Electronic Supplementary Material (ESI) for ChemComm.

*Supporting Information for*

# X-ray photochromism of chalcogenide frameworks linked with metal-amine chelates

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# I. Experimental Section

**Chemicals and Materials.** Tin powder (Sn, 99.99%), zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 99.9%), sulfur powder (S, 99%), 2-(2-Aminoethylamino)ethanol (AEAE, 99%), 1,2-diaminocyclohexane (DAC, 99%)，N,N'-dimethyl-1,2-cyclohexanediamine (DAC-Me), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%) were commercially available and used as received.

### $[Zn(DAC)]_2SnS_4.(H_2O)$ (1)

The mixture of $Zn(CH_3COO)_2{\cdot}2H_2O$ (55 mg, 0.25 mmol), Sn (30 mg, 0.25 mmol), S (96 mg, 3 mmol), DAC (2 mL), AEAE (1 mL), and DBU (3 mL) were stirred in a 23 mL Teflon-lined stainless steel autoclave for 20 mins. After the vessel was sealed and heated at 180 °C for 8 days, the autoclave was taken out and gradually cooled to room temperature. The pale yellowish octahedral crystals were obtained by filtration, washed with ethanol, and dried in vacuum (yield 30.8% based on Zn). The phase purity of the sample was identified by powder X-ray diffraction measurements.

### $[Zn(DAC\text{-}Me)]_2SnS_4.(H_2O)$ (1-Me)

Following the aforementioned procedures, **1-Me** can be obtained by using DAC-Me instead of DAC for solvothermal reaction. A large quantity of clear yellowish crystals was obtained by filtration, washed with ethanol, and dried in vacuum (yield 35.8% based on Zn). The phase purity of the sample was identified by powder X-ray diffraction measurements.

## II. Physical measurements

**Powder X-ray Diffraction Characterization.** The Powder X-ray Diffraction (PXRD) data was collected on a desktop diffractometer (D2 PHASER, Bruker, Germany) using Cu-Kα (λ=1.54056 A) radiation operated at 30 kV and 10 mA. The samples were ground into fine powders for several minutes before the test.

**Single-Crystal X-ray Crystallography.** Intensity data of **1** were recorded on Bruker Photon II CPAD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at 120 K, whereas that of **1-Me** were collected on an Agilent SuperNova Dual system (Cu Kα) at 100 K. Absorption corrections were applied by using the program CrysAlis (multi-scan). The structures were solved by direct method, and nonhydrogen atoms were refined anisotropically by least-squares on $F^2$ using the SHELXTL program. The data collection and refinement parameters for **1** and **1-Me** are summarized in Table S1.

**Elemental Analysis.** Energy dispersive spectroscopy (EDS) analysis was performed on scanning electron microscope (SEM) equipped with EDS detector. An accelerating voltage of 25 kV and 40 s accumulation time were applied. Elemental analysis of C, H, and N was performed on VARIDEL III elemental analyzer.

| | **Elements (*wt.*)** | **N (%)** | **C (%)** | **H (%)** |
|---|---|---|---|---|
| **1** | Calculated | 8.97 | 23.08 | 4.81 |
| | Experimental | 8.91 | 24.02 | 4.57 |
| **1-Me** | Calculated | 8.28 | 28.42 | 5.07 |
| | Experimental | 8.29 | 28.05 | 5.18 |

**Thermogravimetric analysis.** Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 thermal analyzer by heating the sample from room temperature to 800 °C with heating rate of 10 °C /min under $N_2$ flow.

**Fourier transform infrared (FT-IR) measurement.** FT-IR spectra was performed on a Thermo Nicolet Avatar 6700 FT-IR spectrometer with diamond/zinc selenide optics allowing the instrument to observe from 600-4000 $cm^{-1}$.

**UV-vis diffusion reflectance spectra.** Solid-state UV-vis diffusion reflectance spectra (UV-vis DRS) of **1** and **1-Me** were conducted on a SHIMADZU UV-3600 UV-vis-NIR spectrophotometer coupled with an integrating sphere by using $BaSO_4$ powder as the reflectance reference. In order to determine the band edge of the direct-gap semiconductor, the relation between the absorption coefficients ($\alpha$) and the incident photon energy ($hv$) is exhibited as $\alpha hv = A(hv\text{-}Eg)^{0.5}$, where A is a constant that relates to the effective masses associated with the valence and conduction bands, and $Eg$ is the optical transition gap of the solid material. By extrapolating the linear region to the abscissa, the optical gap can be estimated.

