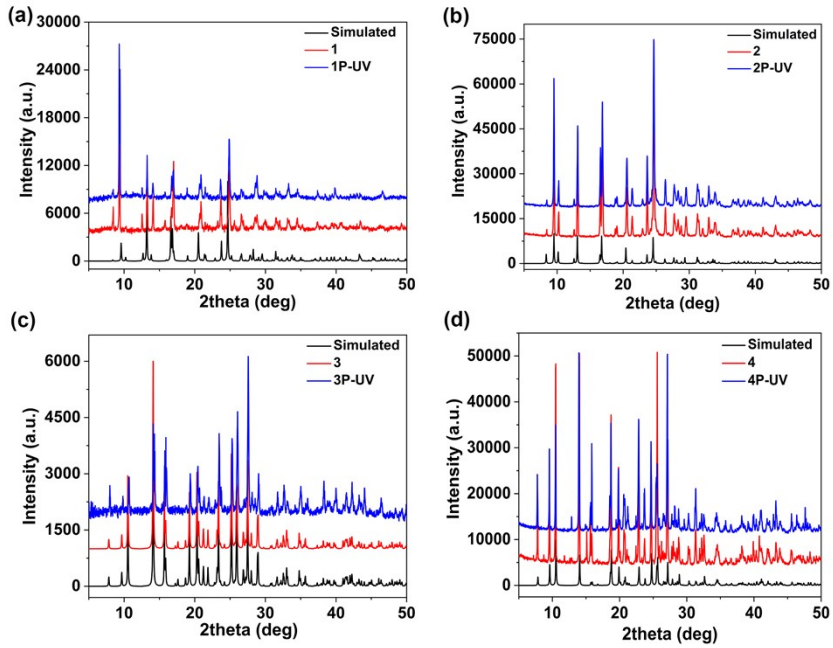


Fig. S3 PXRD patterns of **1**–**4** simulated from the X-ray single-crystal structures, as-synthesized samples and after UV-light irradiation samples.

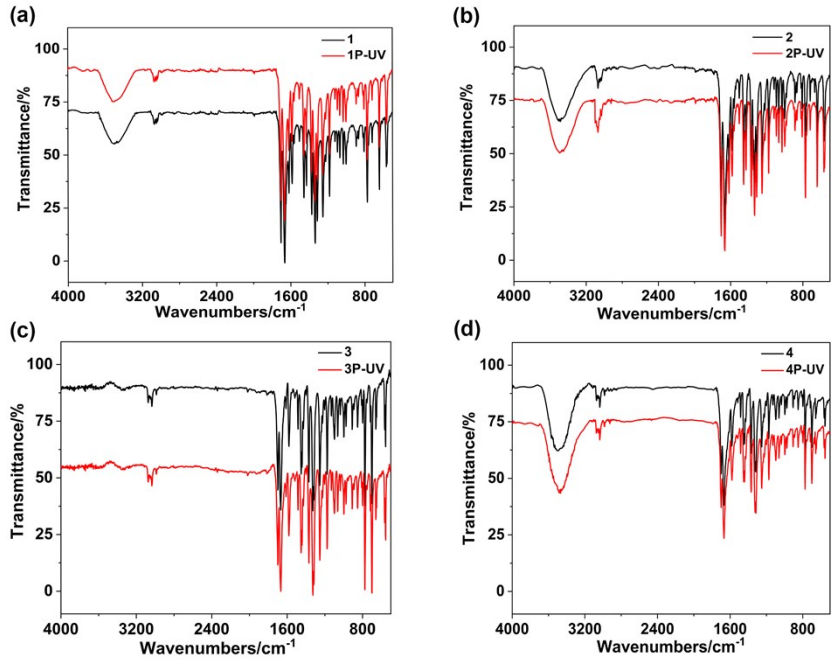


Fig. S4 FT-IR spectra of **1**–**4** as-synthesized samples and after UV-light irradiation samples.

