

# **Two component semiconductive hybrid coordination polymers with controllable photo-induced electron-transfer properties**

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# 1. Experimental Details and Synthesis

## 1.1. Materials and methods:

PbI<sub>2</sub>, CuI, hydroiodic acid (55%, w/w), methanol (analytical reagent grade), naphthalene-1,4,5,8-tetracarboxylic acid, 4-aminopyridine, *N,N*-Dimethylformamide, acetonitrile and methanol in AR grade were purchased commercially and used without further purification. The organic ligand DPNDI was synthesized according to the same procedures reported in the literature [S<sup>1</sup>].

The infrared spectra have been measured in the range of 400-4000cm<sup>-1</sup> by use of a Perkin-Elmer FT-IR spectrophotometer. Powder X-ray diffraction (PXRD) intensities were recorded on a Rigaku Mini Flex-II X-Ray diffractometer. TGA measurements were performed on a TG-209 system with a heating rate of 10 °C/min under an N<sub>2</sub>-atmosphere. The electron spin resonance (ESR) measurements were recorded on a Bruker A300 instrument operating in the X-band at room temperature. The XPS studies were performed with a Thermo Fisher ESCALAB250 X-ray photoelectron spectrometer (powered at 150 W) using Al K $\alpha$  radiation ( $\lambda = 8.357 \text{ \AA}$ ). To compensate for surface charging effects, all XPS spectra were referenced to the C 1s neutral carbon peak at 284.7 eV. UV-Vis diffuse reflectance spectra were recorded at room temperature on a Varian Cary 500 UV-Vis spectrophotometer equipped with an integrating sphere by using BaSO<sub>4</sub> as a white standard in the range of 200-1200 nm.

## 1.2. Synthesis

**Synthesis of [Cu<sub>2</sub>I<sub>2</sub>(DPNDI)]<sub>n</sub> (1).** In a crystallization tube, a solution (5 mL) of MeOH was carefully layered on a DMF (5 mL) solution of DPNDI (0.10 mmol, 0.042 g), CuI, (0.10 mmol, 0.019 g) and 0.2 mL HI (55%, w/w). Dark block crystals of complex **1** were obtained after several days (yield 42% based on DPNDI). IR (KBr, cm<sup>-1</sup>): 3070 (w), 3017 (w), 1722 (s), 1680 (s), 1575 (s), 1506 (m), 1410 (m), 1337 (s), 1247 (s), 1179 (m), 1120 (s), 972 (m), 824 (s), 835 (m), 755 (s), 634 (m), 526 (s).

**Synthesis of [PbI<sub>2</sub>(DPNDI)]<sub>n</sub> (2).** The synthesis procedure of **2** is similar to that of **1**, except CuI was replaced by PbI<sub>2</sub> (yield 65% based on DPNDI). IR data (KBr, cm<sup>-1</sup>): 3092 (w), 3012 (w), 1717 (s), 1675 (s), 1575 (m), 1342 (s), 1247 (s), 1205 (m), 977 (m), 771 (m), 735 (m), 629 (m), 528 (m).

## 2. Molecular orbital calculations

Molecular structures determined by X-ray crystallographic analysis have been used for the

evaluation of their molecular orbital energies through density functional theory (DFT) computations using the Gaussian 03 suite of programs [S2]. A hybrid functional, B3LYP, was used for all calculations. Geometry were optimized using the 6-21G\* basis set.