**X-ray photoelectron spectroscopy.** X-ray photoelectron spectroscopy (XPS) was collected with a Leeman prodigy spectrometer equipped with a monochromatic Al Kα X-ray source and a concentric hemispherical analyzer. All binding energies were calibrated using the C (1s) carbon peak (284.6 eV), which was applied as an internal standard.

**Preparation of 1/ITO Film and 1-Me/ITO Film.** To prepare the working electrode, 2 mg crystals of **1** or **1-Me** were first ground into fine powders, and then added into 60 μL of 0.5% Nafion (D-521 dispersion, 5% in water and 1-propanol). After ultrasonic treatment for 30 minutes, the obtained suspensions were dropped onto the surface of ITO substrate, and then dried at room temperature.

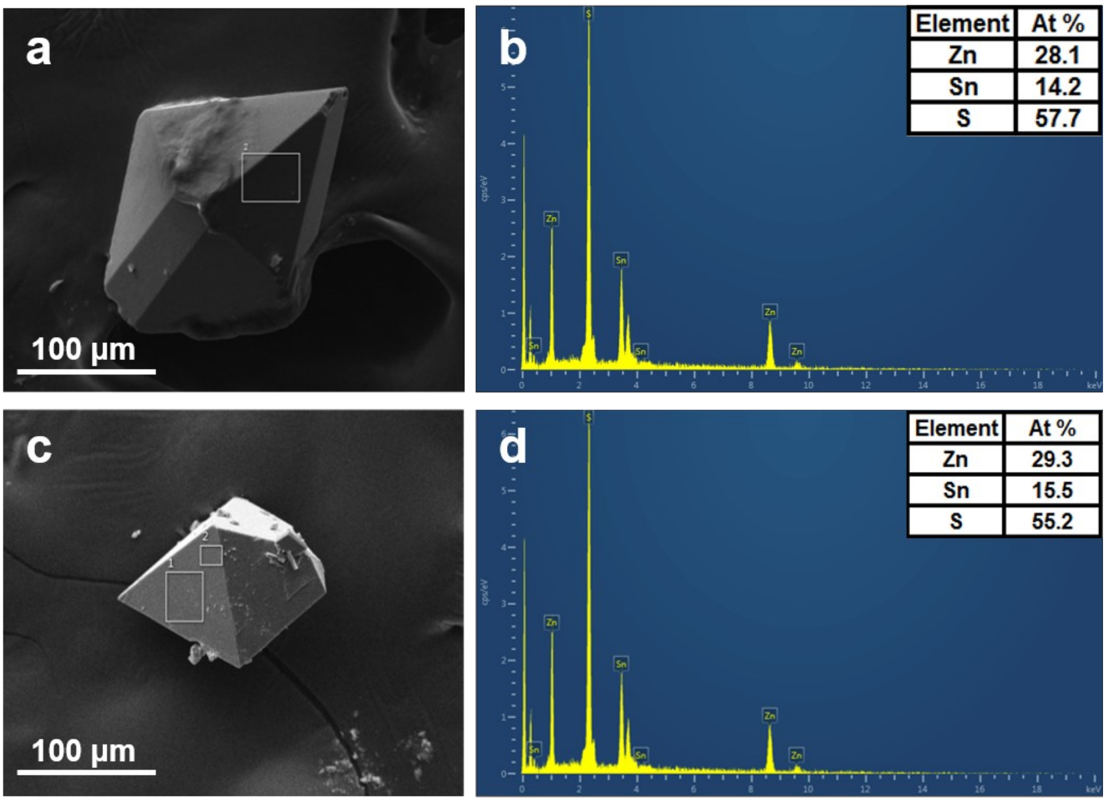
**Transient photocurrent and electrochemical impedance spectroscopy measurement.** The transient photocurrent and electrochemical impedance spectroscopy (EIS) experiments were carried out on a CHI760E electrochemistry workstation in a standard three-electrode configuration. The sample coated ITO glass electrode (effective area about 1 $cm^2$), the saturated calomel electrode (SCE), and the Pt plate electrode were used as the working electrode, reference electrode, and counter electrode, respectively. The light source was a 150 W high pressure xenon lamp with a horizontal of 25 cm away from the surface of the ITO working electrode. Sodium sulphate aqueous solution (0.5 M, 100 mL) was used as the supporting electrolyte.