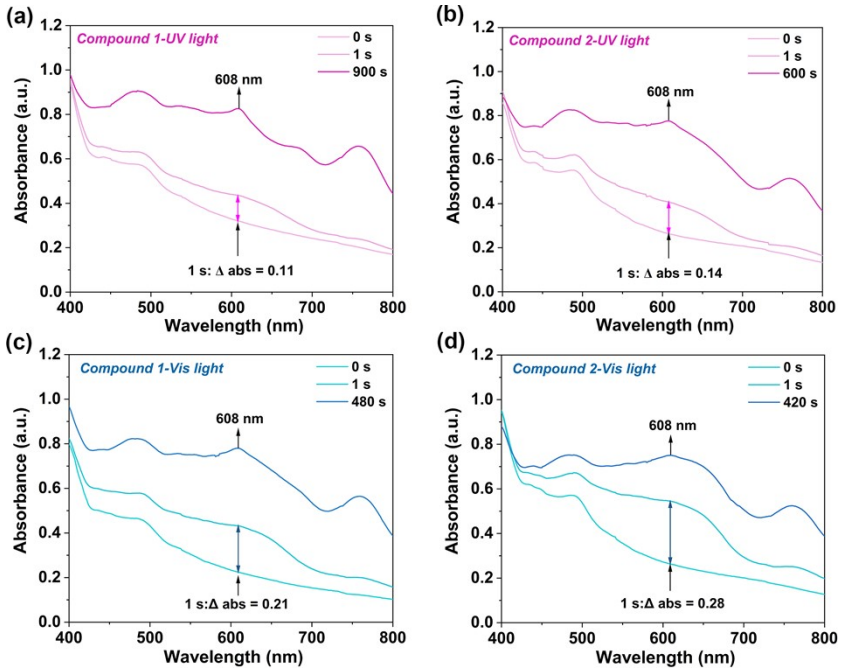


Fig. S5 (a) and (b) The change of absorption in 1 second of **1** and **2** upon UV-light 365 nm irradiation, (c) and (d) The change of absorption in 1 second of **1** and **2** upon Visible-light (> 420 nm) irradiation at RT.

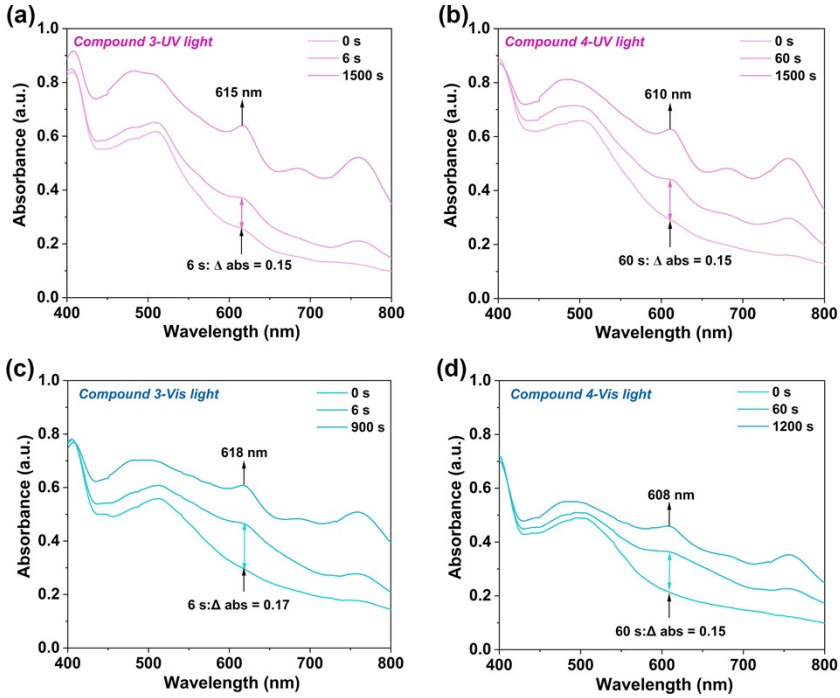


Fig. S6 (a) and (b) The change of absorption in 6 seconds of **3** and 60 seconds of **4** upon UV-light 365 nm irradiation, (c) and (d) The change of absorption in 6 seconds of **3** and 60 seconds of **4** upon Visible-light (> 420 nm) irradiation at RT.

