# **Supporting Information**

# Materials and general methods

Cu<sub>2</sub>O and CuBr<sub>2</sub> were purchased from Tianjin Heowns Biochem LLC (Tianjin, China). P(OEt)<sub>3</sub> was purchased from Energy Chemical (Shanghai, China), and distilled over Na before use. Phosphomolybdic acid (PMA) was purchased from Guoyao Corporation and used as received. CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, CHCl<sub>3</sub>, and DMF were dried over CaH<sub>2</sub> and stored under N<sub>2</sub> atomsphere. TT-TTF was synthesized by following our previous report,<sup>[1]</sup> and TSe-TTF (tetraselenophenythio)-TTF) was synthesized via the same protocol as shown in the following section.

Melting points were determined on WRS-2 melting point apparatus. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance III 400MHz (100 MHz for <sup>13</sup>C) spectrometer. High-resolution mass spectral analysis (HRMS) was carried out on maXis 4G mass spectrometer (Bruker Daltonic Inc.). UV/Vis spectra were measured on Lambda 35 spectrometer (Perkin Elmer). The infrared (IR) spectra were record on the PerkinElmer Spetrum 400 spectrometer with the resolution of 2 cm<sup>-1</sup>. The ESR spectra were measured on a Bruker ER200DSRC10/12 device with microwave frequency of 9.444 GHz and power of 24.127 mW. Differential pulse voltammetry of PMA and TT-TTF was recorded on a RST 5000 electrochemical workstation at a scan rate of 50 mV s<sup>-1</sup>, with glassy carbon discs as the working electrode, Pt wire as the counter electrode, and SCE electrode as the reference electrode. The concentration was  $5 \times 10^{-4}$  mol L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>CN (v/v = 7 : 3), and the supporting electrolyte was (*n*-Bu)<sub>4</sub>N•PF<sub>6</sub> (0.1 mol L<sup>-1</sup>). The measurement was performed at 20 °C after bubbling the solution with N<sub>2</sub> gas for 15 min.

The in-situ investigation of the absorption spectra of TT-TTF under constant potential electrochemical-oxidation was performed on a Zahner CIMPS type photo-electrochemical workstation. Dynamic light scattering (DLS) was measured on BI-200SM (Brookhaven). Thermogravimetric analyses (TGA) were conducted on 1090B type thermal analyzer (Dupont Engineering Polymers).

The X-ray diffraction measurement was carried out on SuperNova (Agilent) type diffractometer. The crystal structure was solved by solved by a direct method  $SIR2004^{[2]}$  and refined by full-matrix least-squares method on  $F^2$  by means of *SHELXL-97*.<sup>[3]</sup> The X-Ray powder diffraction (XRPD) pattern was recorded on X'Pert PRO (PANalytical).

# Synthesis of TSe-TTF



Scheme S1. Synthetic approach of TSe-TTF

#### **Preparation of compound 1**

(TBA )<sub>2</sub>[ Zn ( DMIT )<sub>2</sub> ] (4.6 g, 4.9 mmol), 2-iodoselenophene (5.0 g, 19.5 mmol), Cu<sub>2</sub>O (0.3 g, 2.4 mmol), ethyl acetoacetate (0.2 g, 1.9 mmol), and DMF (6 mL) were placed in a two-necked flask and heated to 100 °C. After stirred at 100 °C for 10 h, the reaction mixture was cooled down to room temperature (r.t.) and poured into 200 mL of dichloromethane (DCM). The resulting mixture was washed with distilled water (6 × 100 mL) and brine (100 mL) successively, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by column chromatography on silica gel (eluent: v/v, DCM : petroleum ether = 1 : 1) to afford compound **1** as yellow solid (2.5 g, yield 61%). Mp: 96–97 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.26(d, *J* = 4 Hz, 1H), 7.54 (d, *J* = 4 Hz, 1H), 7.28 (dd, *J* = 8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  210.62, 139.30, 138.86, 135.99, 134.00, 130.13; HRMS, Calcd. for C<sub>11</sub>H<sub>6</sub>S<sub>5</sub>Se<sub>2</sub>+ H: 458.7476; Found: 458.7461.

#### **Preparation of compound 2**

To a solution of compound 1 (2.3 g, 5.0 mmol) in chloroform (50 mL) was added Hg(OAc)<sub>2</sub> (4.84 g, 15.00 mmol), then stirred at rt for 5 h. The reaction mixture was filtered through celite column and washed with chloroform. The filtrate was washed with saturated NaHCO<sub>3</sub> (2 × 15 mL) and brine (10 mL) successively, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent,

compound **2** was obtained as pale yellow oil (2.18 g, yield 99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.24 (dd, J = 4 Hz, 2H), 7.52 (d, J = 4 Hz, 2H), 7.26(dd, J =4 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  188.69, 138.80, 138.39, 134.88, 129.99, 127.80; HRMS, Calcd. for C<sub>11</sub>H<sub>6</sub>S<sub>5</sub>Se<sub>2</sub>O + H: 442.7705; Found: 442.7693.

