Electronic Supplementary Material (ESI) for Dalton Transactions.

1. Basic analysis

2. Crystallographic analysis

3. Electrical conductivities

1. Basic analysis

1.1 CHN elemental analysis measured for dried sample.

Table S1. CHN elemental analyses.

	Mo_{18}-2	**Mo_{18}-3**	**Mo_{18}-4**
Number of Alkylammonium cation per POM	6	5	5
Number of proton per POM	0	1	1
Composition without crystalline solvents	$[(C_2H_5)_4N]_6[S_2Mo_{18}O_{60}]$ $C_{48}H_{120}N_6Mo_{18}O_{60}S_2$	$[(C_3H_7)_4N]_5H[S_2Mo_{18}O_{60}]$ $C_{60}H_{141}N_5Mo_{18}O_{60}S_2$	$[(C_4H_9)_4N]_5H[S_2Mo_{18}O_{60}]$ $C_{80}H_{145}N_5Mo_{18}O_{60}S_2$
Calculated	C 16.32 H 3.42 N 2.38	C 19.56 H 3.86 N 1.90	C 24.46 H 3.72 N 1.78
Experimental	C 16.26 H 3.51 N 2.37	C 19.68 H 3.83 N 1.84	C 24.26 H 4.64 N 1.81

1.2 Redox titration

Redox titrations were performed using $Ce(IV)(SO_4)_2$ under monitoring IVCT band using UV-vis-NIR spectra. Table S2 summarized experimental conditions and Figure S1 represents plots of absorbance against number of electron.

Table S2. Summary of experimental conditions.

	Mo_{18}-2	**Mo_{18}-3**	**Mo_{18}-4**
Solvent used for titration measurements	DMSO 1 mM $H_2SO_{4\,aq}$	DMSO 1 mM $H_2SO_{4\,aq}$	DMSO 1 mM $H_2SO_{4\,aq}$
Wavelength for monitoring (IVCT band)	909 nm	909 nm	914 nm
Number of electron	**2**	**2**	**2**