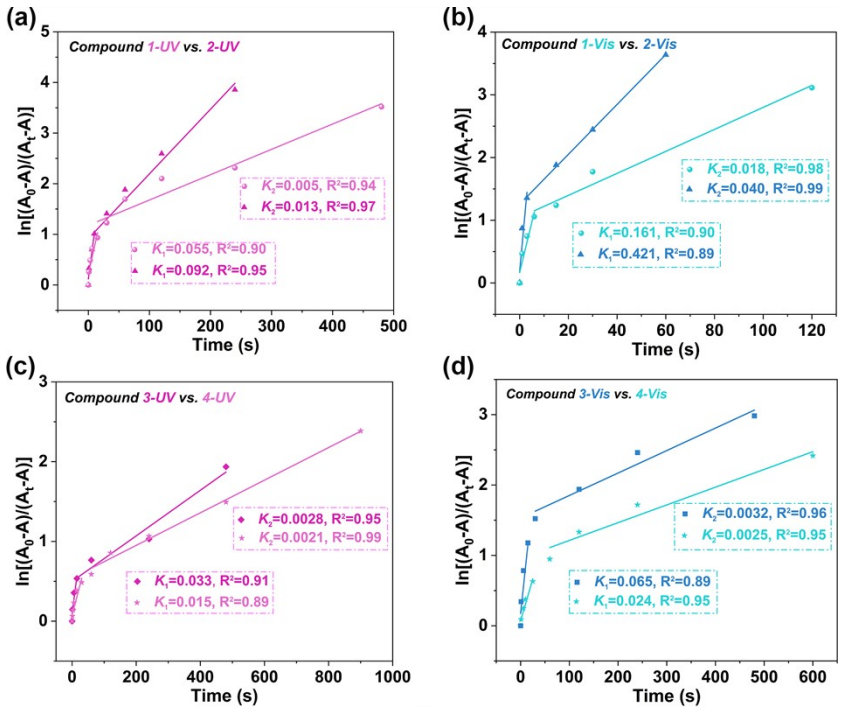


Fig. S7 Photochemical reaction kinetic comparison plots of **1**–**4** monitored at 608, 608, 618 and 608 nm upon visible-light (> 420 nm) irradiation and 608, 610, 615 and 610 upon UV-light (365 nm) illumination respectively under ambient conditions.

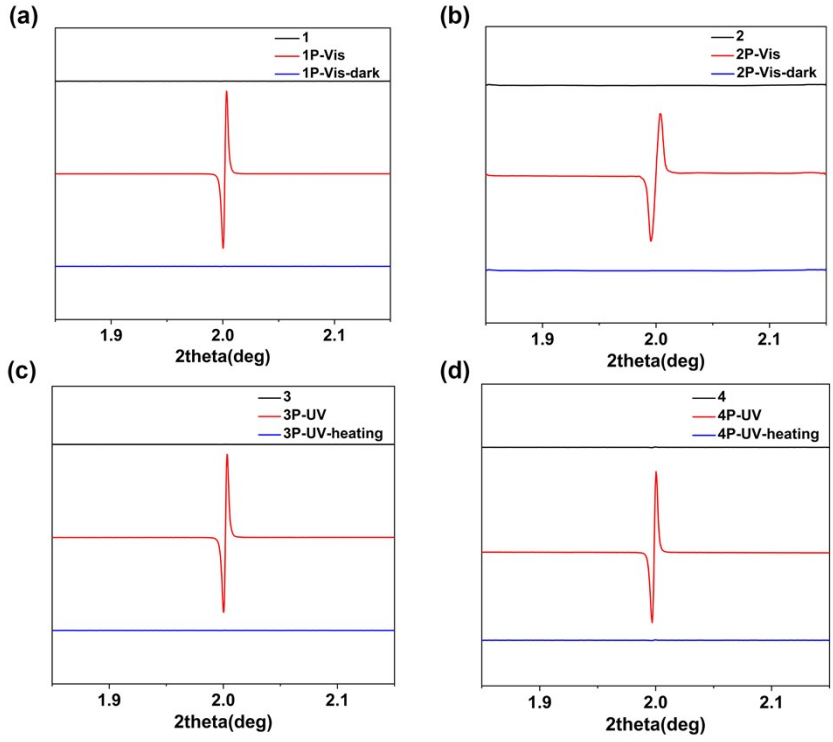


Fig. S8 (a) EPR spectra of **1**, **1P-Vis** and **1P-Vis** after dark treatment. (b) EPR spectra of **2**, **2P-Vis** and **2P-Vis** after dark treatment. (c) EPR spectra of **3**, **3P-UV** and **3P-UV** after heating treatment. (d) EPR spectra of **4**, **4P-UV** and **4P-UV** after heating treatment.