**Electron spin resonance.** Electron spin resonance (ESR) spectra was obtained on the ER200-SRC Bruker X-band spectrometer, which operates at 9.06 GHz under room temperature. Two crystals of equal weight were ground to powders and packed into capillary tubes with a diameter of 0.05 mm and sealed at both ends.

**X-ray irradiation.** X-ray irradiation was produced by medical radiation equipment with tungsten anode X-ray sources (Monoblock® X-ray generators) with a tube voltage of 80 KVp and a tube current that can be adjusted from 1 μA to 0.6 mA, corresponding to calibrated dose rates from 0.705 μGys$^{-1}$ to 423 μGys$^{-1}$. A cumulative irradiation of 150 Gy per material (1.225 Gymin$^{-1}$) was applied, with the same irradiation parameters and time.

For the time-dependent coloration experiment, X-ray irradiation were collected on an X-RAD SmART system equipped with W Kα radiation source with a tube voltage of 225 KVp and a tube current that can be adjusted from 1 mA to 13 mA, corresponding to calibrated dose rates from 1.941 Gymin$^{-1}$ to 26.50 Gymin$^{-1}$. In all these experiments, the dose rate was fixed at 26.50 Gymin$^{-1}$.

# III. Supporting figures



| Element | At % |
|---|---|
| Zn | 28.1 |
| Sn | 14.2 |
| S | 57.7 |

| Element | At % |
|---|---|
| Zn | 29.3 |
| Sn | 15.5 |
| S | 55.2 |

**Figure S1.** a) SEM image and b) EDS pattern of **1** (EDS analysis of the single crystal of **1** revealed a Zn/Sn atomic ratio of 1.98, which is close to the calculated value of 2.00). c) SEM image and d) EDS pattern of **1-Me** (EDS analysis of **1-Me** revealed a Zn/Sn atomic ratio of 1.89, which is close to the calculated value of 2.00).

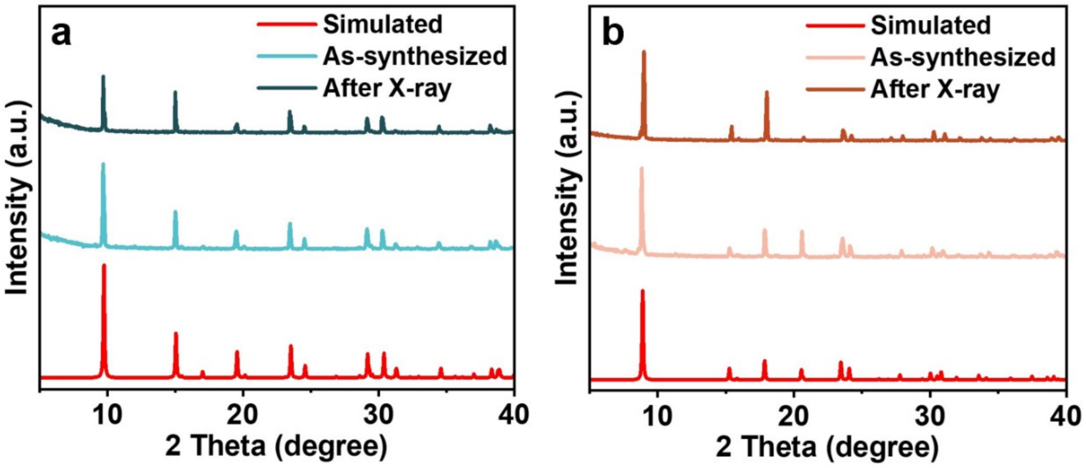


**Figure S2.** The simulated and experimental (as-synthesized and after X-ray irradiation) PXRD patterns of a) **1** and b) **1-Me**.

