Supporting Information For

Structural Transitions from Triangular to Square Molecular Arrangements in the Quasi-One-Dimensional Molecular Conductors (DMEDO-TTF)$_2$*X*F$_6$ (*X* = P, As, and Sb)

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1. Crystal Structure analysis of DMEDO-TTF

The diffraction data of DMEDO-TTF at 100 K were collected on a Rigaku VariMaxSaturn724 CCD system with graphite monochromatized Mo-Kα radiation. Raw frame data were integrated using CrystalClear and no absorption correction was applied. The crystal structures were solved by the direct method (SIR2008)[1] and refined by full-matrix least squares on F^2 (SHELXL-97).[2]

References

(1) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Siliqi, D.; Spagna R. *SIR2008*: Program for the solution of crystal structures from X-ray data, CNR Institute of Crystallography, Bari, Italy, 2007.

(2) Sheldrick, G. M. *SHELXL (SHELX97)*: Program for the refinement of crystal structures; University of Gottingen, Gottingen, Germany, 1996.

Table 1. Crystallographic Data of DMEDO-TTF

formula	$C_{20}H_{20}O_4S_8$
crystal size	$0.12 \times 0.10 \times 0.02$ mm^3
T (K)	100
crystal system	Monoclinic
space group	$P2_1/c$ (#14)
a (Å)	13.462(12)
b (Å)	8.271(7)
c (Å)	11.139(10)
β (°)	110.853(15)
V (Å^3)	1159.0(18)
Z	4
D_{calc} (g cm^{-3})	1.664
independent reflections	2649
observed reflections [$I > 2\sigma(I)$]	2279
$R1$; $wR2$ [$I > 2\sigma(I)$]	0.0505; 0.1117
GOF	1.144