### 3. X-ray Diffraction Analysis

The suitable single crystals of **1** and **2** were mounted on glass fiber for X-ray measurements. Diffraction data were collected on a Rigaku-AFC7 equipped with a Rigaku Saturn CCD area-detector system. The measurements were made using graphic monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 K. The frame data were integrated and absorption correction were calculated the Rigaku *CrystalClear* program package. All calculations were performed with the *SHELXTL-97* program package[S3] and structures were solved by direct methods and refined by full-matrix least-squares against F<sup>2</sup>. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms. The crystal data and structure refinements are summarized in Table S1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 1451074-1451075 for **1-2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1** Crystal Data and Structure Refinement Parameters for **1-2**

Complex	<b>1</b>	<b>2</b>
empirical Formula	C <sub>12</sub> H <sub>6</sub> CuIN <sub>2</sub> O <sub>2</sub>	C <sub>24</sub> H <sub>12</sub> I <sub>2</sub> N <sub>4</sub> O <sub>4</sub> Pb
formula weight	400.63	881.37
crystal system	Monoclinic	Monoclinic
space group	<i>P2<sub>1</sub>/n</i>	<i>C2/c</i>
<i>a</i> (Å)	14.484(3)	25.087(5)
<i>b</i> (Å)	4.1532(8)	4.5640(9)
<i>c</i> (Å)	20.910(4)	25.103(5)
$\alpha$	90	90
$\beta$ (deg)	92.11(3)	111.08(3)
$\gamma$	90	90
<i>V</i> (Å <sup>3</sup> )	1257.0(4)	2682.0(9)
<i>Z</i>	4	4
<i>T</i> (K)	293(2)	293(2)
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	2.117	2.183
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	4.187	8.628
F(000)	760	1616
collected reflections	11114	10434
unique reflections	2844 (0.0310)	3042 (0.0470)

no. of observations	2404	2833
goodness-of-fit on $F^2$	1.043	1.132
$R_1^a, wR_2^b (I > 2\sigma(I))$	0.0443, 0.1193	0.0516, 0.1178
$R_1^a, wR_2^b(\text{all data})$	0.0519, 0.1241	0.0555, 0.1201

#### 4. The packing of compounds 1 and 2

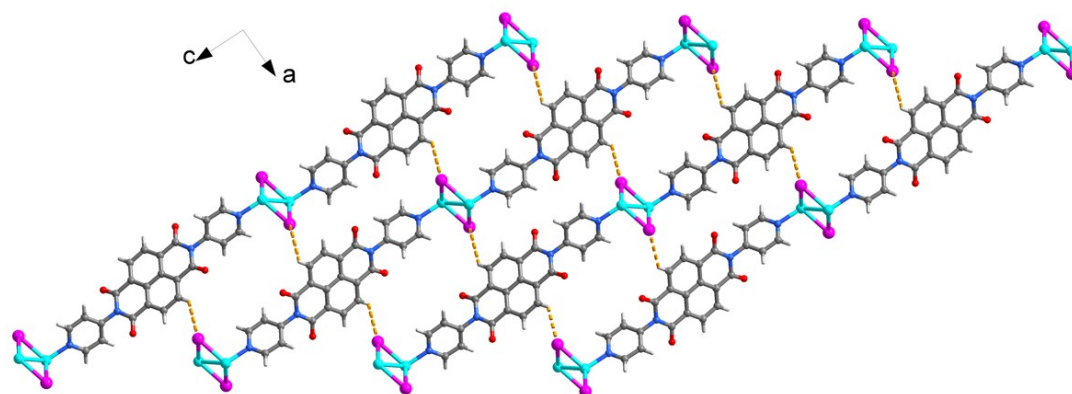


Figure S1. The C-H...I hydrogen bonds of 1.

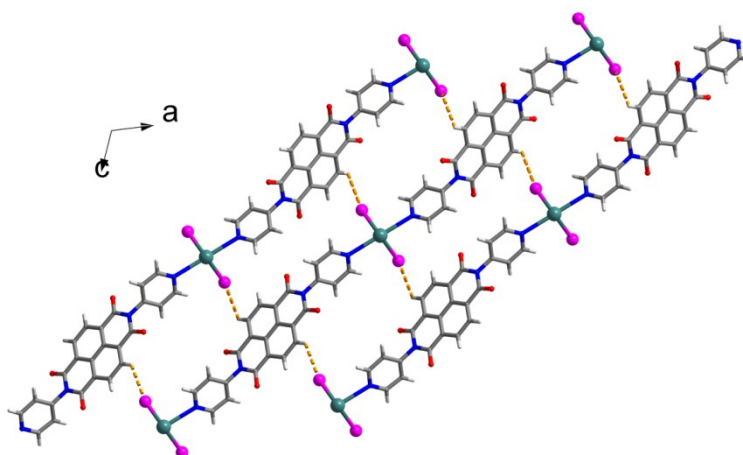


Figure S2. The C-H...I hydrogen bonds of 2.