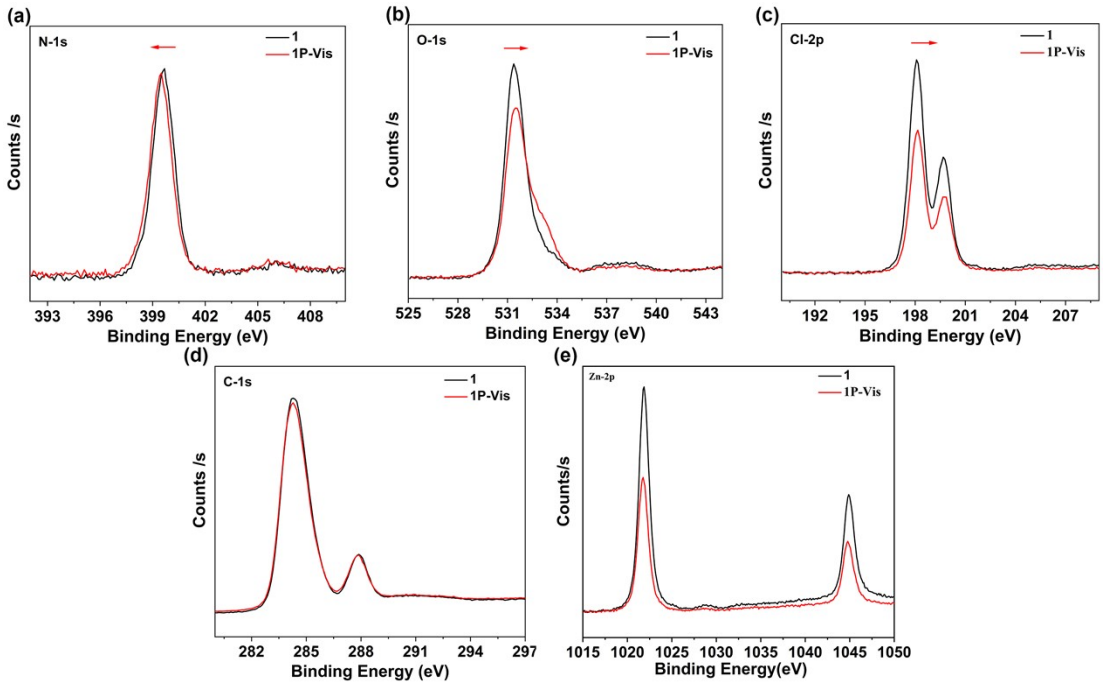


Fig. S9 N 1s (a), O 1s (b), Cl 2p (c), C 1s (d) and Zn 2p (e) XPS core-level spectra of **1** and **1P-Vis**.

