

# Exceptional Photosensitivity of the Polyoxometalate-based Charge Transfer Hybrid Material

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## 1. Materials and Physical Measurements

All chemicals were obtained from commercial sources and used as received without further purification. Powder X-ray diffraction (PXRD) were collected on Rigaku desktop MiniFlex II diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ). IR spectra were recorded in the range 4000–400  $\text{cm}^{-1}$  on a Perkin-Elmer FT-IR spectrum 2000 spectrometer with pressed KBr pellets. Optical diffuse reflectance spectra were measured at room temperature on a Perkin Elmer Lambda-900 UV/Vis/NIR spectrophotometer. XPS studies were performed in Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectrometer. EPR spectra were recorded on a Bruker BioSpin E500 EPR spectrometer with a 100 kHz magnetic field modulation at room temperature equipped with a 16 mW ultraviolet lamp. Thermal analyses were performed on a TGA/DSC 1 STAR<sup>e</sup> system from room temperature to 1000°C with a heating rate of 10K/min under nitrogen. A 300W Xenon arc lamp (PLS-SXE 300/300UV, Beijing Perfectlight, Co. Ltd.) equipped with one filter to make the wavelength be in the range of 400-780 nm (visible light) or 320-400 nm (UV light) was employed as the irradiation source.

## 2. Experimental Section

**Synthesis of N, N'-di(4-pyridyl)-1,4,5,8-naphthalenediimide (DPNDI) ligand.** A mixture of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NDA) (0.8 g, 3 mmol) and 4-aminopyridine (6 mmol) in DMF (20 mL) was heated under reflux for 8 h. When the reaction mixture reached room temperature, a crystalline solid precipitated out, which was collected by filtration. The crude product was purified by recrystallization from DMF to obtain DPNDI as off-white crystalline solids.<sup>S1</sup>

**Synthesis of compound 1.** A solution (1mL) of DMA/MeCN (1:1, v/v) was carefully layered over a DMA (4mL) solution of DPNDI tectons (0.03 mmol, 0.0126 g) and 4,4'-bipyridine (0.025 mmol, 0.0037 g), and then the solution of ZnSiF<sub>6</sub> (0.057 mmol, 0.0127 g) and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (0.017 mmol, 0.05 g) in MeCN/MeOH (3:1, v/v) (4mL) mixture was carefully added as a second layer. Yellow crystals that appeared after several days were collected and washed with MeCN in ca. 15% yield (based on Zn). Elemental analyses of C, H and N were carried out with a Vario EL III elemental analyzer. Anal. Calcd for C<sub>64</sub>H<sub>60</sub>F<sub>3</sub>N<sub>12</sub>O<sub>52</sub>PW<sub>12</sub>Zn<sub>2</sub>: C 18.06, H 1.47 N 3.95%. Found: C 21.31, H 2.11, N 5.44%. The difference was probably because of the volatile solvent molecules in the frameworks. Combined with Molecular Weight Calculator, the result we calculated is that there are approximately five MeCN and two DMAc molecules. Calcd: C 21.25, H 2.07, N 5.74%. Elemental analyses of Zn and W were carried out with a Ultima2 Inductively Coupled Plasma OES spectrometer (ICP). Anal. Calcd for C<sub>64</sub>H<sub>60</sub>F<sub>3</sub>N<sub>12</sub>O<sub>52</sub>PW<sub>12</sub>Zn<sub>2</sub>: Zn 2.87, W 47.37% (including five MeCN and two DMAc molecules). Found: Zn 2.82, W 47.59%. IR( $\text{cm}^{-1}$ ): 3396(m), 2952(w), 1612(s), 1508(w), 1348(s), 1249(m), 1192(w), 1075(m), 979(s), 819(s), 752(m), 515(w).

## 3. Crystallographic data collection and refinement

Suitable single crystal of compound **1** was mounted on glass fiber for the X-ray measurement.