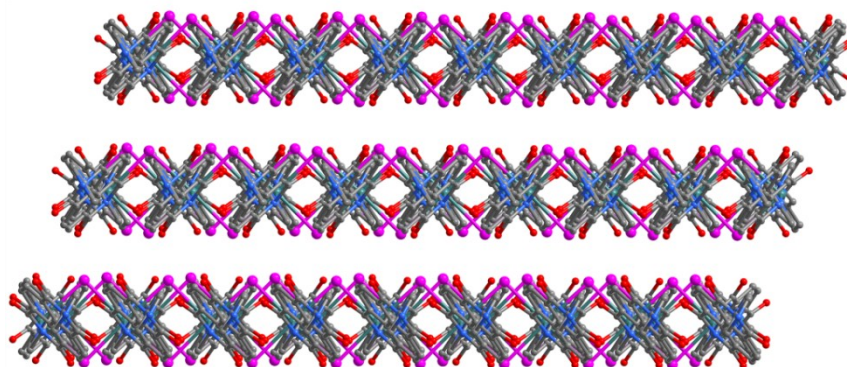
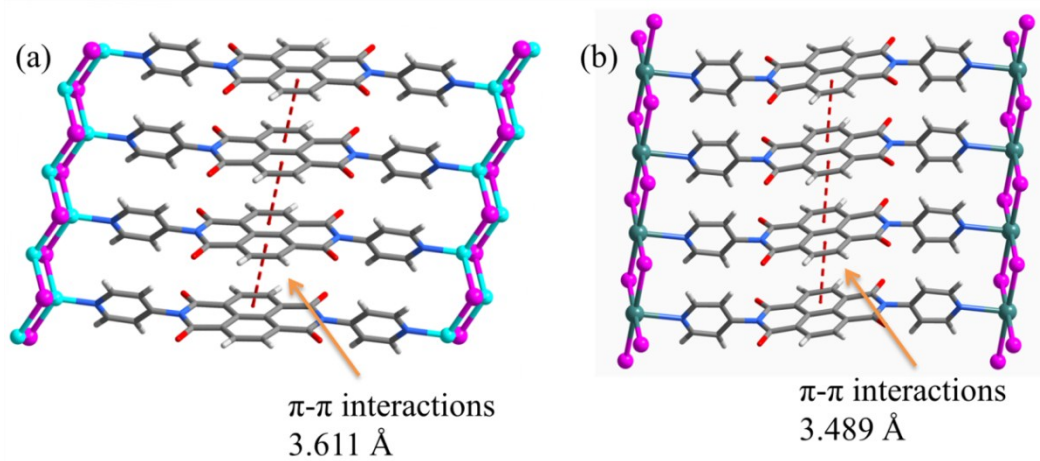
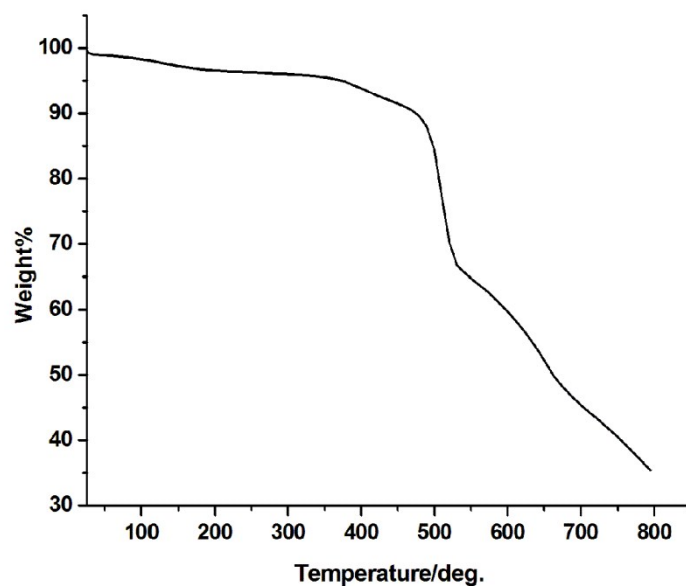