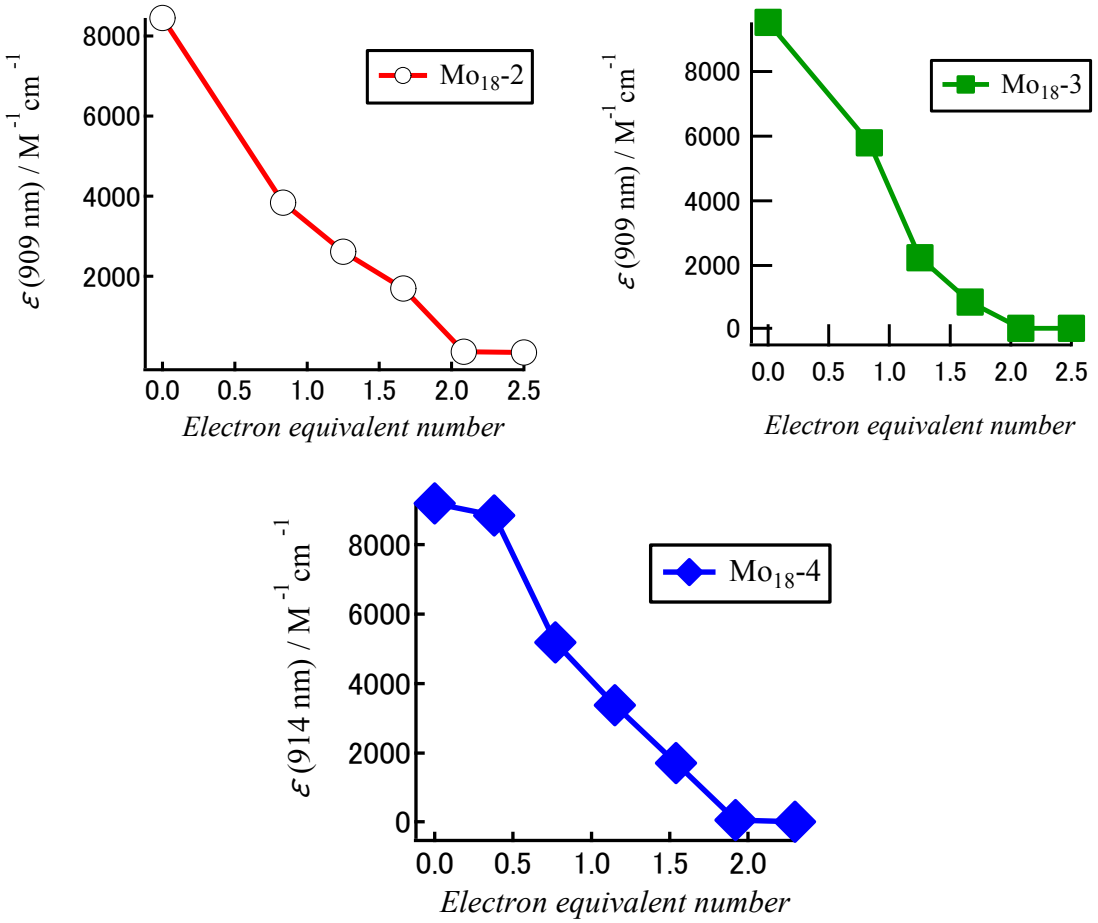


Figure S1. Plots of absorbance originated from IVCT band with number of electron.

1.3 FTIR

FTIR spectra (absorption) were characterized in the KBr discs and summarized in table S3 with peak assignments. Peaks of Mo=O vibration mode were not shifted by chain-length.

Table S3. Summary and assignments of FTIR.

	Mo_{18}-2	**Mo_{18}-3**	**Mo_{18}-4**
ν_{as}(Mo=O) / cm^{-1}	964	968	966
ν(Mo-Oc-Mo) / cm^{-1}	791 759	796 754	796 755
ν(Mo-Oe-Mo) / cm^{-1}	889	889	894

Oc and Oe; O of corner-sharing octahedral and edge-sharing octahedral, respectively

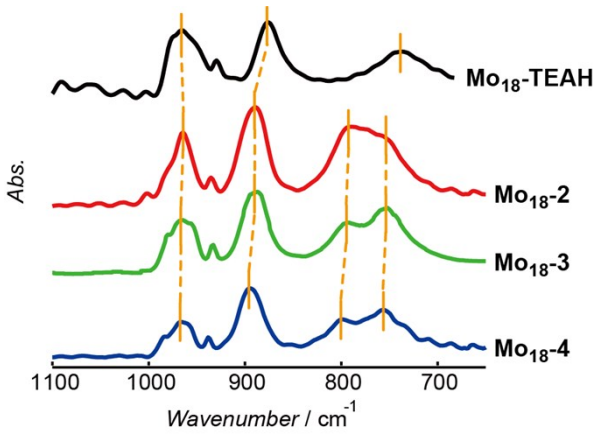


Figure S1-2. FTIR spectra of TEAH salt of $[Mo^{V}_{2}Mo^{VI}_{16}O_{54}(SO_3)_2]^{6-}$ and **Mo_{18}-*n***.

2. Crystallographic analysis

Single crystal X-ray diffraction analysis was performed using a Rigaku MARCURY with graphite monochromated Mo-Kα radiation. The data were collected at 173 K. The structure was determined by direct methods and expanded using Fourier techniques.

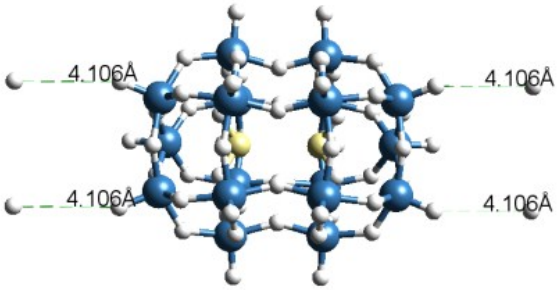
Hirshfeld analyses

Hirshfeld analyses were performed using crystallographic data from which data for counter cation and solvent were removed.