Diffraction data was collected on SuperNova (Dual source) diffractometer equipped with the CrysAlis<sup>pro</sup> X-ray crystallography data systems. The measurement was made by using graphic monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.54184\text{\AA}$ ) at 173 K under a cold nitrogen stream. All calculations were performed with the SHELXTL-97 program package<sup>S2</sup>, and structures were solved by direct methods and refined by full-matrix least-squares against  $F^2$ . All non-hydrogen atoms except for the disordered moieties were refined anisotropically, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms. The crystal has very large pores containing badly disordered solvent molecules, which contributed to an A-level alert. SQUEEZE routine implemented on PLATON was used to remove electron densities corresponding to disordered solvent molecules. Crystallographic data has been deposited at the Cambridge Crystallographic Data Center with reference number CCDC 1471310. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

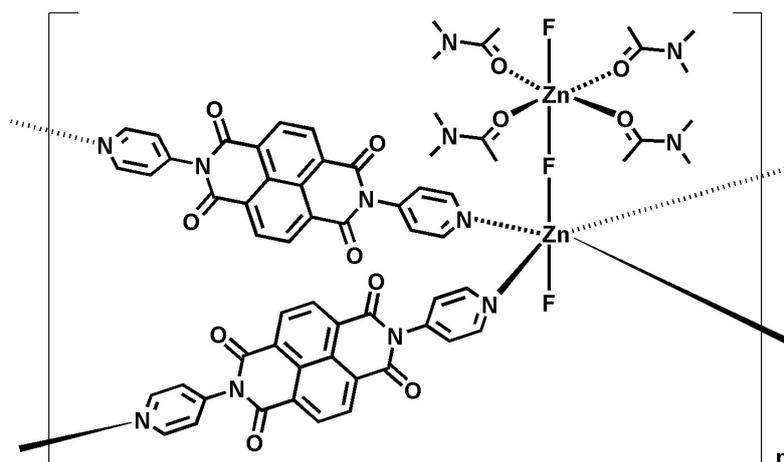
#### 4. Crystal data for compound 1

**Table S1.** Crystal Data and Structure Refinement Parameters for Compound 1

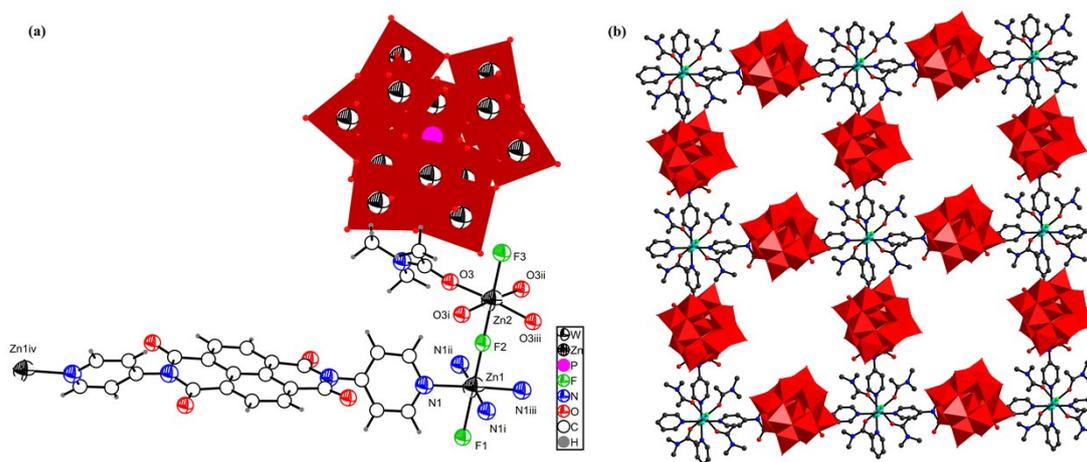
| Compound reference   | Compound 1  |
|--|---|
| Chemical formula   | C <sub>64</sub> H <sub>60</sub> F <sub>3</sub> N <sub>12</sub> O <sub>52</sub> PW <sub>12</sub> Zn <sub>2</sub> |
| Formula Mass   | 4254.15   |
| Crystal system   | Tetragonal  |
| <i>a</i> /Å  | 19.5965(3)  |
| <i>b</i> /Å  | 19.5965(3)  |
| <i>c</i> /Å  | 16.0780(3)  |
| $\alpha$ /°  | 90.00   |
| $\beta$ /°   | 90.00   |
| $\gamma$ /°  | 90.00   |
| Unit cell volume/Å <sup>3</sup>  | 6174.32(18)   |
| Temperature/K  | 173(2)  |
| Space group  | <i>P4/n</i>   |
| No. of formula units per unit cell, <i>Z</i>   | 2   |
| No. of reflections measured  | 18135   |
| No. of independent reflections   | 6320  |
| <i>R</i> <sub>int</sub>  | 0.032   |
| Final <i>R</i> <sub><i>I</i></sub> <sup>a</sup> values ( <i>I</i> > 2σ( <i>I</i> ))        | 0.0340  |
| Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>b</sup> values ( <i>I</i> > 2σ( <i>I</i> )) | 0.0727  |
| Final <i>R</i> <sub><i>I</i></sub> <sup>a</sup> values (all data)                          | 0.0442  |
| Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>b</sup> values (all data)                   | 0.0765  |
| Goodness of fit on <i>F</i> <sup>2</sup>   | 1.064   |