#### **Preparation of TSe-TTF**

Compound 7 (1.50 g, 4.48 mmol) was suspended in freshly distilled P(OEt)<sub>3</sub> (20 mL) under N<sub>2</sub> atmosphere and stirred at 80 °C for 6 h. After cooling down to rt, 20 mL CH<sub>3</sub>OH was added to the reaction mixture and kept at around 5 °C overnight. The resulting orange-red solid (that is TSe-TTF) was collected by suction, washed with CH<sub>3</sub>OH, then dried in vacuo (1.23 g, 1.4 mmol, 86%), which was recrystallized in dichloromethane and petroleum ether to obtain TSe-TTF as orange-red crystals. Mp: 169.3–170.3 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.17 (d, *J* = 4 Hz, 1H), 7.43 (s,1H), 7.21(s, 1H); HRMS, Calcd. for C<sub>22</sub>H<sub>12</sub>S<sub>8</sub>Se<sub>4</sub>O + H: 849.5344; Found:849.5353.

#### References

[1] a) J. Sun, X. Lu, J. Shao, X. Li, S. Zhang, B. Wang, J. Zhao, Y. Shao, R. Fang, Z. Wang, W. Yu,
X. Shao, *Chem. Eur. J.* 2013, **19**, 12517; b) J. Sun, X. Lu, J. Shao, Z. Cui, Y. Shao, G. Jiang, W. Yu,
X. Shao, *RSC Adv.* 2013, **3**, 10193.

[2] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. de Caro, C. Giacovazzo, G. Polidori, R. Spagna, J. Appl. Cryst. 2005, 38, 381–388.

[3] G. M. Sheldrick, *SHELXL-97, A Program for Crystal Structure Refinement*. University of Göttingen, Göttingen, Germany, 1997.

# **Spectroscopy study**



**Fig. S1** Titration of TT-TTF with CuBr<sub>2</sub>. For the titration, the concentration of TT-TTF is  $10^{-5}$  mol L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>, and that of CuBr<sub>2</sub> is  $3 \times 10^{-3}$  mol L<sup>-1</sup> in CH<sub>3</sub>CN. The absorption spectra indicate that CuBr<sub>2</sub> could oxidize TT-TTF to its cation radical form, regarding the appearance of the absorption bands at 400–500 nm and 650–1000 nm. On the other hand, the resulting mixed solution is rather stable at ambient conditions, and dynamic light scattering indicates that there is no aggregation in the solution. The solid state complex of (TT-TTF)-(CuBr<sub>2</sub>) was only obtained by slow evaporation of the mixed solution at  $20 \pm 2$  °C. The evaluation of the structure and property of this complex, and those of other TTFs with CuBr<sub>2</sub> as well, are in progress.



**Fig. S2** IR spectra for  $(TT-TTF)_3[PMo_{12}O_{40}]$  along with those of TT-TTF and  $(n-Bu_4N)_3[PMo_{12}O_{40}]$  for comparison. The red star marked frequency belongs to the typical vibration of  $[PMo_{12}O_{40}]$  cluster as summarized in Table S1.

Assignment <sup>[2-4]</sup>	$(n-Bu_4N)_3[PMo_{12}O_{40}]$	(TT-TTF) <sub>3</sub> [PM0 <sub>12</sub> O <sub>40</sub> ]	(TSe-TTF) <sub>3</sub> [PMo <sub>12</sub> O <sub>40</sub> ]
Mo–O–Mo (edge sh)	$806 \text{ cm}^{-1}$	803 cm <sup>-1</sup>	804 cm <sup>-1</sup>
Mo–O –Mo (corner sh)	$880 \text{ cm}^{-1}$	877 cm <sup>-1</sup>	876 cm <sup>-1</sup>
Mo=O (terminal)	955 cm <sup>-1</sup>	955 cm <sup>-1</sup>	955 cm <sup>-1</sup>
Р-О	$1062 \text{ cm}^{-1}$	$1060 \text{ cm}^{-1}$	1061 cm <sup>-1</sup>

**Table S1** Frequency values and assignment of FTIR bands for  $(n-Bu_4N)_3[PMo_{12}O_{40}]$ , (TT-TTF)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>](CH<sub>2</sub>Cl<sub>2</sub>), and (TSe-TTF)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>](CH<sub>2</sub>Cl<sub>2</sub>)<sup>[1]</sup>

[1] The IR spectra of (TSe-TTF)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>](CH<sub>2</sub>Cl<sub>2</sub>) is shown in Fig S15.

[2] M. Fournier, C. Rocchiccioli-Deltchef, L. P. Kazansky, Chem. Phys. Lett. 1994, 223, 297.