Figure S3. packing diagram of 2 shows layer structure.

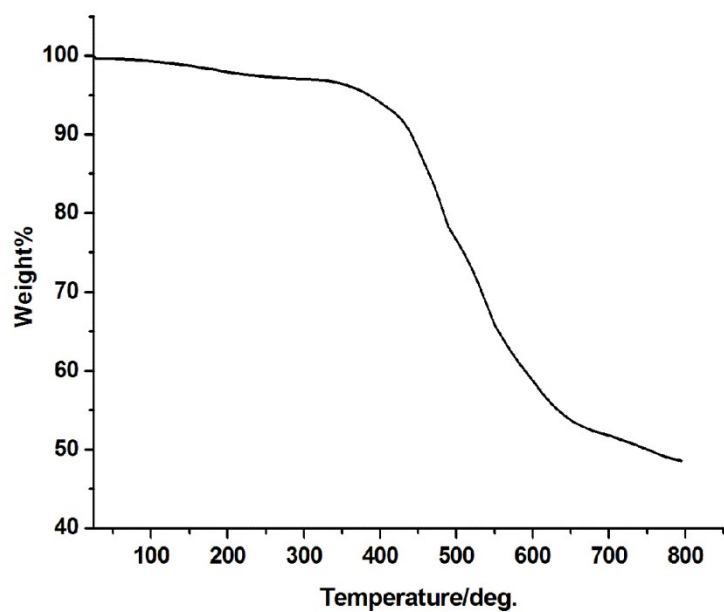


**Figure S4.** The  $\pi$ - $\pi$  interactions in crystals **1** (a) and **2** (b).

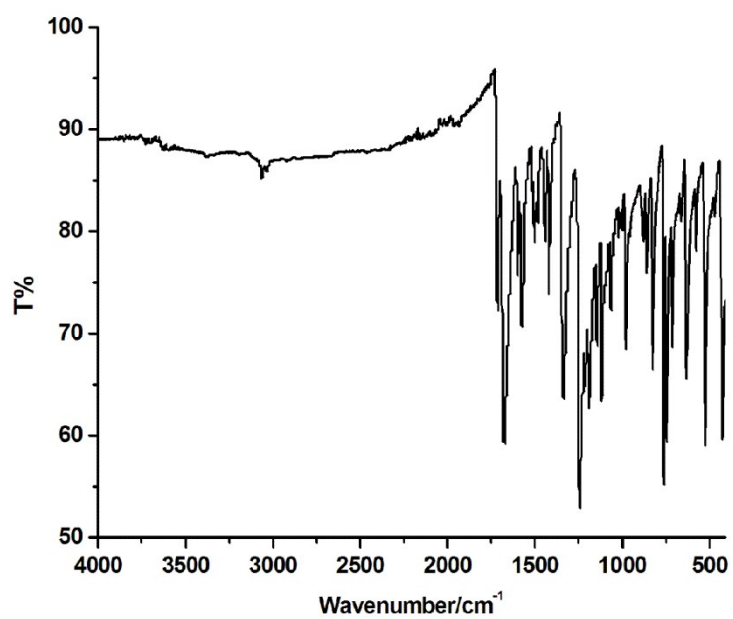
## 5. Other patterns of compounds **1** and **2**