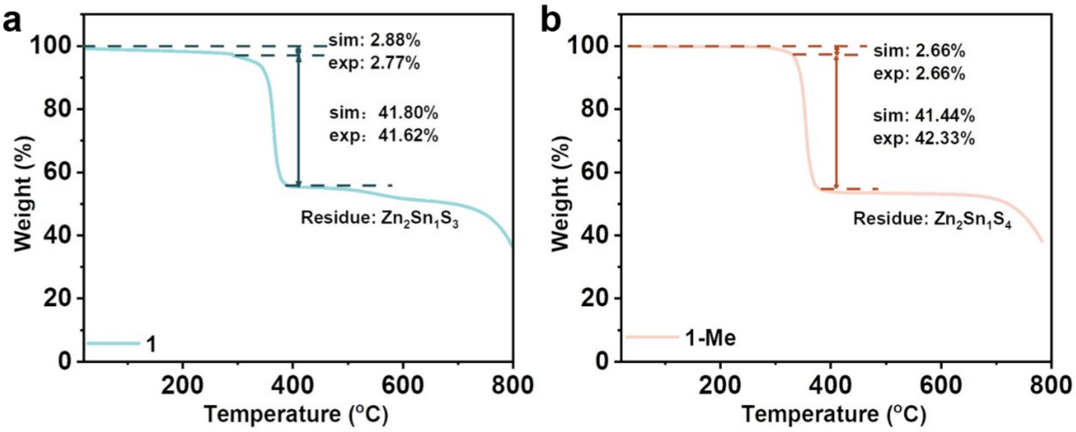


**Figure S3.** TGA curves of a) **1** and b) **1-Me**.

The two chalcogenide frameworks are stable below 300 °C. The first weight loss below 300 °C is attributed to the desorption of one $H_2O$ molecule. The weight loss from 300-400 °C corresponds to the collapse of the framework and the loss of organic ligands.