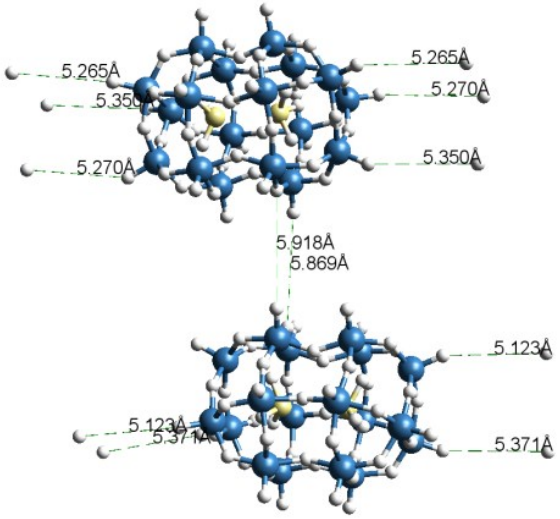
Concerning to Hirshfeld analyses, since the method usually utilized for a data with fully solved crystallographic data for investigates intermolecular interaction in the crystal, we employed the method for analyzing inter-cluster interactions. Any of molecules other than cluster are removed from data. Hirshfeld surface were mapped with normalized interatomic distances (d_{norm}), where values represent interatomic distances shorter than the sum of the van der Waals radii (red), positive values represent distances longer than the sum of the van der Waals radii (blue). In all case, blue surface were appeared in Hirshfeld surface, showing any of cluster were not interacted with each other. In the figure S2-1 and S2-2, O and Mo atoms that positioned with distances below 7.0 Å from surface of considering cluster were only shown.

Concerning to 2D fingerprint plots, distance from the Hirshfeld surface to an internal nucleus (d_i) is plotted against the distance of the Hirshfeld surface to an external nucleus (d_e). These plots can be determined for pairs of nuclei inside and outside the Hirshfeld surface (e.g., O inside for concerning cluster shown, O outside for outer cluster). Comparison of 2D-fingerprint plots clearly showed cluster-to-cluster spacing are elongated with *n*.

Mo_{18}-2



Mo_{18}-3



Mo_{18}-4

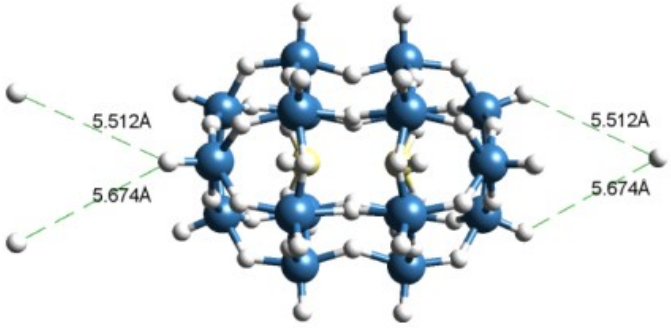
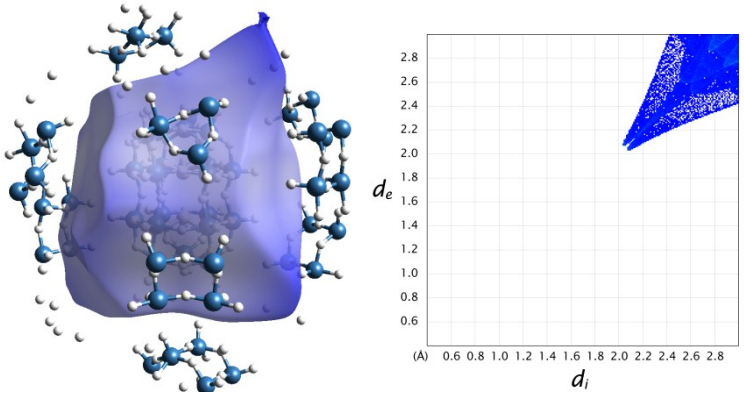
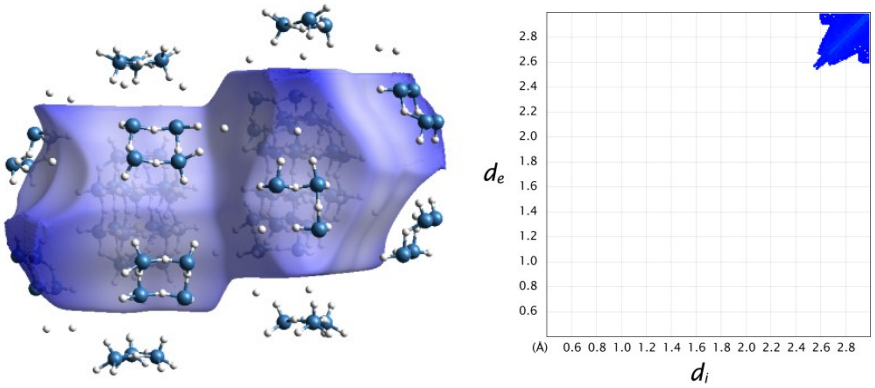


Figure S2-1. shortest inter-cluster spacing (blue=Mo, yellow=S and white=O)