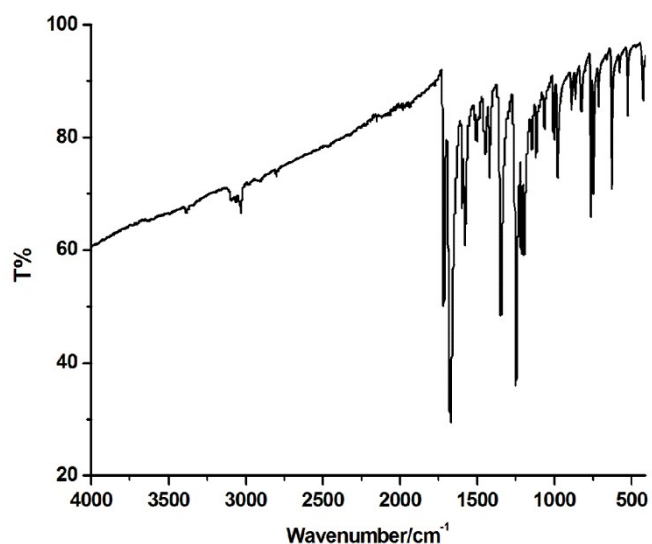
**Figure S5.** Thermogravimetric analyses of crystals **1** in  $N_2$  with a ramp rate of 10 K/min.



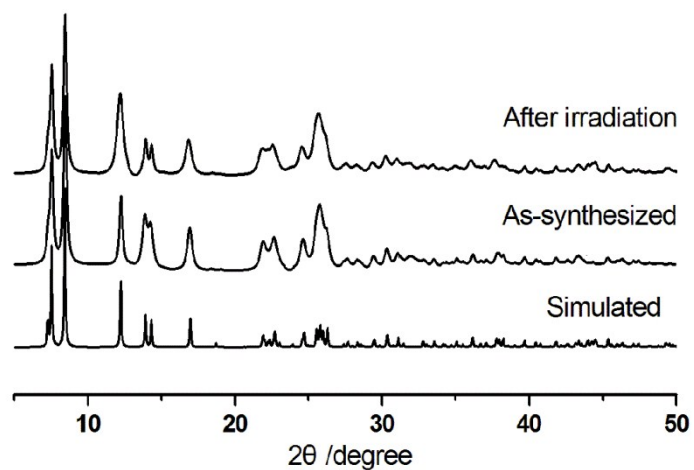
**Figure S6.** Thermogravimetric analyses of crystals **2** in N<sub>2</sub> with a ramp rate of 10 K/min.



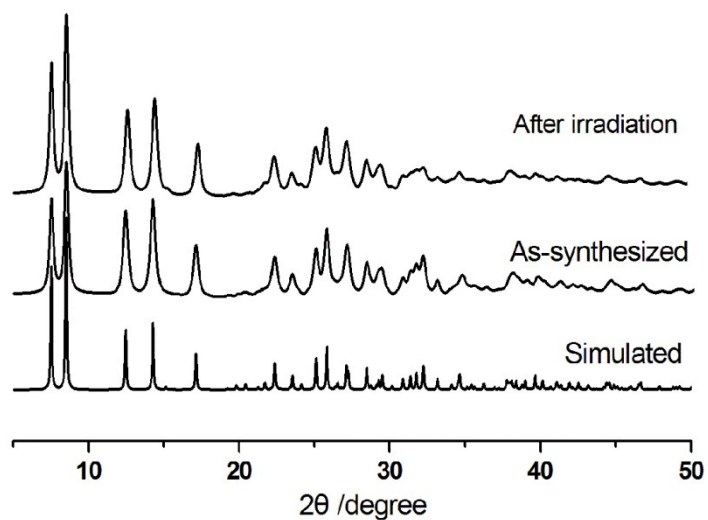
**Figure S7.** IR spectra of crystals **1**.