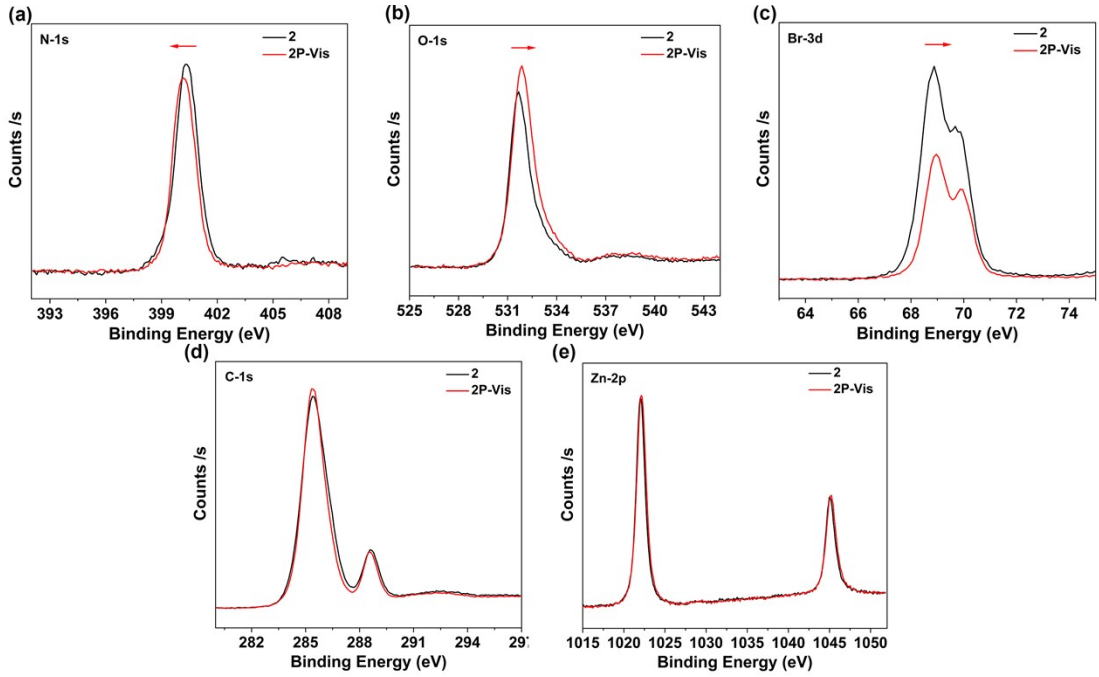


Fig. S10 N 1s (a), O 1s (b), Br 3d (c), C 1s (d) and Zn 2p (e) XPS core-level spectra of **2** and **2P-Vis**.

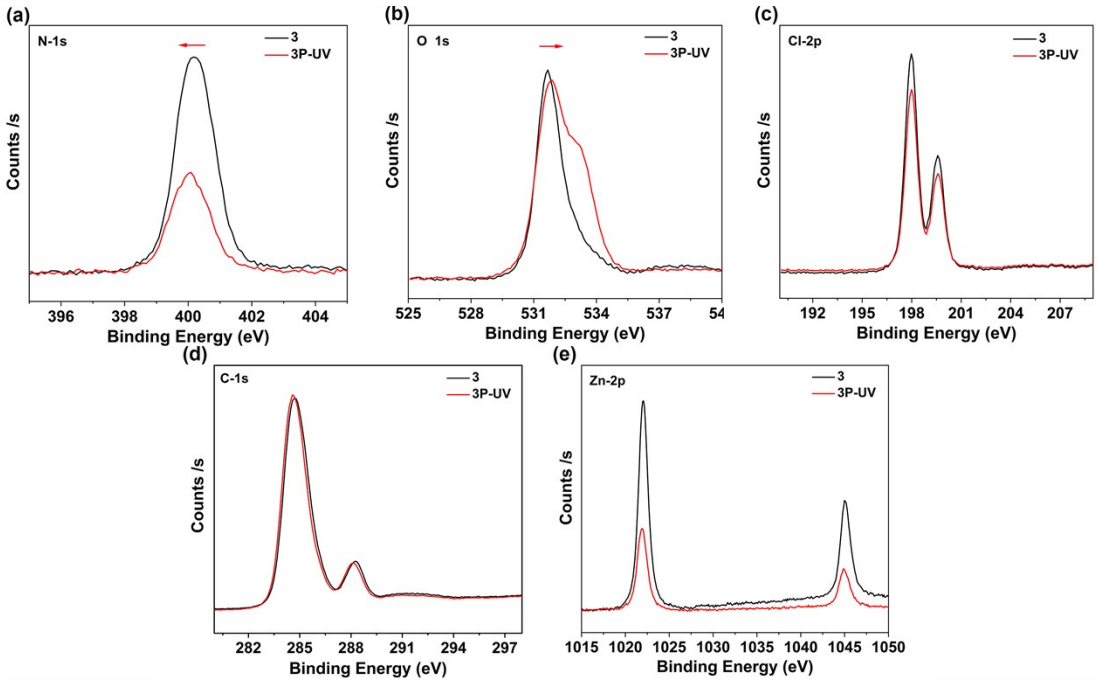


Fig. S11 N 1s (a), O 1s (b), Cl 2p (c), C 1s (d) and Zn 2p (e) XPS core-level spectra of **3** and **3P-UV**.