Mo_{18}-2



Mo_{18}-3



Mo_{18}-4

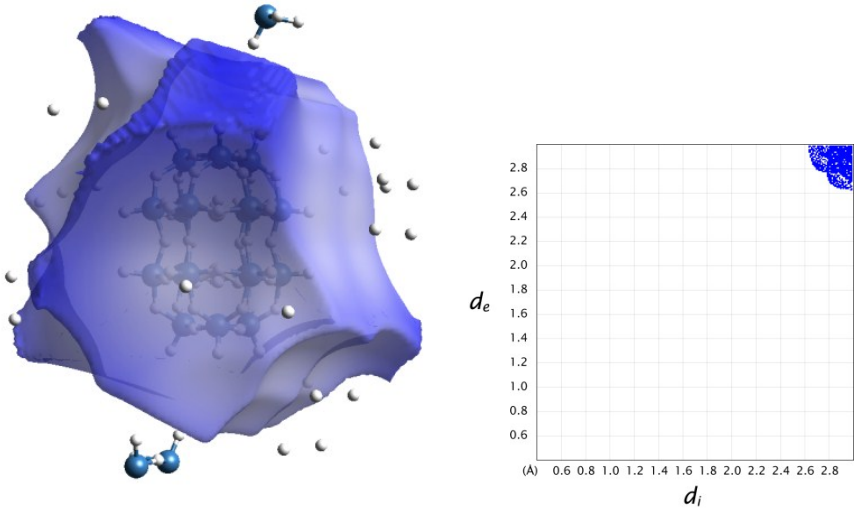


Figure S2-2. Hirshfeld surface with their 2D fingerprint plots (blue=Mo, yellow=S and white=O)

3. Electrical conductivity measurements

3.1 Measurements for single crystals

Current-time measurements were performed for single crystalline samples at constant voltage (V) at 15, 10 and 5 V for each positive and negative polar. Since all samples are considered to an insulator, charging and absorption currents were not negligible that were observed as time dependent components in electric current at constant voltage. To analyze the time dependent current for intrinsic conductivity, parallel RC equivalent circuit were considered in which model total current (I [A]) was represented by sum of time dependent current by capacitor components ($I_a(t)$) and time constant bulk electric conduction (I_G) were estimated (Figure S3-1 and -2).

$$I(t) = I_a(t) + I_G$$

$$I_G \approx I(\infty)$$

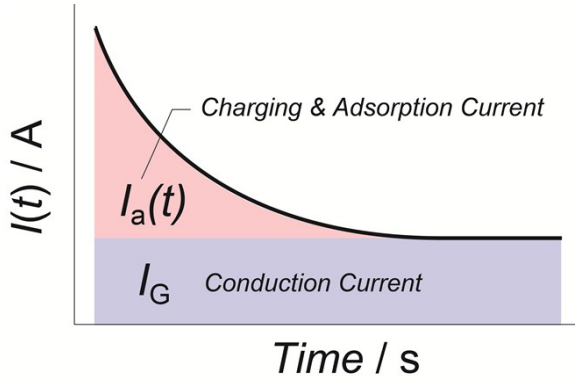


Figure S3-1. Time dependent electric current.

With increases in temperature and chain length, total current showed time dependent behaviors due to insulating characteristics of samples. Conductance (G [S]) was estimated from slop of I_G and V for each temperature (Figure S3-3). Ohmic relation between current and electric field were observed.

$$d(I_G)/dV = G$$

Conductivity (σ [S/cm]) was estimated with dimension factor of cross sectional area s [cm^2] and inter-electrode distance d [cm].