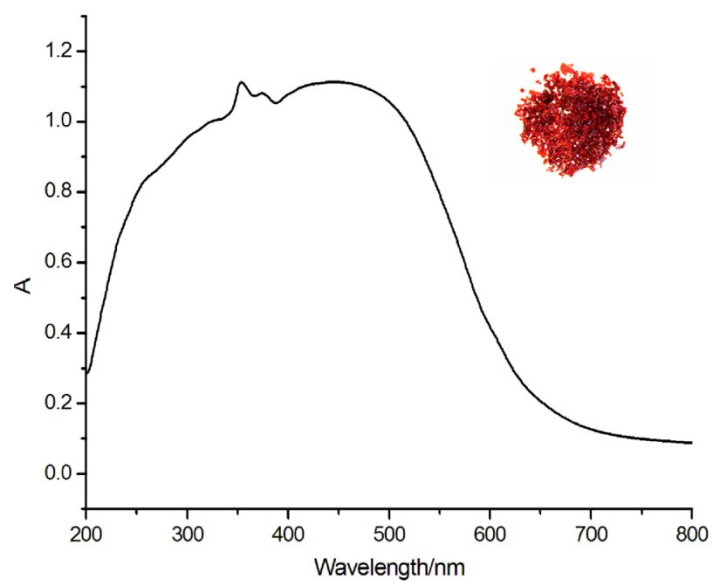
**Figure S8.** IR spectra of crystals **2**.



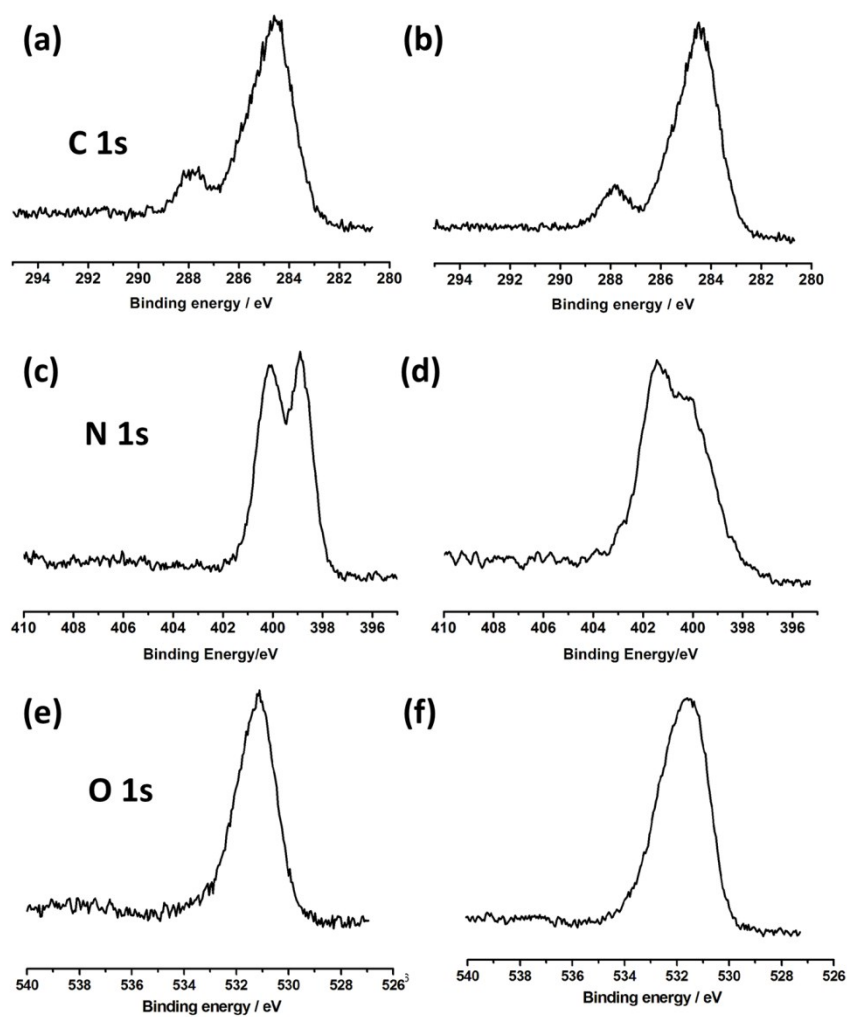
**Figure S9.** Comparison of the simulated and synthesized PXRD for **1**



**Figure S10.** Comparison of the simulated and synthesized PXRD for **2**.



**Figure S11.** UV/Vis diffuse reflectance spectrum of  $(\text{H}_2\text{DPNDI})\cdot(2\text{I})$  at room temperature<sup>[S4]</sup>.