[3] M. Hasik, A. Pron, J. Pozniczek, A. Bielanski, Z. Piwowarska, K. Kruczala, R. Dziembaj, J. Chem. Soc., Faraday Trans. 1994, **90**, 2099.

[4] M. Lira-Cantú, P. Gómez-Romero, Chem. Mater. 1998, 10, 698.

# Bulk crystals of (TT-TTF)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>](CH<sub>2</sub>Cl<sub>2</sub>)

### Preparation

The bulk crystals of  $(TT-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$  were prepared through the diffusion method by means of a three-layered technique as shown in Fig S6. In a typical condition, a dichloromethane solution (5 mL) of TT-TTF (6 mg, 0.010 mmol) was placed at the bottom layer of a glass tube, freshly distilled acetonitrile (CH<sub>3</sub>CN, 5 mL) was added dropwisely into the tube as the middle layer, and the solution of phosphomolybdic acid (PMA, 30mg, 0.016 mmol) in CH<sub>3</sub>CN (2 mL) was slowly charged in the tube as the upper layer. The tube was then placed in the dark hood and kept quietly. After around one week, the black hexagonal single crystals (see Figure S7) of (TT-TTF)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>](CH<sub>2</sub>Cl<sub>2</sub>) were obtained (2.4 mg, yield: 11%). It should be noted that in this synthesis, the microcrystals were simultaneously formed to show the hexagonal shapes, similar to those obtained in the mixed solution of TT-TTF : PMA = 1 : 1 in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>CN (v/v, 7 : 3). The bulk crystals were dried in vacuo at 60 °C for 6 hours before the X-ray diffraction measurement, which is to remove the solvent molecules in the nano-channel formed by thienyl groups



Fig. S3 Schematic depiction of the three-layer diffusion for TT-TTF and PMA.



Fig. S4 Photographs for the bulk crystals of  $(TT-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$ , where the red grid represents 1 mm.

## Crystallographic data

Empirical formula,  $C_{67}H_{36}Cl_2Mo_{12}O_{40}PS_{36}$ ; formula weight, 3888.27; temperature, 103(2) K; irradiation, Mo-Ka (0.71073 Å); crystal system, trigonal; spacegroup, *P*-3; *a* = 23.7742(3) Å; *b* = 23.7742(3) Å; *c* = 13.7571(2) Å; *V* = 6733.94(19) Å<sup>3</sup>; *Z* = 2;  $\mu$  = 1.753 mm<sup>-1</sup>; 2 $\theta$  = 57.32°; reflections, 10406; parameters, 516; *GoF*, 1.079; final *R* and *R*<sub>w</sub> for *I* ≥ 2 $\sigma$ (*I*) were 0.026 and 0.0569, respectively; the highest difference peak is 0.91 eV and the deepest hole is –0.59 eV; CCDC number 1037985.

**Crystal structure refinement details:** The thienyl groups on TT-TTF in this complex show the orientational disorder, which cannot be suppressed even at lower temperature. This means the disorder is caused by statistic reason rather than the rotational one. It should be noted that the rotational disorder of thienyl groups have also been observed in the crystal structure of neutral TT-TTF (J. Sun, *et al., Chem. Eur. J.* 2013, **19**, 12517), and those of the inclusion complex [(TT-TTF)- $C_{60}$ ] (which will be published in due course).



**Fig. S5** Comparison of the molecular geometry of TT-TTF in its neutral state and in the complex  $(TT-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$ . The top, short-axis, and long axis are defined with respect to the mean plane of the central TTF core. The light grey, light cyan, and dark green spheres represent C, H, and S atoms, respectively. The crystallographic data for neutral TT-TTF can be obtained in our previous report (J. Sun, *et al., Chem. Eur. J.* 2013, **19**, 12517) or from CCDC (No. 922065).

In comparison with neutral state, the TT-TTF in the complex show the significant variations in (1) the bond length of the central C=C bond as shown in the top view and (2) the spatial alignment of the peripheral thienyl groups, which would be mainly induced by the geometry of the counter component [PMo<sub>12</sub>O<sub>40</sub> cluster] because the peripheral aryls in this type of TTFs show the large rotational freedom and also very sensitive to the environmental variations (J. Sun, *et al., Chem. Eur. J.* 2013, **19**, 12517).



**Fig. S6** Packing structure of  $(TT-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$  viewed along the crystallographic *c*-axis. The present figure is drawn in the space-filled style to show the one-dimensional channel formed by the organic component TT-TTF. The light grey, light cyan, dark green, red, blue, and cyan spheres represent the C, H, S, O, Cl, and Mo atoms respectively.