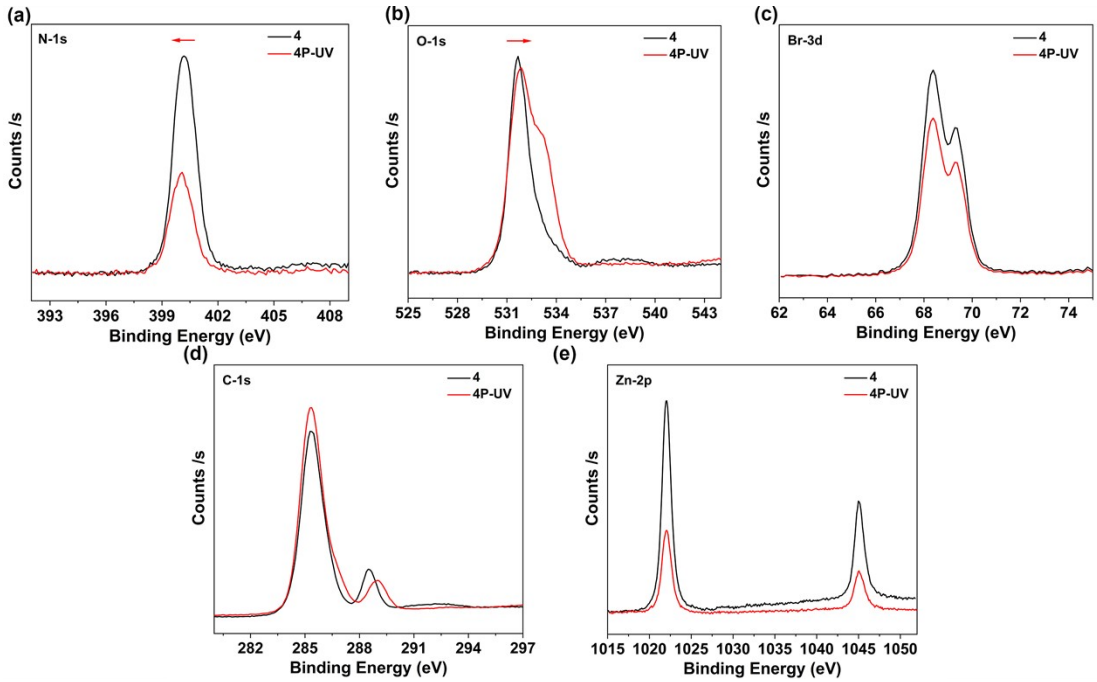


Fig. S12 N 1s (a), O 1s (b), Br 3d (d), C 1s (d) and Zn 2p (e) XPS core-level spectra of **4** and **4P-UV**.

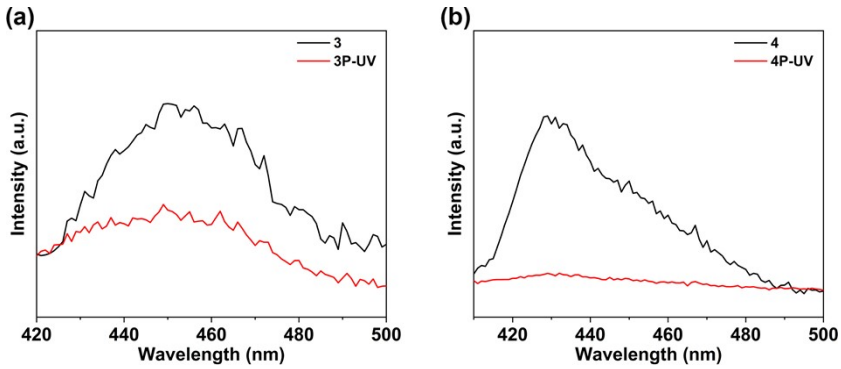


Fig. S13 (a). Luminescence spectra of **3**, **3P-UV**, λ_{ex} = 365 nm; (b) Luminescence spectra of **4**, **4P-UV**, λ_{ex} = 365 nm.