**Figure S12.** C 1s (a, b), N 1s (c, d) and O 1s (e, f) XPS core-level spectra of **1** before and after irradiation.



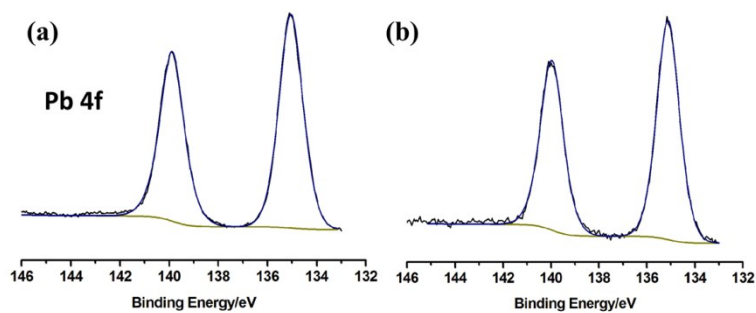


Figure S13. Pb 4f XPS core-level spectra of **2** before (a) and after (b) irradiation.

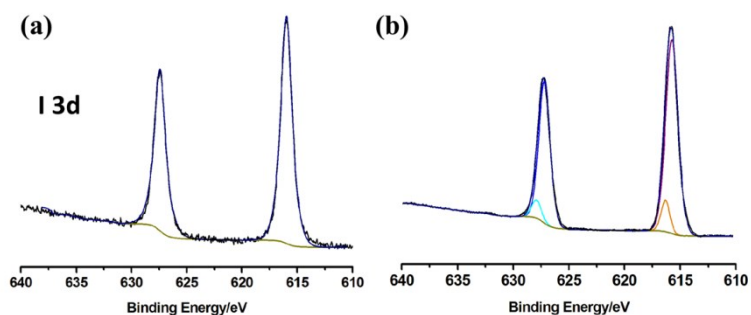


Figure S14. I 3d XPS core-level spectra of **2** before (a) and after (b) irradiation.