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

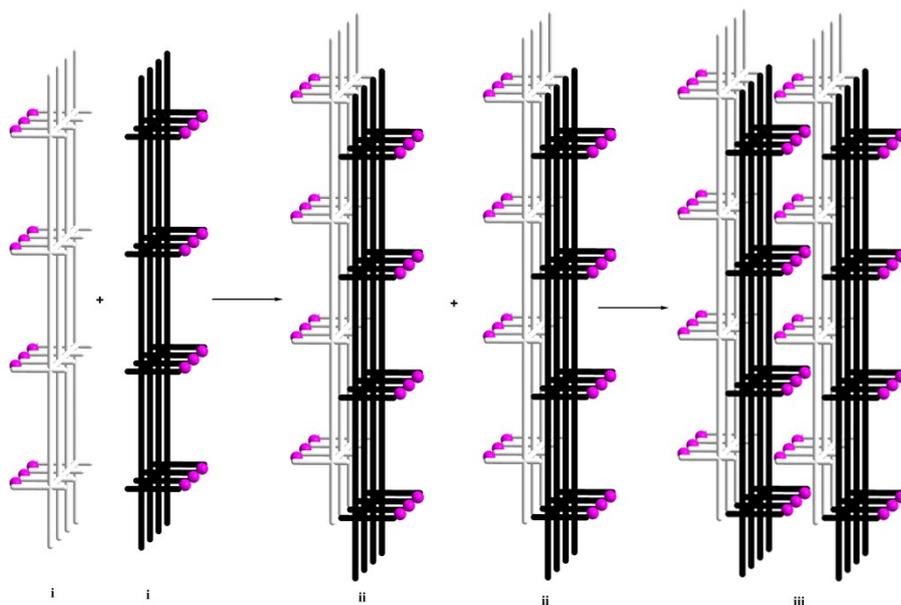
#### 5. Figures of compound 1



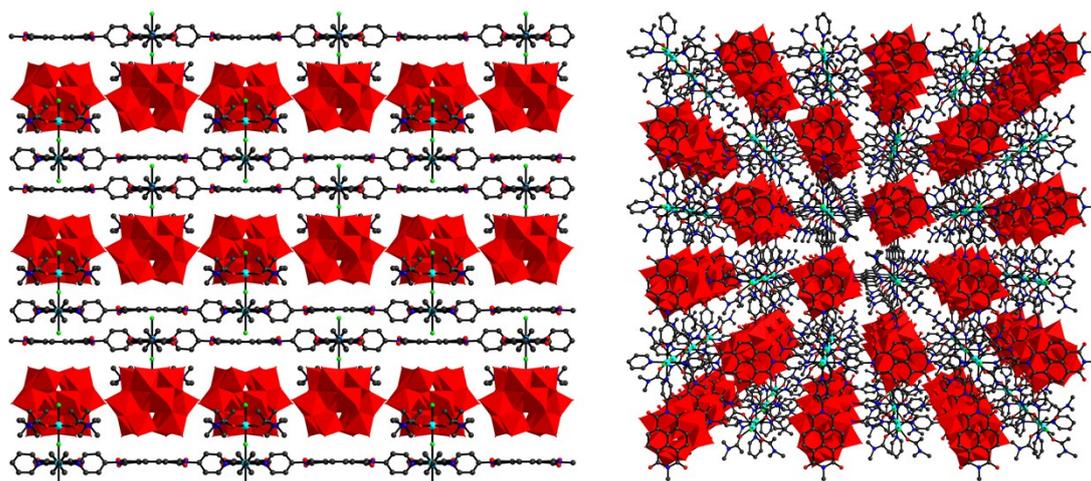
**Scheme S1.** The host unit of compound **1** (POMs guest molecules reside directly over the  $\pi$ -electron-deficient naphthalenic ring centroid which are omitted for clarity).