3. Tables

Table S1 The rate constants in the first stage and second stage of **1**–**4** under UV-light and visible light irradiation respectively.

Compounds	UV-K_1	UV-K_2	Vis-K_1	Vis-K_2
1	0.055	0.005	0.161	0.018
2	0.092	0.013	0.421	0.040
3	0.033	0.0028	0.065	0.0032
4	0.015	0.0021	0.024	0.0025

Table S2 Distance Parameters for weak interactions for **1**–**4**.

Compounds	**1**	**2**	**3**	**4**
π-π interactions (Å)	--	--	$d_{\pi\text{-}\pi}$ = 3.8219	$d_{\pi\text{-}\pi}$ =3.9290
X-π interactions (Å)	$d_{Cl\text{-}\pi}$ = 3.3189	$d_{Br\text{-}\pi}$ = 3.3324	--	--
O-π interactions (Å)	--	--	$d_{o\text{-}\pi}$ = 3.6055	$d_{o\text{-}\pi}$ = 3.7192
Ionic radius (Å)	Cl: 1.81	Br: 1.95	--	--
X-centroid net distance (Å)	1.51	1.38	--	--
Eletronegativity of X	Cl: 3.16	Br: 2.96	--	--

Table S3 Crystallographic data and refinement of **2**–**4**.

Compounds	**2**	**3**	**4**
CCDC code	2412670	2412671	2412672
Temperature (K)	273.15(10)	293(2)	296.75(10)
Empirical formula	$C_{26}H_{20}ZnN_4O_6Br_2$	$C_{26}H_{16}ZnN_4O_4Cl_2$	$C_{26}H_{16}ZnN_4O_4Br_2$
Formula weight	709.65	584.70	673.62
Crystal size (mm)	0.25 × 0.08 × 0.03	0.493 ×0.108 × 0.023	0.24 × 0.16 × 0.06
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C2/c*	*C2/c*	*C2/c*
a (Å)	13.4928(17)	23.565(2)	23.497(2)
b (Å)	18.563(2)	5.2731(5)	5.4400(5)
c (Å)	11.3130(13)	19.1074(18)	19.1936(17)
α (°)	90	90	90
β (°)	107.371(3)	106.827(3)	106.576(2)
γ (°)	90	90	90
V (Å^3)	2704.3(6)	2272.6(4)	2351.5(4)
Z	4	4	4
ρ_c (g cm^{-3})	1.743	1.709	1.903
μ (mm^{-1})	3.912	1.361	4.487
F (000)	1408.0	1184.0	1328.0
Reflections collected	18602	13634	16194
Independent reflections	3395	2808	2923
R_{int}	0.0679	0.0310	0.0351
Goodness-of-fit on F^2	1.144	1.030	1.023
R_1/wR_2, [$I \geq 2\sigma(I)$][a,b]	0.0679/0.1368	0.0319/0.0776	0.0264/0.0747

R_1/wR_2, (all data)	0.1061/0.1469	0.0484/0.0842	0.0360/0.0797

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

Table S4 Selected bond lengths (Å) and angles (°) for **2**–**4**.

