

# Supporting Information

## UV-vis/X-ray/thermo-induced synthesis and UV–SWIR photoresponsive property of a mixed-valence viologen-based - molybdate semiconductor

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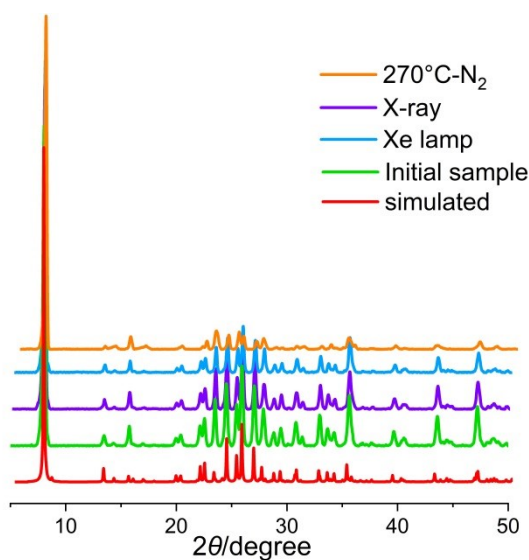
# 1.Methods

**Materials.**  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in Ar grade was purchased commercially. It was directly used without further purification. Water was deionized and distilled before use.  $\text{EVBr}_2$  ( $\text{EV}^{2+}$  = ethyl viologen cation) was synthesized according to the same procedure reported in the literature. Synthesis of **1** was the same as the literature <sup>1</sup>.

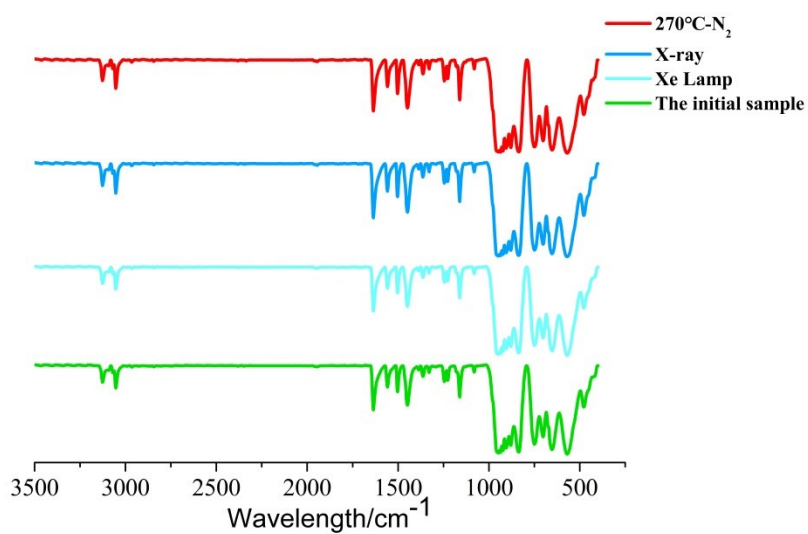
**Measurements.** Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Desktop MiniFlex 600 diffractometer using  $\text{Cu } K_\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) powered at 40 kV and 15 mA. IR spectra were measured on a PerkinElmer Spectrum One FT-IR spectrometer using KBr pellets in the range of 4000–450  $\text{cm}^{-1}$ . Thermogravimetric analysis was recorded on a Mettler TOLEDO simultaneous TGA/DSC apparatus. Elemental analyses of C, H and N were conducted on an ULTIMA 2 ICP Optical Emission Spectrometer. Diffuse reflectance spectra were measured on a PerkinElmer Lambda 900 UV/vis/NIR spectrophotometer in the wavelength range of 200–2600 nm at room temperature. A  $\text{BaSO}_4$  plate was used as the reference (100% reflection), on which the finely ground powder of the sample was coated. Electron spin resonance (ESR) spectra were collected on a Bruker ER-420 spectrometer with 100 kHz magnetic field in the X band at room temperature. Photoirradiation for

coloration was carried out with a PLS-SXE300D 50-W xenon lamp system and Cu  $K_{\alpha}$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) powered at 40 kV and 15 mA. An OPOTEK Vibrant laser (10 Hz; 10 ns pulse width; spot size, ca. 1–2 cm $\phi$ ) and a Newport Co. Pulseo GKNQL-355-3-30 diode pumped solid state (DPSS) laser (355nm; 70 kHz; 39 ns pulse width; spot size, ca. 1.5 cm $\phi$ ) were used for photocurrent tests. Photocurrent tests were recorded in a Keithley 4200-SCS semiconductor parameter analyzer using pellet samples by the two-probe method using silver paste.