**Figure S1.** a) Coordination environment of the Zn(II) ionic centre in compound **1** (POMs : red polyhedron). Symmetry codes: i)  $x, 0.5-y, z$ ; ii)  $0.5-x, y, z$ ; iii)  $0.5-x, 0.5-y, z$ ; iv)  $x, 1+y, z$ . b) The 2D layer structure of compound **1**, Zn (turquoise), F (yellow-green), C (black), O (red), N (blue), POMs (red polyhedron).

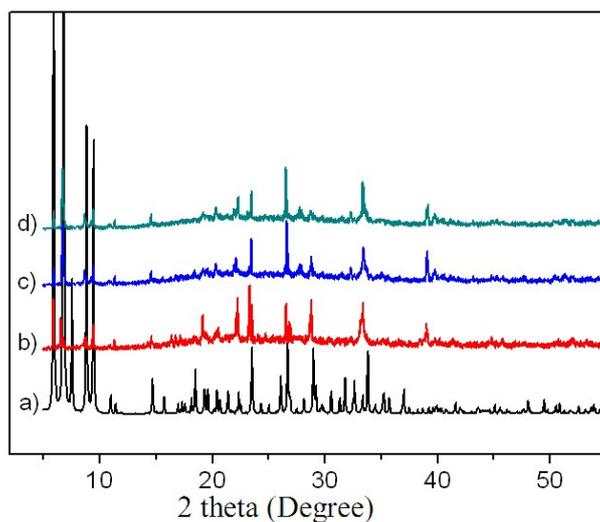


**Figure S2.** Adjacent layers are staggered along a axis.



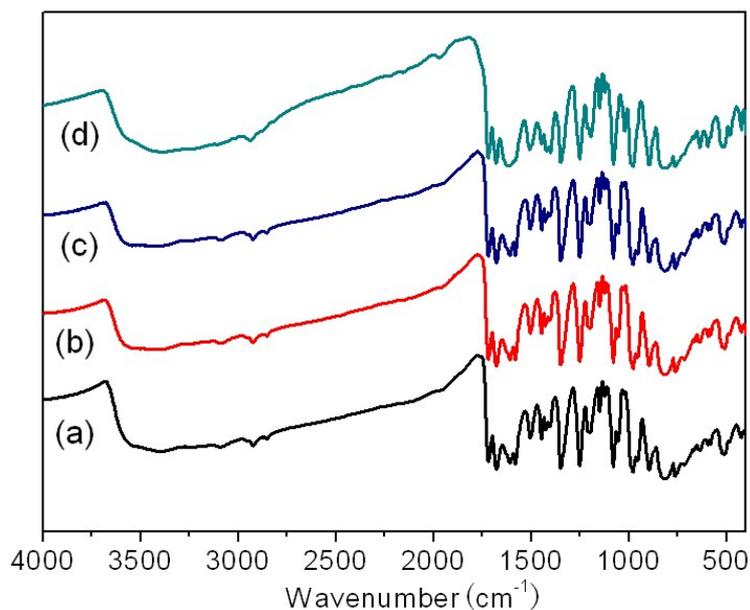
**Figure S3.** View of the 3D framework structure of compound **1** (left: along b axis; right: along c axis). Other guests (they are disordered) and all H atoms are omitted for clarity. Zn (turquoise), F (yellow-green), C (black), O (red), N (blue), P (purple), W (teal), POMs (red polyhedron).

## 6. X-ray Powder Diffraction



**Figure S4.** (a) The simulated PXRD pattern based on the single crystal **1**; (b) PXRD pattern of the as-synthesized coordination compound **1**; (c) for **1** after irradiated by visible light; (d) for **1** after irradiated by ultraviolet light.