$$\sigma = G \cdot d/s$$

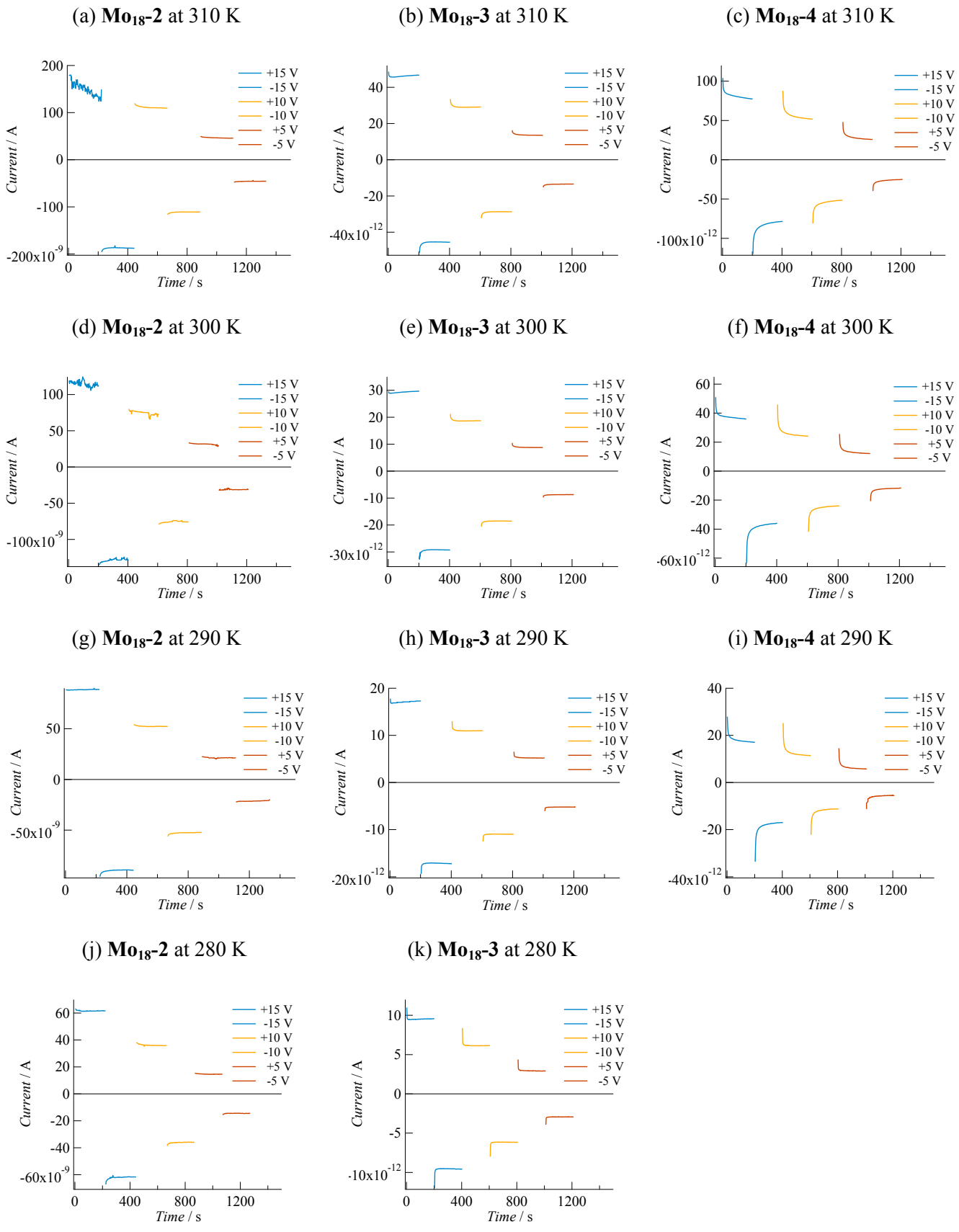
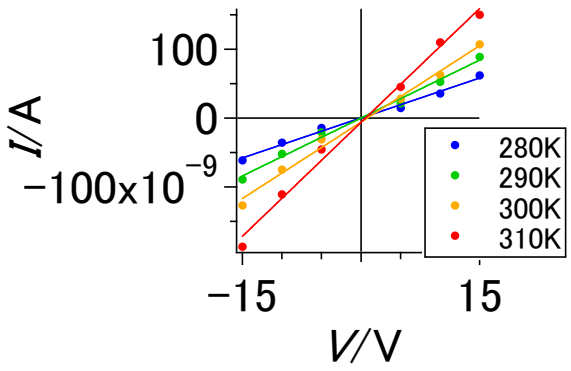
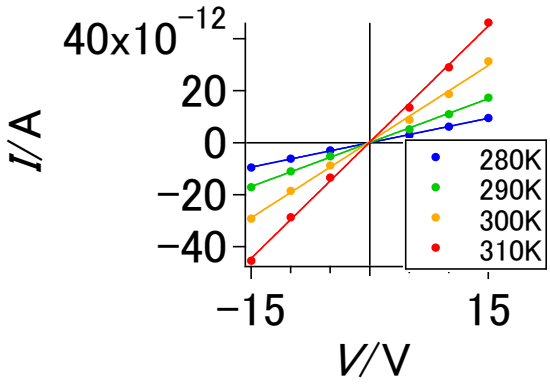


Figure S3-2. Plot of electric current and time (sec) at constant electric field.