Compound **2**			
Br(1)-Zn(1)	2.3368(8)	C(3)-C(4)	1.378(8)
Zn(1)-N(1)#1	2.062(5)	C(3)-C(6)	1.513(8)
Zn(1)-N(1)	2.062(5)	C(4)-C(5)	1.380(8)
Br(1)#1-Zn(1)-Br(1)	119.27(6)	N(2)-C(6)-C(3)	110.3(4)
N(1)-Zn(1)-Br(1)#1	111.94(13)	O(2)-C(7)-N(2)	120.1(5)
N(1)-Zn(1)-Br(1)	106.59(12)	O(2)-C(7)-C(8)	122.2(5)
N(1)#1-Zn(1)-Br(1)#1	106.59(12)	N(2)-C(7)-C(8)	117.7(5)
N(1)#1-Zn(1)-Br(1)	111.94(13)	C(9)-C(8)-C(7)	120.3(5)
N(1)#1-Zn(1)-N(1)	98.6(3)	C(9)-C(8)-C(10)	120.1(5)
#1: -X, +Y, 1/2-Z; #2: 1/2-X, 3/2-Y, 1-Z			
Compound **3**			
Zn(1)-Cl(1)	2.2226(6)	C(2)-C(6)	1.503(3)
Zn(1)-Cl(1)#1	2.2226(6)	C(3)-C(4)	1.372(4)
Zn(1)-N(1)	2.0687(18)	C(4)-C(5)	1.369(4)
Zn(1)-N(1)#1	2.0687(18)	C(7)-C(8)	1.484(3)
Cl(1)#1-Zn(1)-Cl(1)	128.69(4)	N(2)-C(6)-C(2)	112.26(18)
N(1)#1-Zn(1)-Cl(1)	107.61(6)	O(2)-C(7)-N(2)	120.7(2)
N(1)-Zn(1)-Cl(1)#1	107.61(6)	O(2)-C(7)-C(8)	122.6(2)
N(1)-Zn(1)-Cl(1)	103.46(5)	N(2)-C(7)-C(8)	116.71(18)
N(1)#1-Zn(1)-Cl(1)#1	103.47(6)	C(9)-C(8)-C(7)	119.7(2)
N(1)#1-Zn(1)-N(1)	103.62(10)	C(13)-C(8)-C(7)	119.79(18)
#1: -x, +Y, 1/2-Z			
Compound **4**			
Br(1)-Zn(1)	2.3575(3)	C(1)-C(2)	1.376(3)
Zn(1)-Br(1)#1	2.3576(3)	C(7)-C(8)	1.483(3)
Zn(1)-N(1)#1	2.071(2)	C(2)-C(6)	1.503(3)
Zn(1)-N(1)	2.071(2)	C(2)-C(3)	1.379(4)
Br(1)-Zn(1)-Br(1)#1	126.06(2)	C(3)-C(2)-C(6)	122.3(2)
N(1)#1-Zn(1)-Br(1)#1	107.94(6)	C(8)-C(9)-C(9)#2	119.8(3)
N(1)-Zn(1)-Br(1)	107.94(6)	C(8)-C(9)-C(10)	121.4(2)

N(1)-Zn(1)-Br(1)#1	104.38(6)	C(10)-C(9)-C(9)#2	118.9(2)
N(1)#1-Zn(1)-Br(1)	104.38(6)	C(12)-C(8)-C(7)	119.64(19)
N(1)#1-Zn(1)-N(1)	104.35(11)	C(12)-C(8)-C(9)	120.4(2)

#1: -X, +Y, 1/2-Z, #2: 1/2-X, 3/2-Y, 1-Z

Table S5 Hydrogen bonds of for **2**–**4** (Å and °)

Compound **2**				
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C1-H1···Br1	0.93	3.05	3.645(5)	122.9
C2-H2···O2	0.93	2.64	3.268(6)	125.7
C2-H2···O1	0.93	2.78	3.373(7)	123.0
C6-H6A···O1#1	0.97	2.78	3.507(6)	132.8
C6-H6B···O1#2	0.97	2.44	3.306(6)	147.8
C9-H9···Br1	0.93	2.86	3.721(5)	154.7

#1: -X, +Y, 1/2-Z; #2: 1/2-X, 3/2-Y, 1-Z

Compound **3**				
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C1-H1···C11	0.93	2.91	3.490(2)	122.1

Compound **4**				
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C12-H12···O2	0.93	2.61	3.532(3)	173.0
C1-H1···Br1	0.93	3.00	3.599(2)	123.8
C1-H1···O2	0.93	2.71	3.316(2)	123.7
C6-H6#1···O2	0.97	2.92	3.648(3)	132.7
C6-H6 #2···O2	0.97	3.06	3.858(3)	140.6
C13-H13···Br1	0.93	3.14	3.718(3)	122.2
C5-H5···O1	0.93	3.04	3.841(4)	145.1

#1: -X, +Y, 1/2-Z, #2: 1/2-X, 3/2-Y, 1-Z