## 7. IR spectroscopy

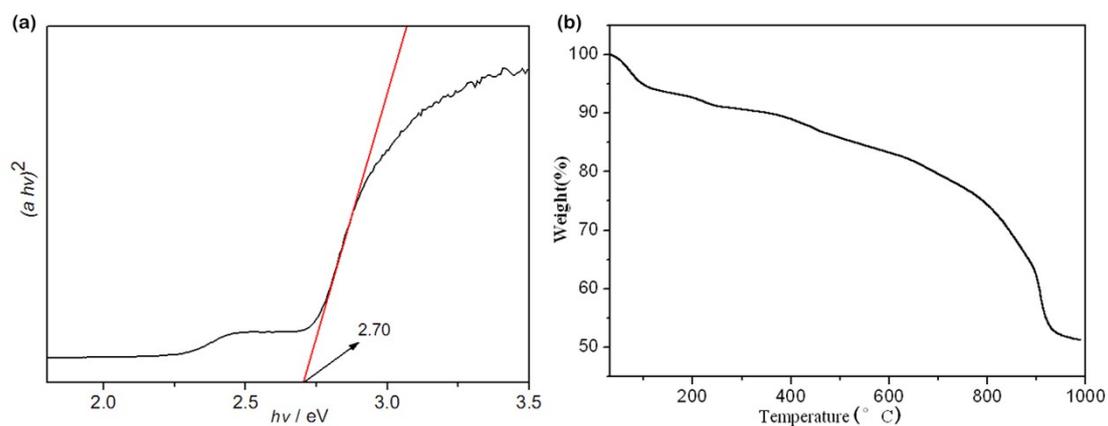


**Figure S5.** The IR spectra of crystal **1**; (a) the IR spectra of crystal **1** before irradiation; (b) for **1** after irradiated by x-ray; (c) for **1** after irradiated by ultraviolet light; and (d) for **1** after irradiated by visible light.

## 8. Thermogravimetric analyses and the estimated energy band gap

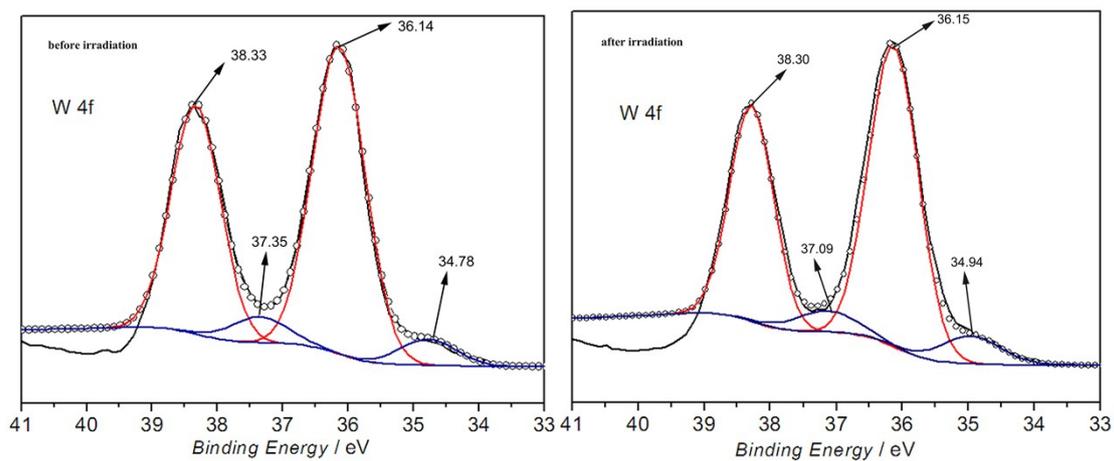
TGA of an air-dried ground sample of compound **1** was conducted on a TGA/DSC 1 STAR<sup>e</sup> system with a heating rate of 10 °C/min under an N<sub>2</sub>-atmosphere. Thermogravimetric analyses revealed that **1** exhibits relatively poor thermal stability (Figure S6b), which can be mainly attributed to the structure feature of non-interpenetrated coordination polymer that bearing large

void ratio. The fraction of volumes accessible for the inclusion of guest solvent molecules is 31.4% (calculated by PLATON).