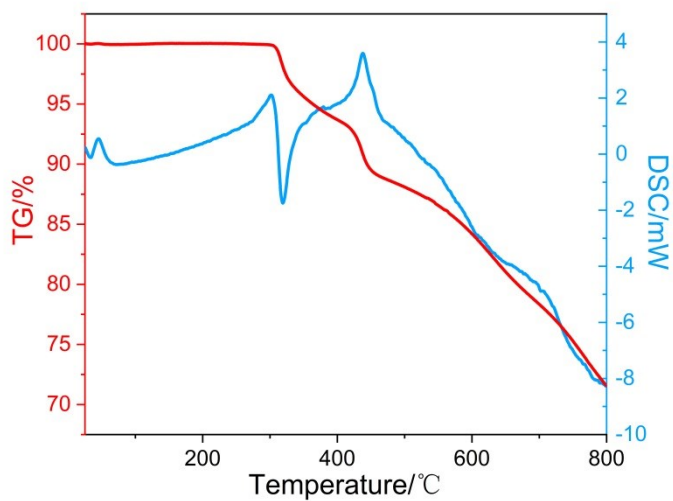
## 2. Supplementary Figures



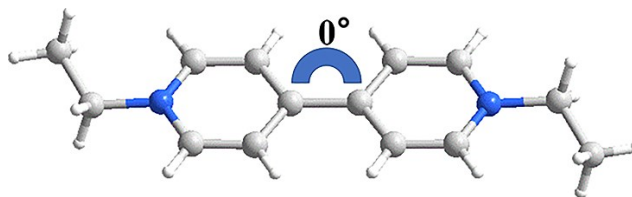
**Fig. S1** PXRd for initial sample and other samples that obtained by different modes.



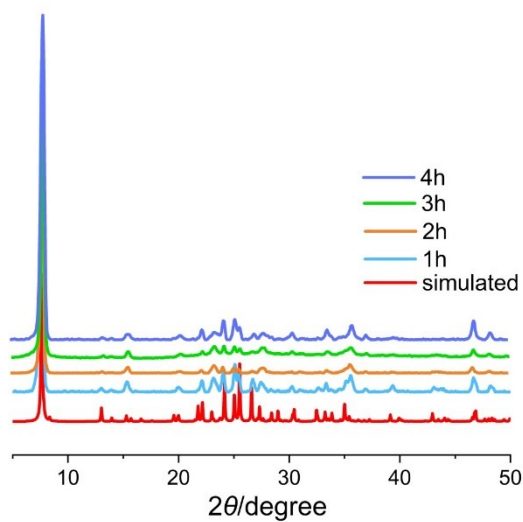
**Fig. S2** IR spectra for initial sample and other samples that obtained by different modes.



