Supporting Information

Significant enhancement of conductance for a hybrid layered molybdate semiconductor by light or heat

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Index:

1. EXPERIMENTAL SECTION

2. ADDITIONAL FIGURES

Fig. S1 Power X-ray diffraction patterns of 1
Fig. S2 Thermogravimetric curve of 1
Fig. S3 IR spectra of 1
Fig. S4 XPS of O 1s for 1A, 1B and 1C
Fig. S5 Temperature-dependent electrical conductivities of 1B and 1C.
Arrhenius law: \( \ln \sigma = -\frac{E_a}{k_B T} + \text{constant} \), where \( E_a \) is the activation energy.
1. EXPERIMENTAL SECTION

Materials and measurements

All commercially available chemicals were of analytical reagent grade and used as received without further purification. Elemental analyses for C, H, N and O were carried out on a Vario MICRO CHNOS Elemental Analyzer. IR spectra were measured on a PerkinElmer Spectrum One FT-IR spectrometer using KBr pellets. UV–vis absorption spectra were measured in the diffuse reflectance mode on a PerkinElmer Lambda 950 UV/vis/near-IR spectrophotometer equipped with an integrating sphere, and a BaSO4 plate was used as the reference. PXRD patterns were recorded using Cu–Kα radiation on a Rigaku Desktop MiniFlexII diffractometer powered at 30 kV and 15 mA. Thermogravimetric analyses (TGA) were performed on a on a Mettler TOLECO TGA apparatus with a heating rate of 10 °C/min in nitrogen atmosphere. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker ER-420 spectrometer with a 100 kHz magnetic field in the X band at room temperature. XPS studies were performed in a ThermoFisher ESCALAB 250Xi X-ray photoelectron spectrometer (powered at 150 W) using Al-Kα radiation. Temperature-dependent electrical conductivities and I–V curves were measured in a Keithley 4200-SCS semiconductor parameter analyzer using pellet samples by the two probe method using silver paste.

Synthesis of EV[Mo₉O₂₈] (I, EV²⁺ = ethyl viologen cation). Na₂MoO₄·2H₂O (0.36 g, 1.5 mmol), EVBr₂ (0.20 g, 0.1mmol) was dissolved in 20 mL H₂O. The pH was adjusted with 4 M HCl to 1. The mixture was then stirred at room temperature for a few minutes and sealed in a 30 mL Teflon-lined autoclave (120 °C, 72 h, autogenous pressure). The resulting colorless crystals of 1 were filtered off, washed with H₂O and EtOH, and dried in air at room temperature. Yield in Mo: 32%. Calcd. ( % ) for C₁₄H₁₈O₂₈N₂Mo₉: C, 11.02; H, 1.19; N, 1.84; O, 29.35. Found: C, 11.13; H, 1.14; N, 1.92; O, 29.32.

Single-crystal structure determination

Suitable single crystal of compound 1 was carefully selected and glued to thin glass fibers with epoxy resin. Intensity data for single crystal were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073Å). The empirical absorption corrections were performed using the CrystalClear program.¹ The structure was solved and refined on F² by full-matrix leastsquares technique using the SHELX-97 program package.² Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms bonded to the carbon atoms of EV²⁺ were generated geometrically.
**Computational approach**

The crystallographic data of 1 was used to build calculation model. Plane wave-based density functional theory (DFT) calculations of the total and partial densities of states were performed using the Cambridge Sequential Total Energy Package (CASTEP) code. The exchange-correlation energy was described by the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).

**References**


2. ADDITIONAL FIGURES

![Fig. S1 Power X-ray diffraction patterns of 1](image1)

Fig. S1 Power X-ray diffraction patterns of 1

![Fig. S2 Thermogravimetric curve of 1](image2)

Fig. S2 Thermogravimetric curve of 1
Fig. S3 IR spectra of 1

Fig. S4 XPS of O 1s for 1A, 1B and 1C
Arrhenius law:
\[ \ln \sigma = -\frac{E_a}{k_B T} + \text{constant} \], where \( E_a \) is the activation energy.

**Fig. S5** Temperature-dependent electrical conductivities of 1B and 1C. Arrhenius law:
\[ \ln \sigma = -\frac{E_a}{k_B T} + \text{constant} \], where \( E_a \) is the activation energy.