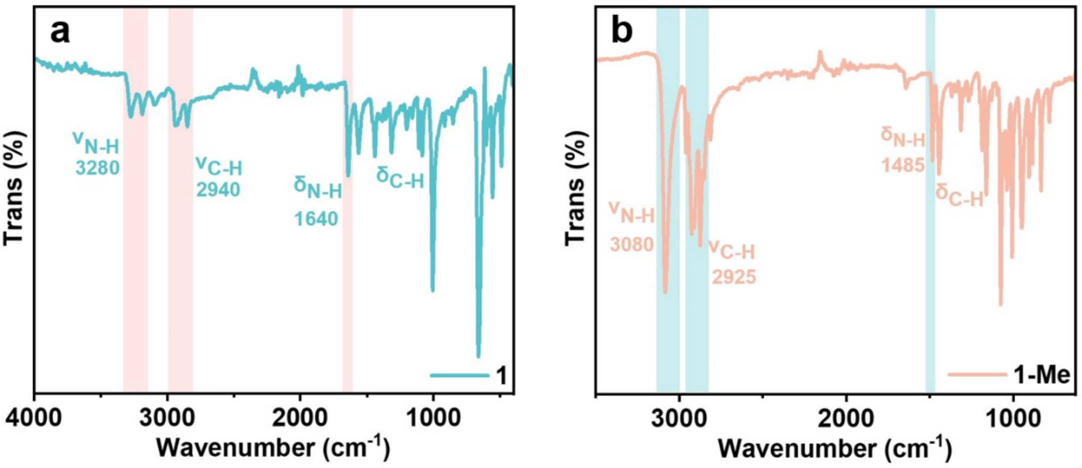


**Figure S4.** FT-IR spectra of a) **1** and b) **1-Me**.

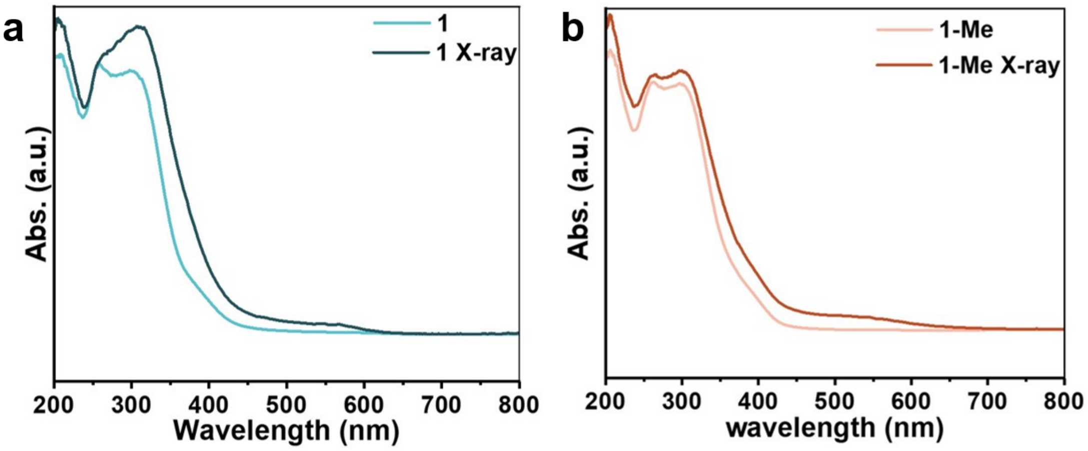


**Figure S5.** Solid-state diffuse reflectance spectra of a) **1** and b) **1-Me** before and after X-ray irradiation.

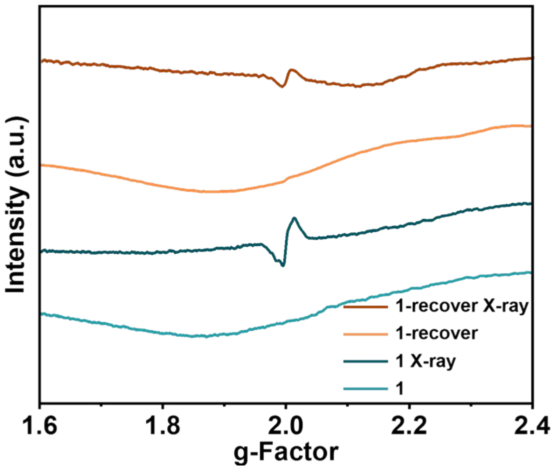


**Figure S6.** ESR spectra for **1** of before and after X-ray irradiation, and recovered upon heating treatment and then re-irradiation.

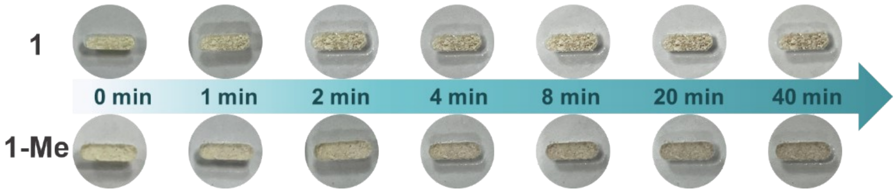


**Figure S7.** Time-dependent color change of crystal samples of **1** and **1-Me** (6 mm × 2 mm × 0.5 mm) under irradiation (W Kα radiation source with a tube voltage of 225 KVp and a dose rate of 26.50 Gymin$^{-1}$).

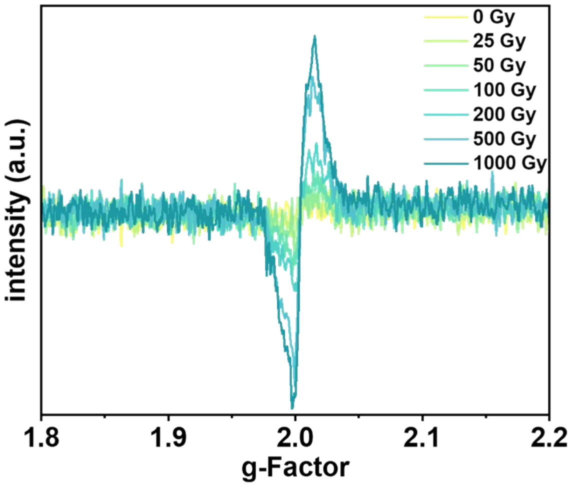


**Figure S8.** ESR spectra of **1** upon X-ray irradiation with different radiation dosages (W Kα radiation source with a tube voltage of 225 KVp and a dose rate of 26.50 Gymin$^{-1}$).