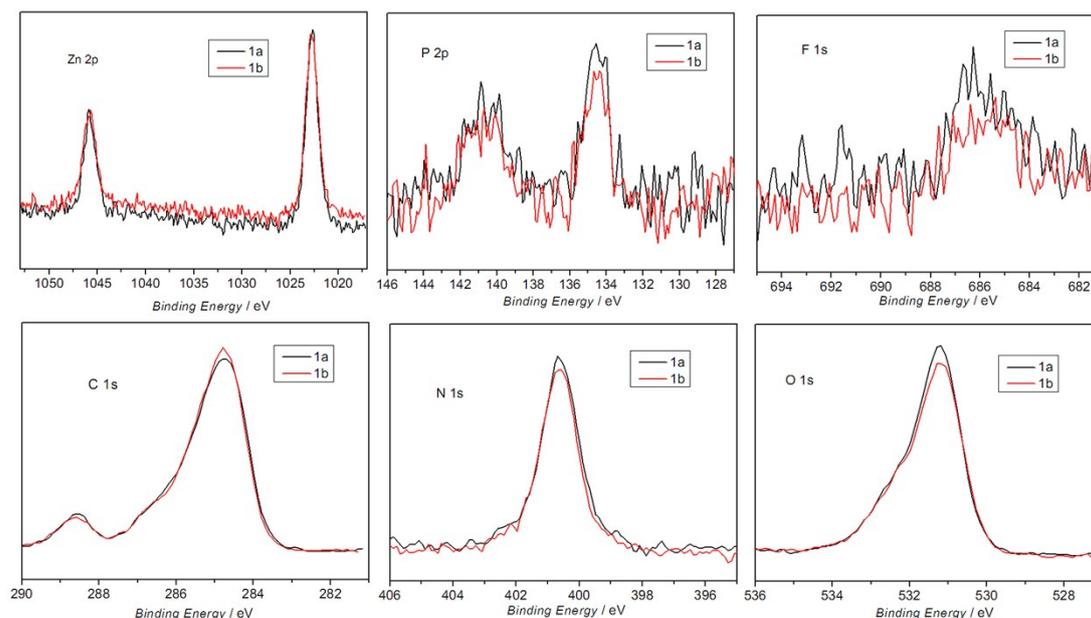


**Figure S6.** (a) The estimated energy band gap by the UV-Vis DRS based on the Kubelka-Munk Function; (b) TGA curve of **1**.

### 9. X-ray Photoelectron Spectroscopy



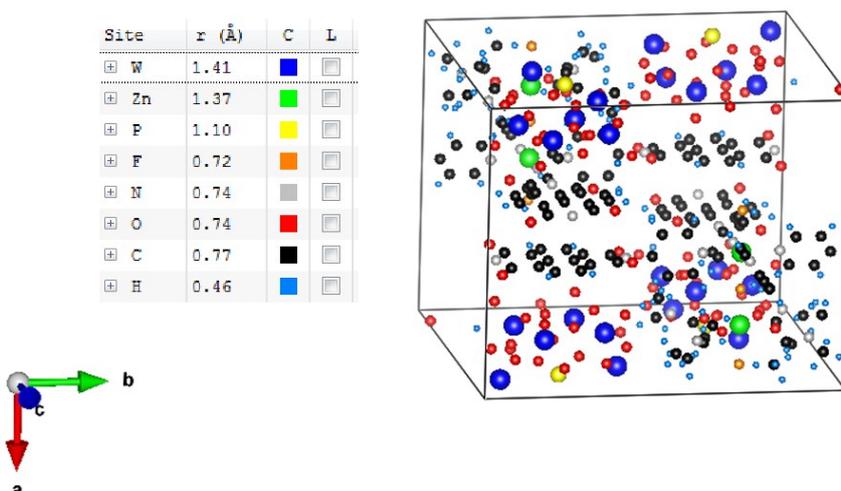
**Figure S7.** Resolved W4f XPS core-level spectra of **1**.