(a) **Mo_{18}-2**



(b) **Mo_{18}-3**



(c) **Mo_{18}-4**

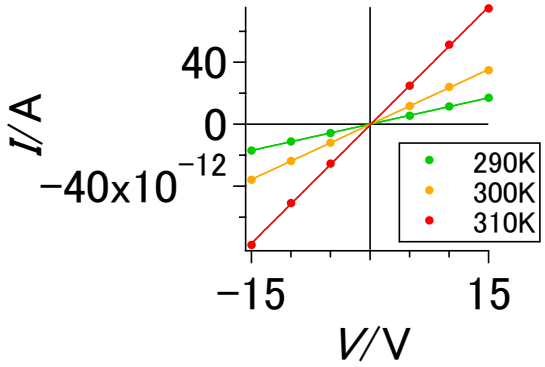


Figure S3-3. *I-V* characteristics (current *I* was plotted with I_G from figure S3-1).

3.2 Measurements for powder pellets

In addition to electrical conductivity measurements using single crystal, DC two probe measurements were also performed with dried pellets. Gold paste was utilized for electrodes and electrical contacts were made using gold wires. Temperature dependence were measured under a vacuumed condition using a commercially available cryostat with a temperature control system over the range indicated in the main text. The current was monitored with a Keithley 6517 electrometer with a constant bias voltage ranging at −10 and +10 V (conductivities were given by their averages). Ohmic contact was validated by current–voltage (*I*–*V*) characteristics (Figure S3-4 to S3-6).

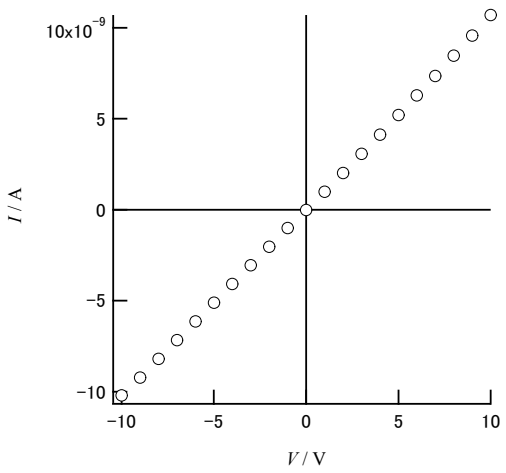


Figure S3-4. *I-V* characteristic at 307 K of **Mo_{18}-2**

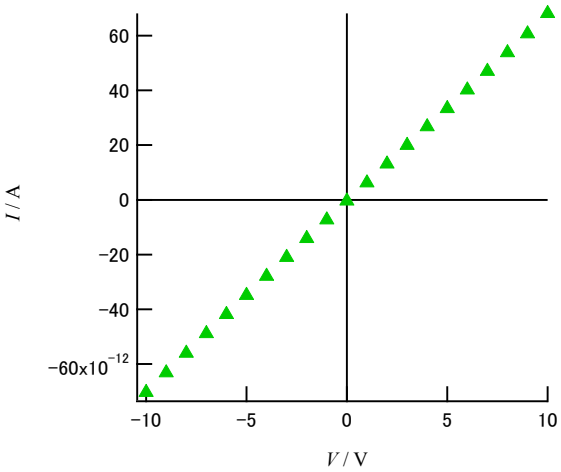


Figure S3-5. *I-V* characteristic at 313 K of **Mo_{18}-3**

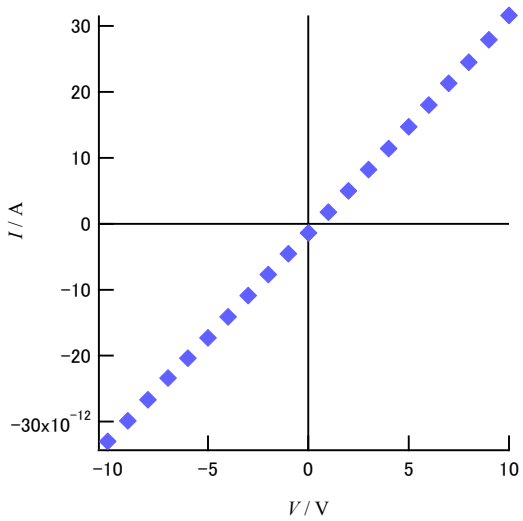


Figure S3-6. *I-V* characteristic at 307 K of **Mo_{18}-4**