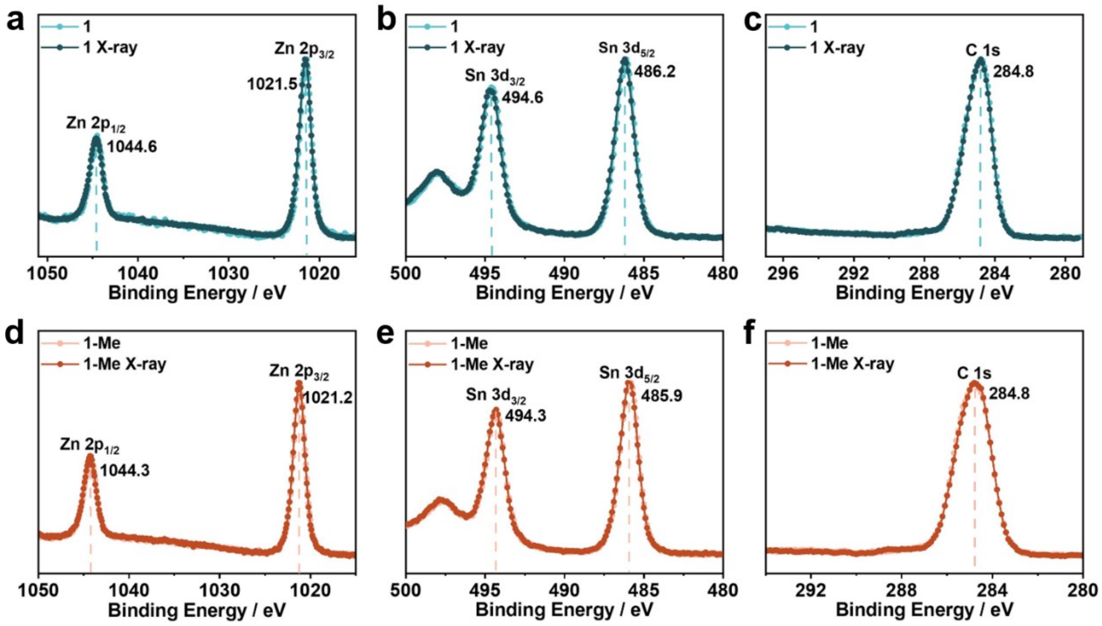


**Figure S9.** High resolution XPS spectra of **1** a) Zn 2p, b) Sn 3d and c) C 1s and **1-Me** d) Zn 2p, e) Sn 3d, and f) C 1s before and after X-ray irradiation.

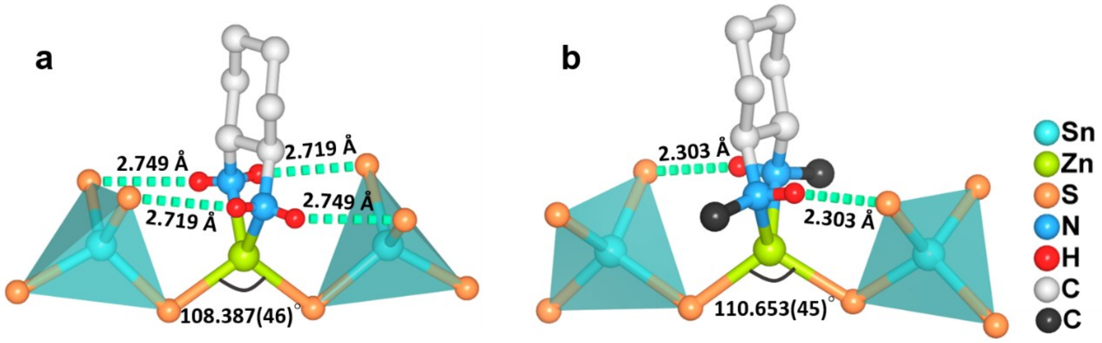


**Figure S10.** a) The [Zn(DAC)] bridged two T1-$SnS_4$ motif in **1** showing the N−H···S hydrogen bonds. b) The [Zn(DAC-Me)] bridged two T1-$SnS_4$ motif in **1-Me** showing the N−H···S hydrogen bonds.