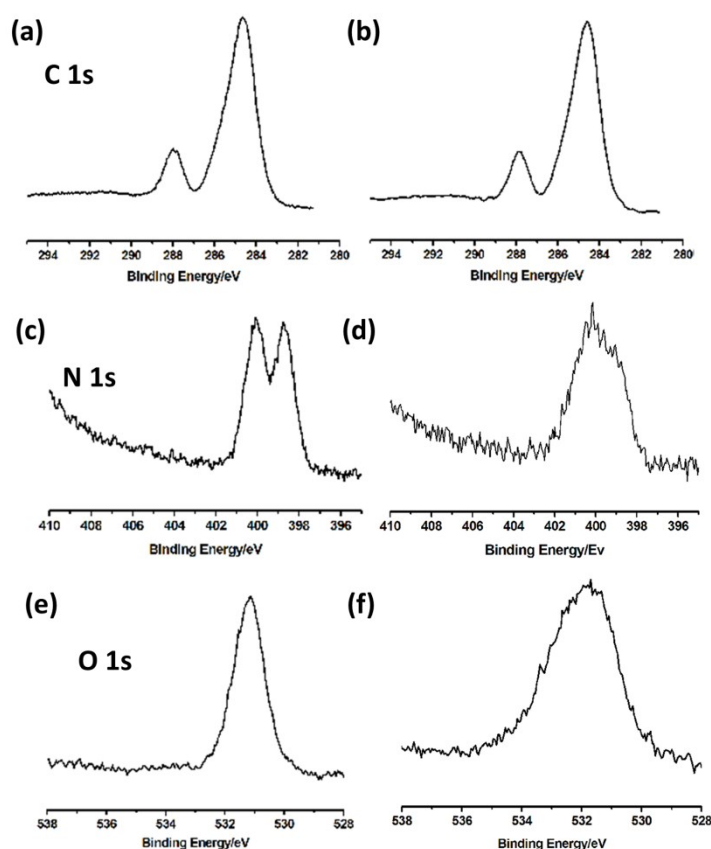
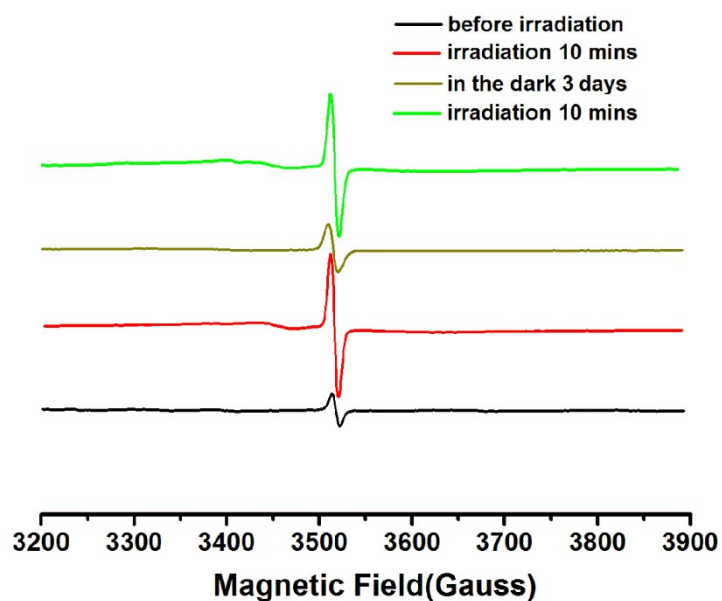
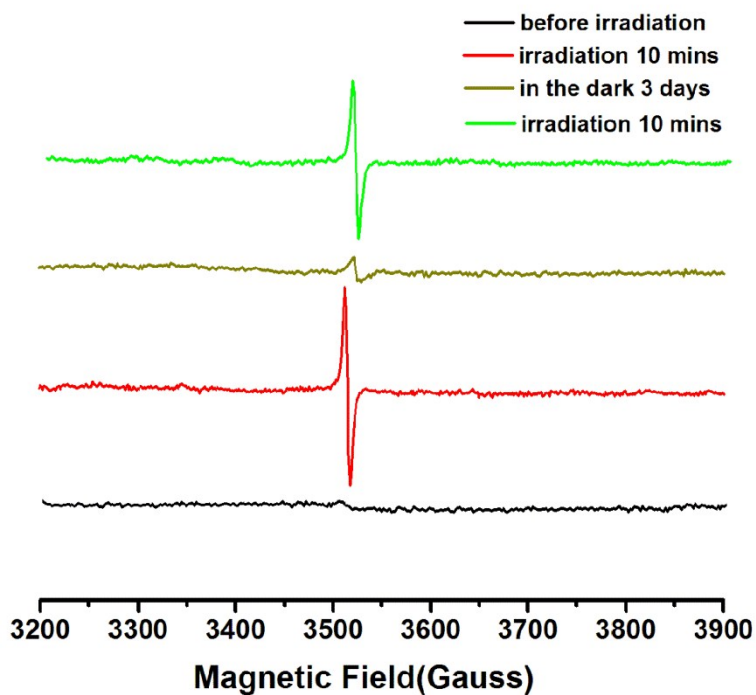


Figure S15. C 1s (a, b), N 1s (c, d) and O 1s (e, f) XPS core-level spectra of **2** before and after irradiation.



**Figure S16.** ESR spectra of **1** at room temperature before and after irradiation.



**Figure S17.** ESR spectra of **2** at room temperature before and after irradiation.

## References

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