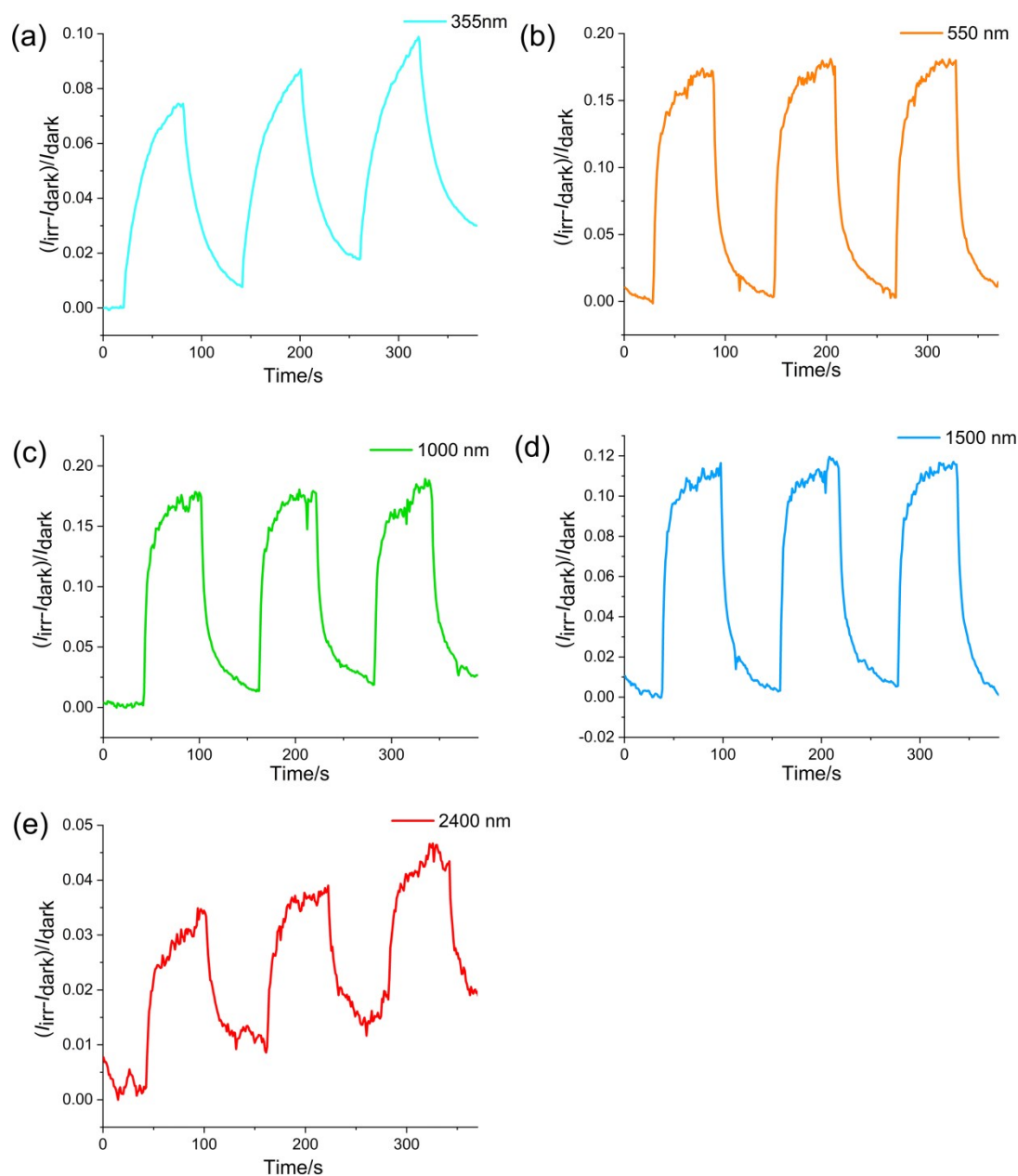
**Fig. S3** Thermogravimetric analysis (TGA) of the initial sample in the N<sub>2</sub> atmosphere.