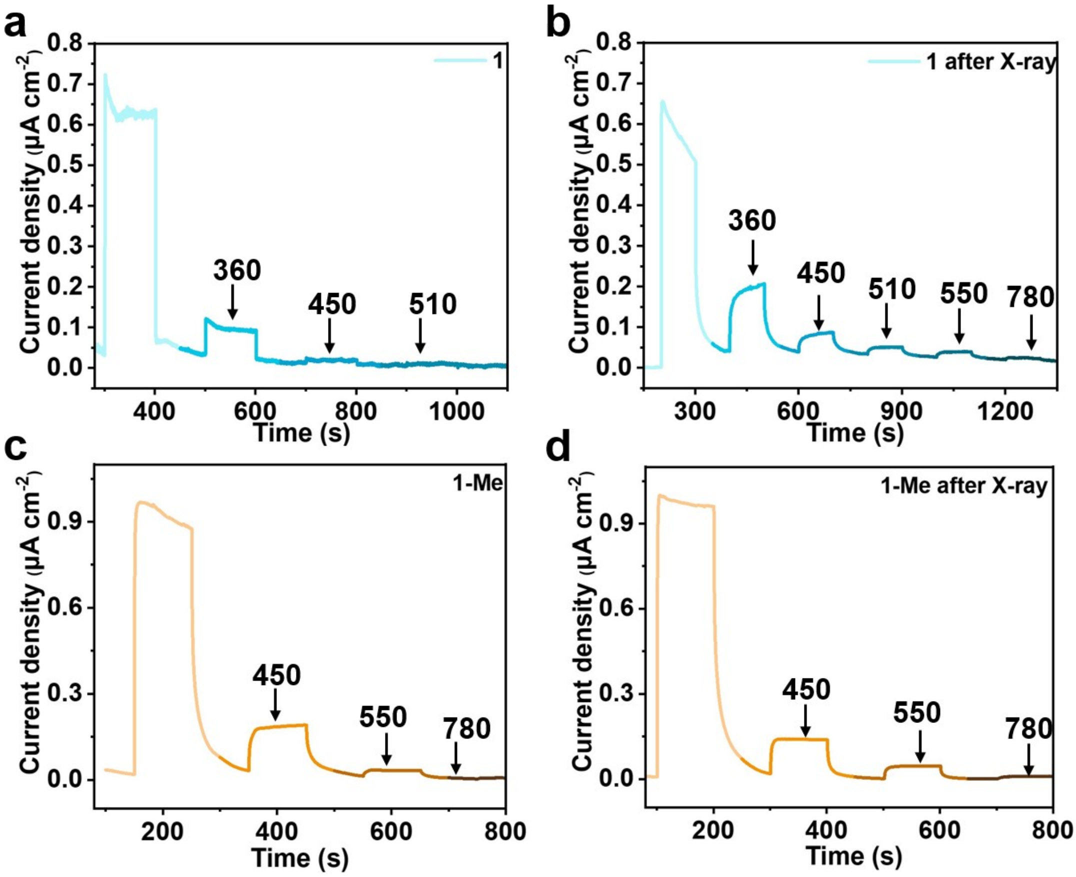


**Figure S11.** Photo response spectra of **1** a) before and b) after X-ray irradiation and **1-Me** c) before and d) after X-ray irradiation with different wavelength of the filters.

**Table S1.** Crystallographic data and structure refinement parameters for **1** and **1-Me**.

| **Compounds** | **1** | **1-Me** |
|---|---|---|
| **Framework Formula** | $C_{12}H_{28}N_4S_4SnZn_2 \bullet H_2O$ | $C_{16}H_{36}N_4S_4Zn_2Sn_1 \bullet H_2O$ |
| **Crystal system** | Tetragonal | Tetragonal |
| **Space group** | *I*-42*d* | *I*-42*d* |
| $\boldsymbol{Z}$ | 16 | 16 |
| $\boldsymbol{a}$ **(Å)** | 10.0687(4) | 13.44118(7) |
| $\boldsymbol{b}$ **(Å)** | 10.0687(4) | 13.44118(7) |
| $\boldsymbol{c}$ **(Å)** | 20.8088(7) | 14.28207(11) |
| $\boldsymbol{\alpha}$ **(deg.)** | 90 | 90 |
| $\boldsymbol{\beta}$ **(deg.)** | 90 | 90 |
| $\boldsymbol{\gamma}$ **(deg.)** | 90 | 90 |
| $\boldsymbol{V}$ **(Å$^3$)** | 2109.57(18) | 2580.27(3) |
| **GOF on $\boldsymbol{F^2}$** | 1.130 | 1.129 |
| $\boldsymbol{R_1, wR_2\ (I>2\sigma(I))}$ | 0.0254, 0.0549 | 0.0266, 0.0749 |
| $\boldsymbol{R_1, wR_2}$ **(all data)** | 0.0300, 0.0588 | 0.0266, 0.0750 |