Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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

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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-*K*α 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 ℃/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-*K*α 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[Mo_9O_{28}] (**1**, EV^{2+} = ethyl viologen cation).* Na_2MoO_4 $2H_2O$ (0.36 g, 1.5 mmol), $EVBr_2$ (0.20 g, 0.1mmol) was dissolved in 20 mL H_2O. 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 ℃, 72 h, autogenous pressure). The resulting colorless crystals of **1** were filtered off, washed with H_2O and EtOH, and dried in air at room temperature. Yield in Mo: 32%. Calcd. (%) for $C_{14}H_{18}O_{28}N_2Mo_9$: 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 *K*α radiation (λ = 0.71073Å). The empirical absorption corrections were performed using the CrystalClear program.[1] The structure was solved and refined on F^2 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 EV^{2+} 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.[3] The exchange-correlation energy was described by the Perdew−Burke−Eruzerhof (PBE) functional within the generalized gradient approximation (GGA).[4]

References

1) Molecular Structure Corporation and Rigaku, 2000. *CrystalClear*. **Version 1.36**. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.

2) (a) G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, 1997.

3) S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, M. C. *Z.* Payne, *Kristallogr.*, 2005, **220**, 567.

4) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

2. ADDITIONAL FIGURES

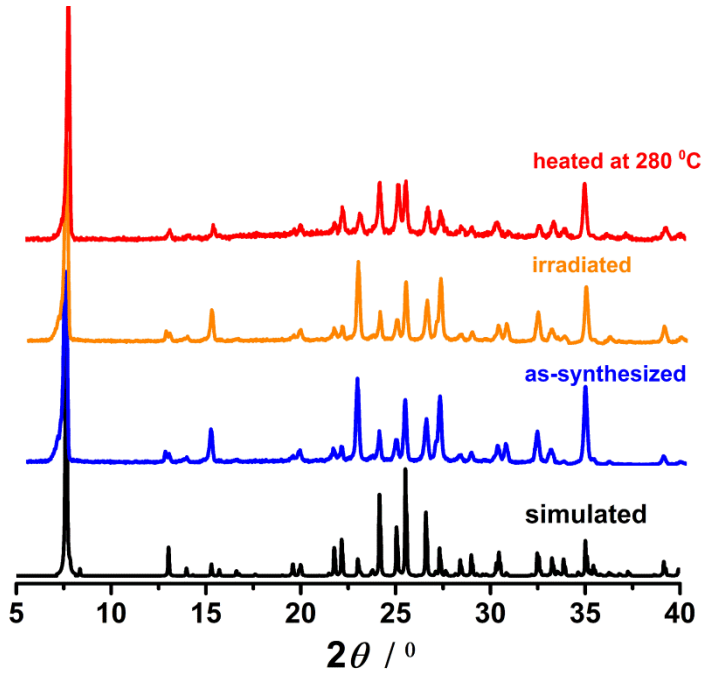

Fig. S1 Power X-ray diffraction patterns of **1**

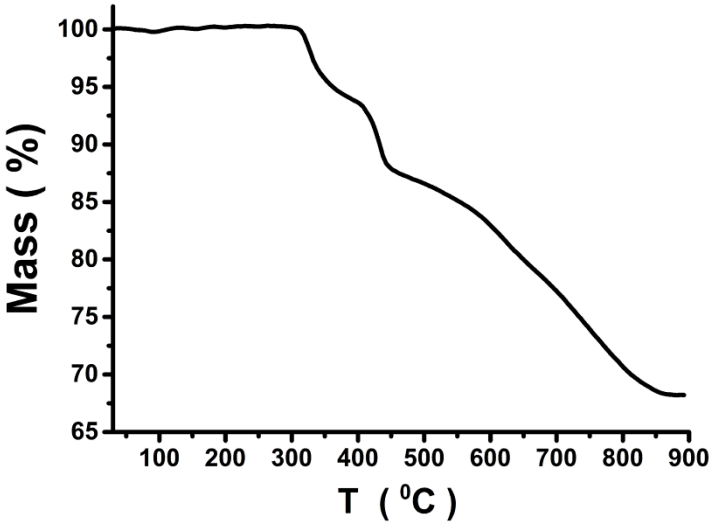

Fig. S2 Thermogravimetric curve of **1**

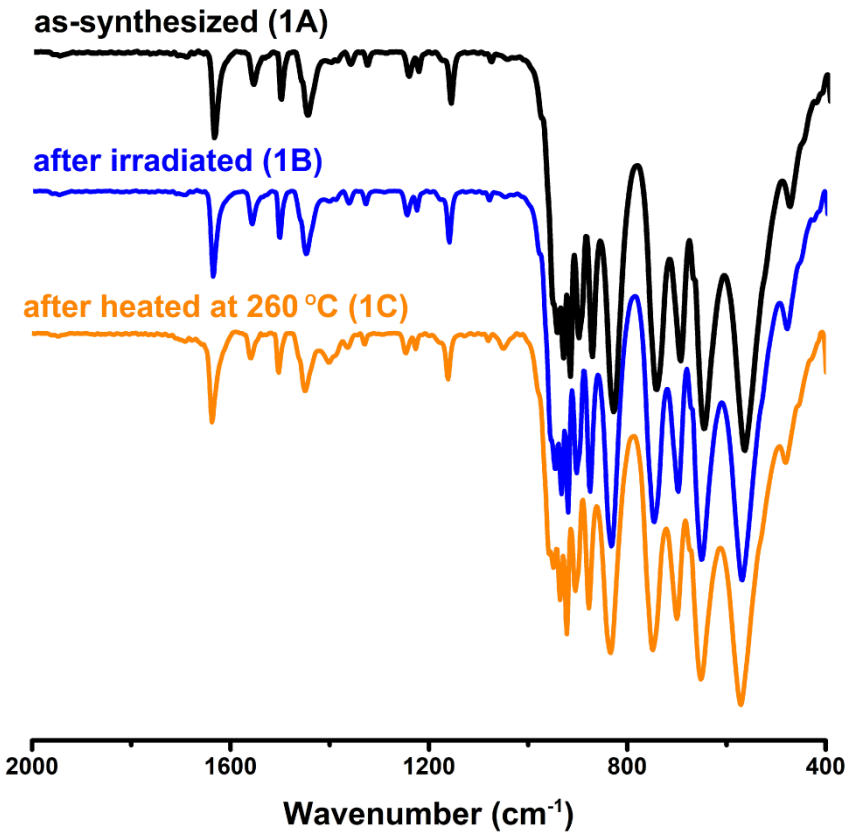

Fig. S3 IR spectra of **1**

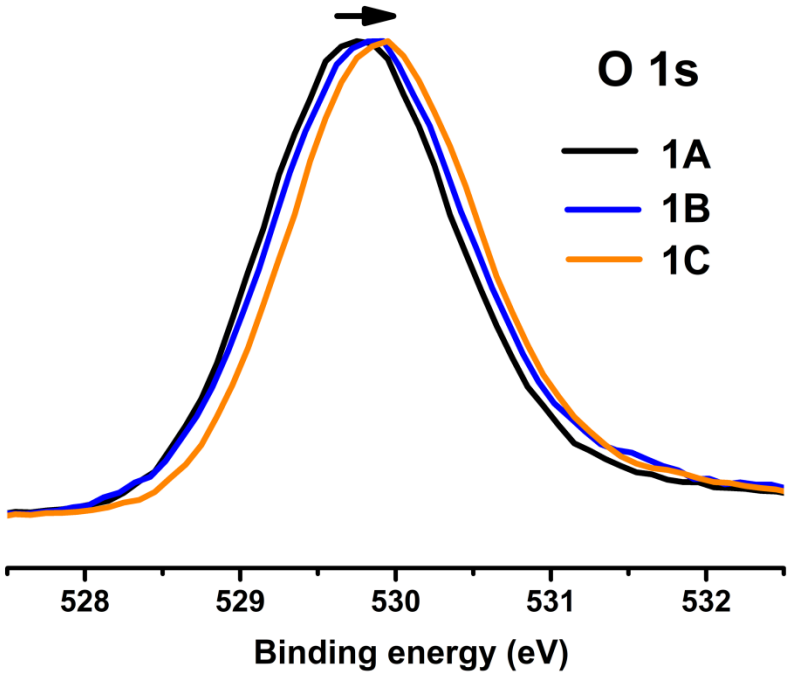

Fig. S4 XPS of O 1s for **1A**, **1B** and **1C**

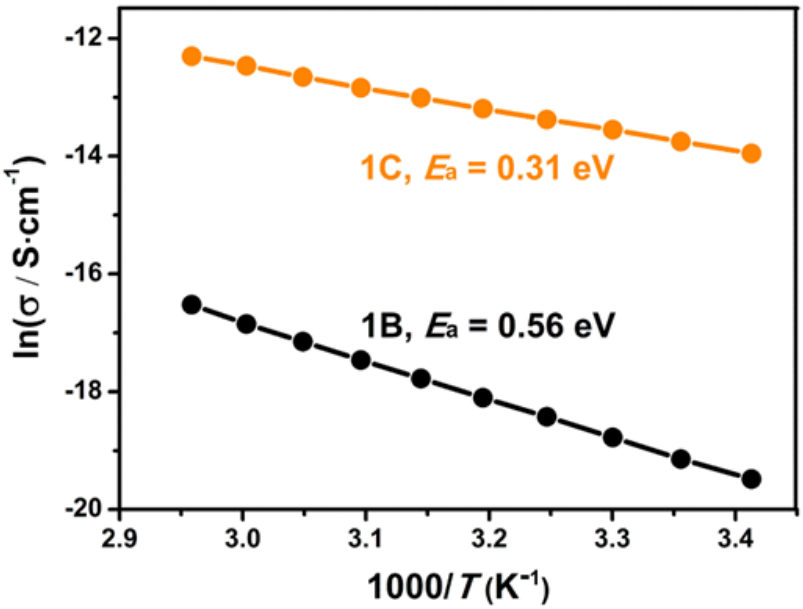

Fig. S5 Temperature-dependent electrical conductivities of **1B** and **1C**. Arrhenius law: $\ln\sigma = -E_a/k_BT$ + constant, where E_a is the activation energy.