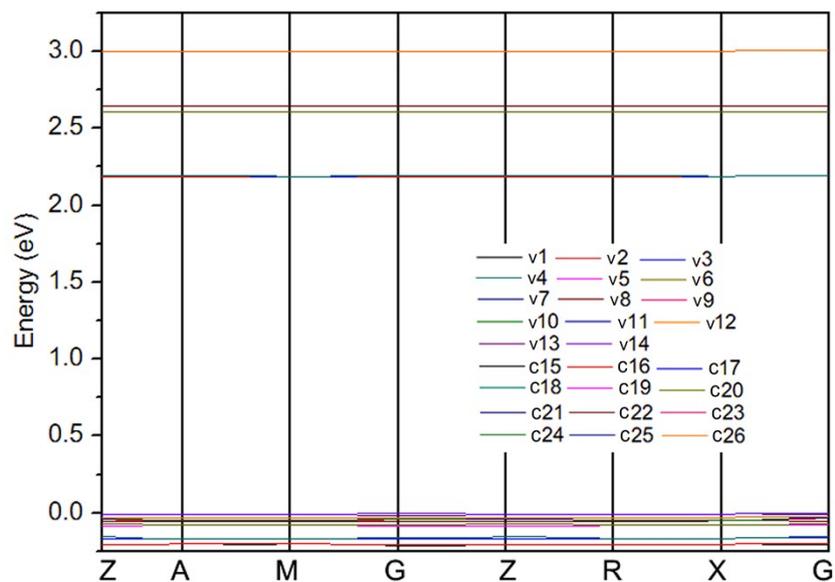
**Figure S8.** XPS core-level spectra of **1** (**1a**: before irradiation; **1b**: after irradiation).

## 10. Computational studies

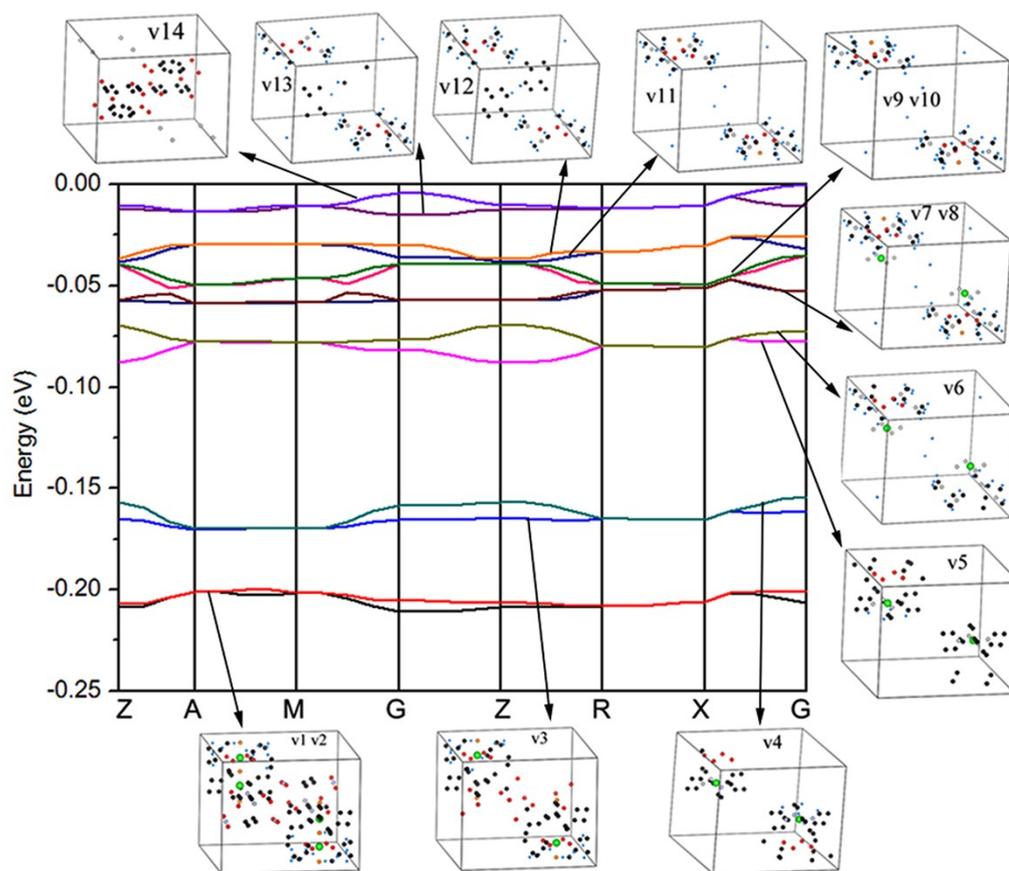
All calculations were performed with the *Vienna ab initio simulation package* (VASP)<sup>S3,S4</sup> and Perdew-Burke-Ernzerhof (PBE)<sup>S5</sup> type generalized gradient approximation (GGA) to describe the exchange-correlation energy. We have used a projector-augmented-wave (PAW) method<sup>S6</sup> for the ionic pseudo-potentials. Monkhorst-Pack meshes<sup>S7</sup> of  $(2 \times 2 \times 2)$  was used to sample the reciprocal space. The energy cutoff and convergence criteria for energy and force were set to be 500 eV,  $1 \times 10^{-5}$  eV, and  $0.001$  eV/Å, respectively.