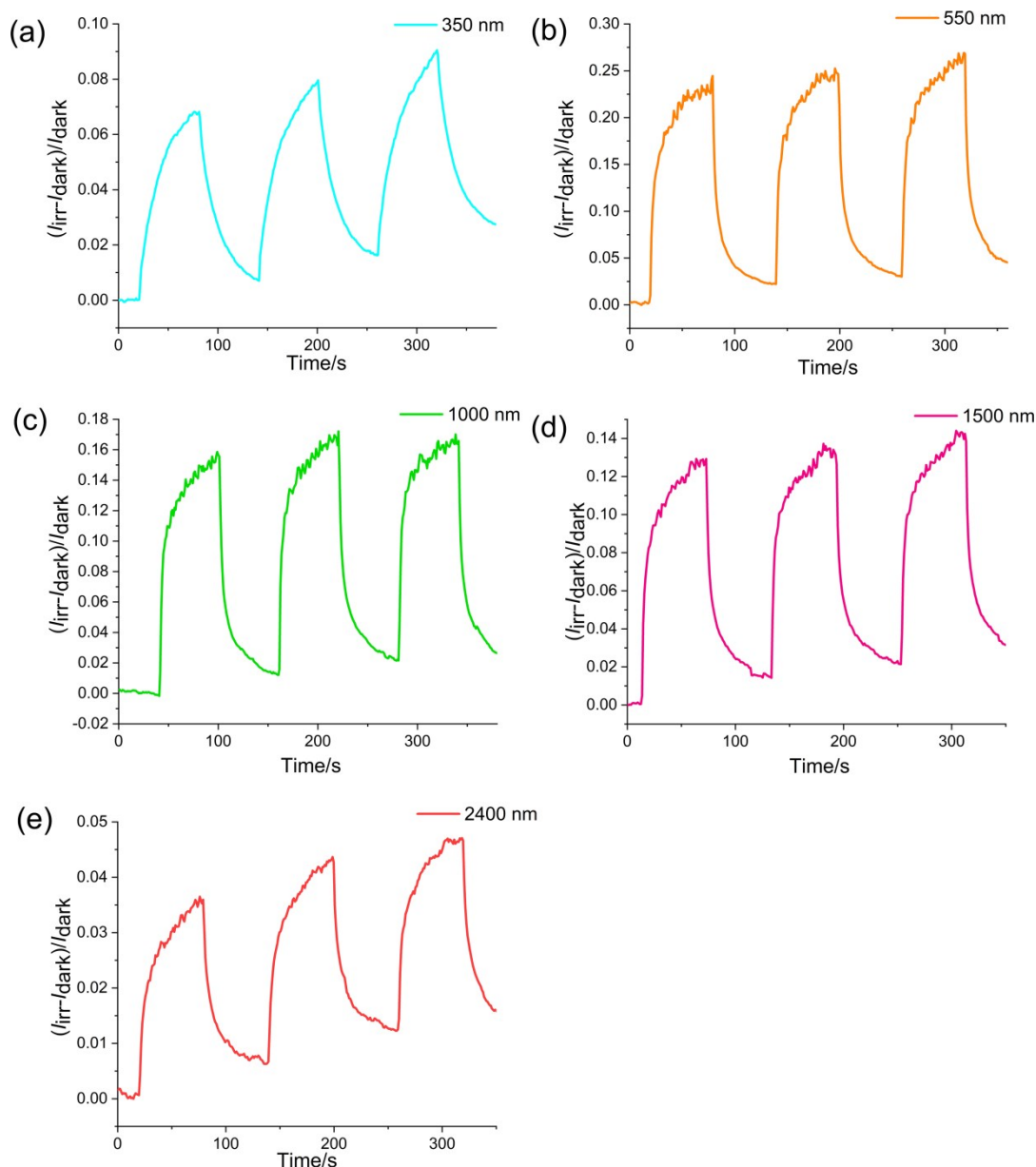
**Fig. S4** The dihedral angle between two pyridyl rings in **1**.



**Fig. S5** The PXRD of the semiconductors obtained by thermal annealing for different times.



**Fig. S6.** Photoswitching behavior for sample 2 of semiconductor obtained by thermal annealing. A Newport Co. Pulseo GKNQL-355-3-30 diode pumped solid-state laser (70 kHz, 39 ns pulse width) and OPO laser (10 Hz, 10 ns pulse width) are used for 355 nm and 550–2400 nm light, respectively. Powers for each wavelength: 355 nm, 55mW; 550 nm, 31 mW; 1000 nm, 30 mW; 1500 nm, 29 mW; 2400 nm, 6 mW.



**Fig. S7** Photoswitching behavior for sample 3 of semiconductor obtained by thermal annealing. A Newport Co. Pulseo GKNQL-355-3-30 diode pumped solid-state laser (70 kHz, 39 ns pulse width) and OPO laser (10 Hz, 10 ns pulse width) are used for 355 nm and 550–2400 nm light, respectively. Powers for each wavelength: 355 nm, 55mW; 550 nm, 31 mW; 1000 nm, 30 mW; 1500 nm, 29 mW; 2400 nm, 6 mW.

## References

1. Y.-Q. Wei, C. Sun, Q.-S. Chen, M.-S. Wang and G.-C. Guo, *Chem. Commun.* 2018, **54**, 14077–14080.