**Fig. S7** View of a single nanosheet along the *a*-axis for  $(TT-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$ . The thickness (*l*) of a single layer is calculated by " $l = D_c + 2 O_{vdW}$ ".  $D_c$  means the distance between the outer oxygen atoms  $O_{12}$  and  $O_{12a}$  along the crystallographic *c*-axis. Thus,  $D_c = (Z_{O12} - Z_{O12a}) \times c = [1.2221 - (-0.2221)] \times 13.7571$  Å = 19.8680 Å, with  $Z_{O12}$  as the coordination of  $O_{12}$  along *c*-axis direction, *c* is the length of unit cell *c*-axis.  $O_{vdW}$  is the van der Waals radii of oxygen atom, 1.52 Å (A. Bondi, *J. Phys. Chem.* 1964, **68**, 441). Thus, l = 19.8680 Å + 2 × 1.52 Å = 2.29 nm.



**Fig. S8** Crystal structure of  $(TT-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$ . This figure depict the view of two neighboring  $[PMo_{12}O_{40}]$  along the crystallographic *b*-axis to show the position of solvent molecule CH<sub>2</sub>Cl<sub>2</sub> (space-filled depiction in this figure). The light grey, light cyan, dark green, red, blue, and cyan spheres represent the C, H, S, O, Cl, and Mo atoms respectively.

### **Complexation of TSe-TTF with PMA**

The complexation of TSe-TTF with PMA shows almost identical phenomena in absorption spectroscopic aspect, including the titration and the gradual aggregation. Moreover, by employing the same strategy, the black hexagonal bulk crystals of  $(TSe-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$  can be obtained (see Fig S12).

The single crystal X-ray diffraction analysis for this complex was performed, whereas the selenophene rings on TSe-TTF show the even larger disorder than those of the thiophene rings in  $(TT-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$ . Consequently, we could not make the satisfied analysis result for this complex, as one of the selenophene rings is severely disordered. However, the packing motif of this complex could be clearly and also definitely evaluated on the present data. Preliminary structure analysis afforded the following data: Empirical formula,  $C_{67}H_{36}Cl_2Mo_{12}O_{40}PS_{24}Se_{12}$ ; formula weight, 4451.07; temperature, 149(2) K; irradiation, Cu-Ka (1.5418 Å); crystal system, trigonal; spacegroup, *P*-3; *a* = 23.7418(9) Å; *b* = 23.7418(9) Å; *c* = 13.9109(7) Å; *V* = 6790.7(7) Å^3; Z = 2;  $\mu = 4.771$  mm<sup>-1</sup>;  $2\theta = 141.31^{\circ}$ ; reflections, 8546; parameters, 415; *GoF*, 1.026; final *R* and  $R_w$  for  $I \ge 2\sigma(I)$  were 0.081 and 0.2265, respectively; the highest difference peak is 4.09 eV and the deepest hole is -5.528 eV. The large residue peaks are ascribable to the non-positive definition of one of the selenophene rings.



Fig. S9 Photographs for the bulk crystals of  $(TSe-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$ , where the red grid reprensents 1 mm.



**Fig. S10** Packing structure in space-filled style for the complex  $(TSe-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$  viewed along the crystallographic *c*-axis. The light grey, dark green, pink, red, blue, and cyan spheres represent the C, S, Se, O, Cl, and Mo atoms respectively.



**Fig. S11** View of a single nanosheet along the *a*-axis for (TSe-TTF)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>](CH<sub>2</sub>Cl<sub>2</sub>).



**Fig. S12** IR spectra for  $(TSe-TTF)_3[PMo_{12}O_{40}]$  along with those of TSe-TTF and  $(n-Bu_4N)_3[PMo_{12}O_{40}]$  for comparison. The red star marked frequency belongs to the typical vibration of  $[PMo_{12}O_{40}]$  cluster as summarized in Table S1.

### **Thermogravimetric Analyses (TGA)**

Both complexes  $(TT-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$  and  $(TSe-TTF)_3[PMo_{12}O_{40}](CH_2Cl_2)$  show the gradually decomposition when temperature is higher than 150 °C. The first step decomposition occurs at 150 – 200 °C, and about 4% of weight is lost, reflecting the release of the solvent molecule  $CH_2Cl_2$  from the crystal matrix. The following decomposition is ascribable to the decomposition of the organic components under the high temperature, as TT-TTF and TSe-TTF are decomposed at 300 °C. Ultimately, about 65% of complex remained at 800 oC, which corresponds to the inorganic component  $[PMo_{12}O_{40}]^{3-}$  ions.



Fig. S13 Thermogravimetric analysis of (TT-TTF)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>](CH<sub>2</sub>Cl<sub>2</sub>)



Fig. S14 Thermogravimetric analysis of (TSe-TTF)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>](CH<sub>2</sub>Cl<sub>2</sub>)



Fig. S15 The TEM image of the microcrystals of (TT-TTF)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>](CH<sub>2</sub>Cl<sub>2</sub>)