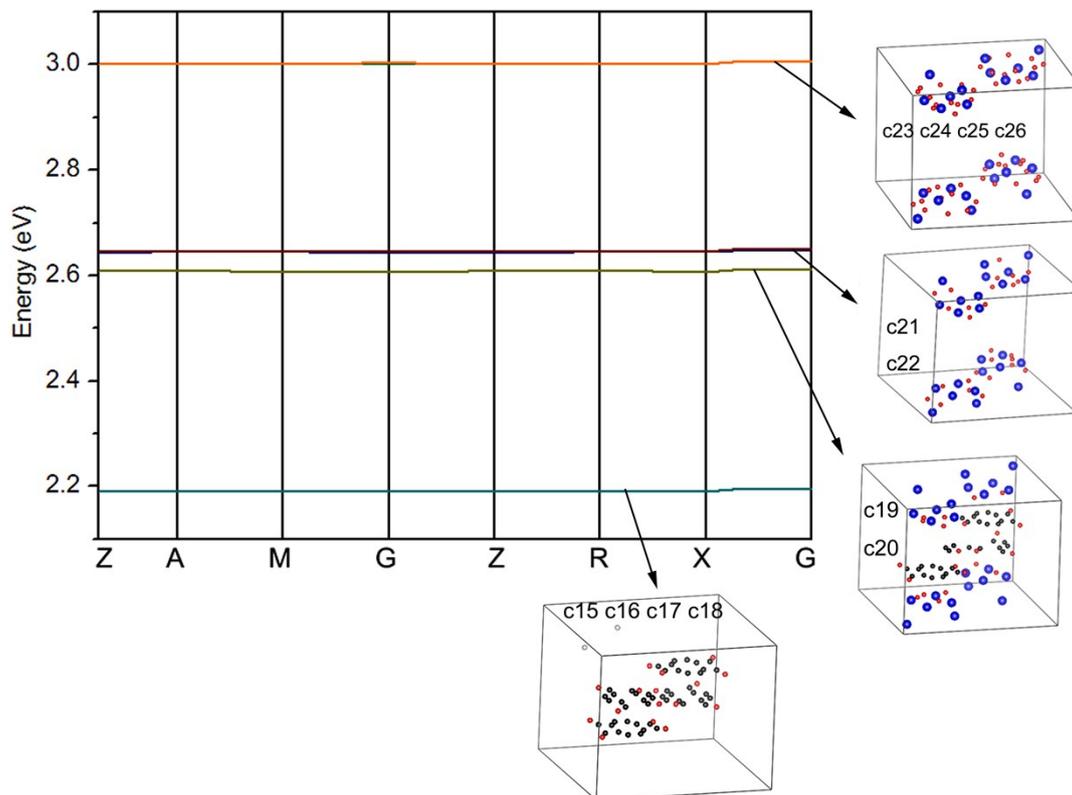
**Figure S9.** The unit cell of **1** is used for computational studies and the corresponding color of the atoms.



**Figure S10.** The electronic band structure of **1** (Fermi level located at 0 eV).



**Figure S11.** The valence band structure of **1**.



**Figure S12.** The conduction band structure of **1**.

## 11. References

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