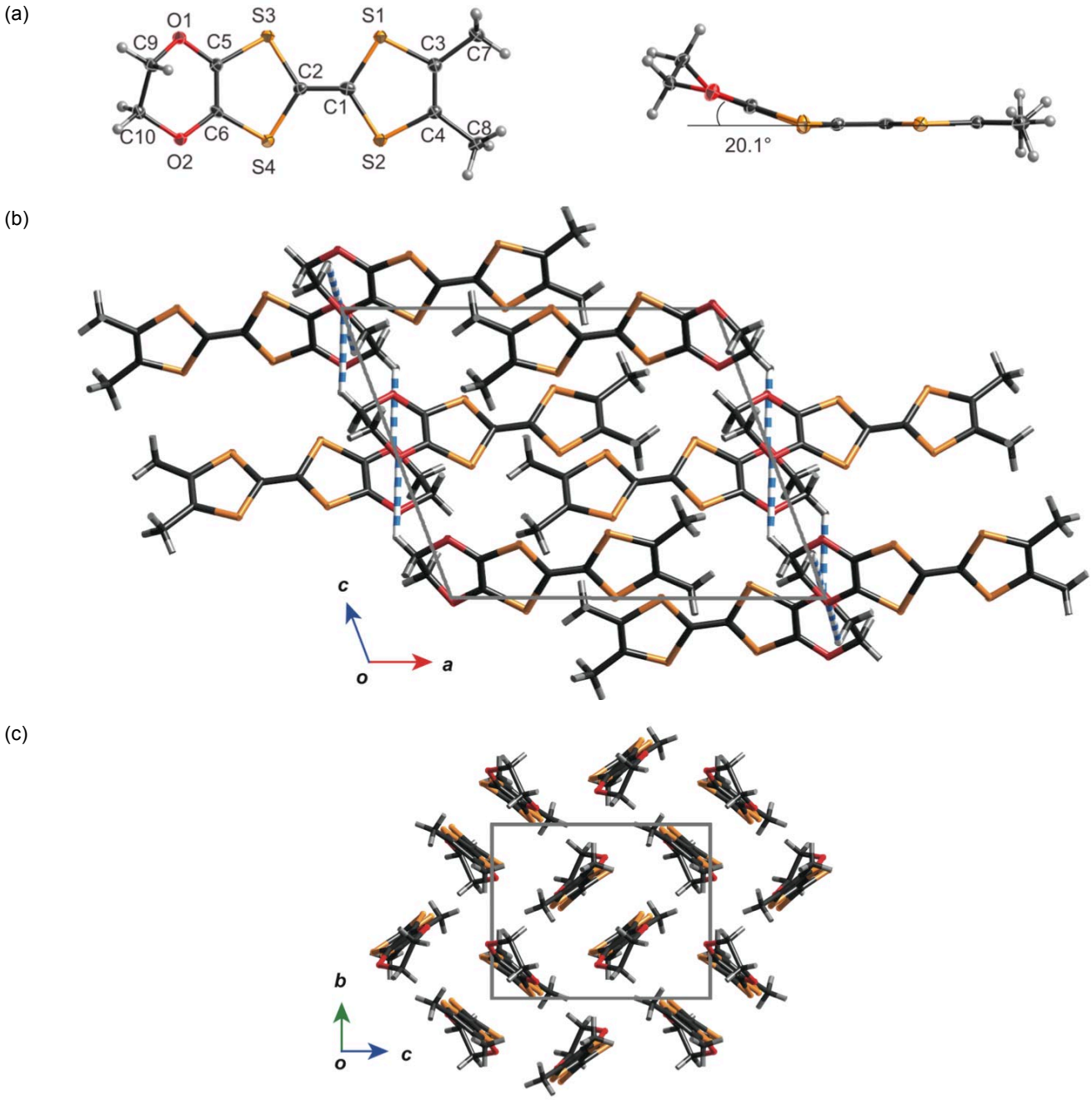

Figure S1. Crystal structure of DMEDO-TTF: (a) molecular structures; (b) crystal packing diagram viewed along the crystallographic *b*-axis, blue dashed lines indicate short CH···O contacts shorter than 2.9 Å; (c) κ-type layer structure viewed along the crystallographic *a*-axis.

2. ESR measurements of $(DMEDO\text{-}TTF)_2PF_6$ (Figure S2, S3)

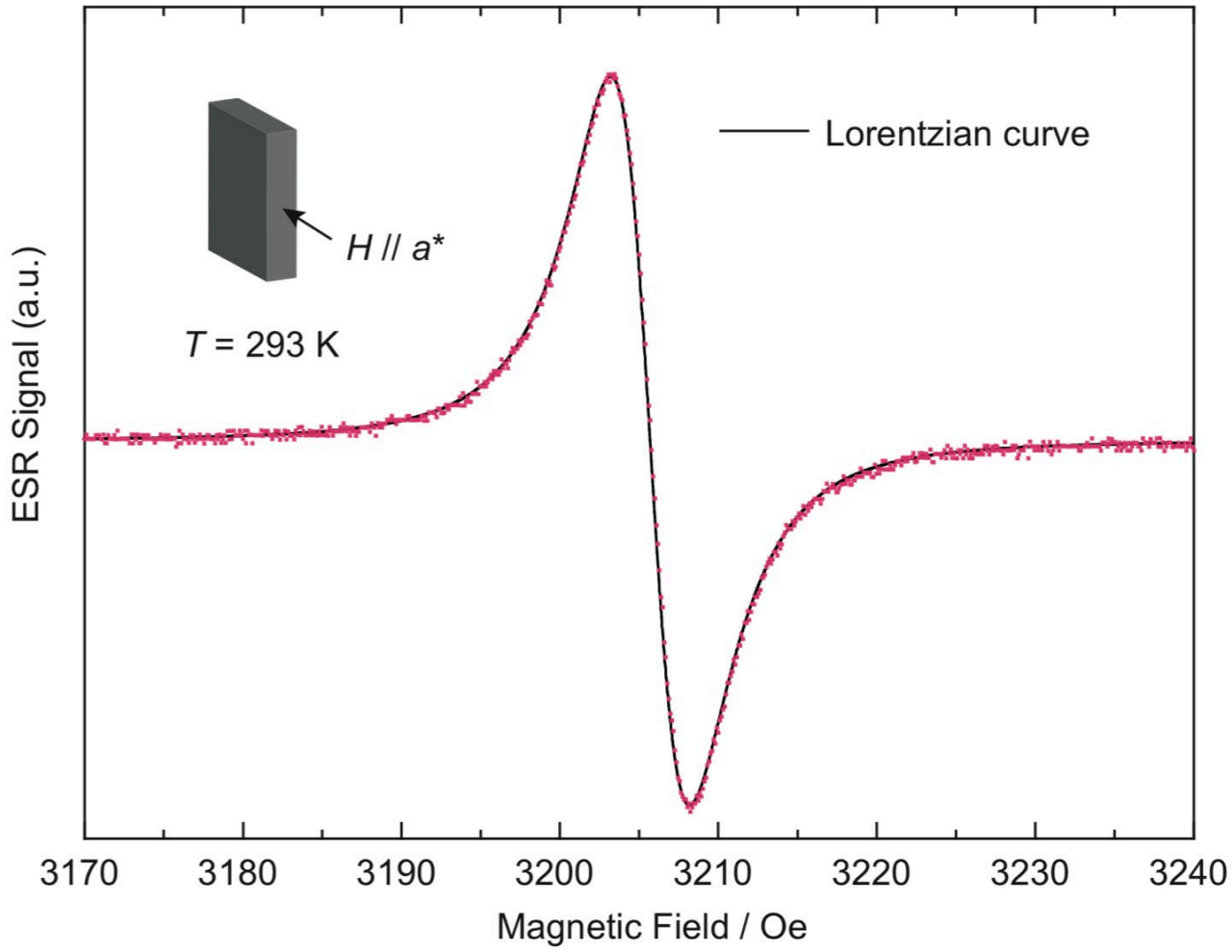

Figure S2. Line shape of ESR spectra in $(DMEDO\text{-}TTF)_2PF_6$ at 293 K. The solid line is fit to the Lorentzian curve. The inset shows relation between the crystal shape and applied magnetic field.

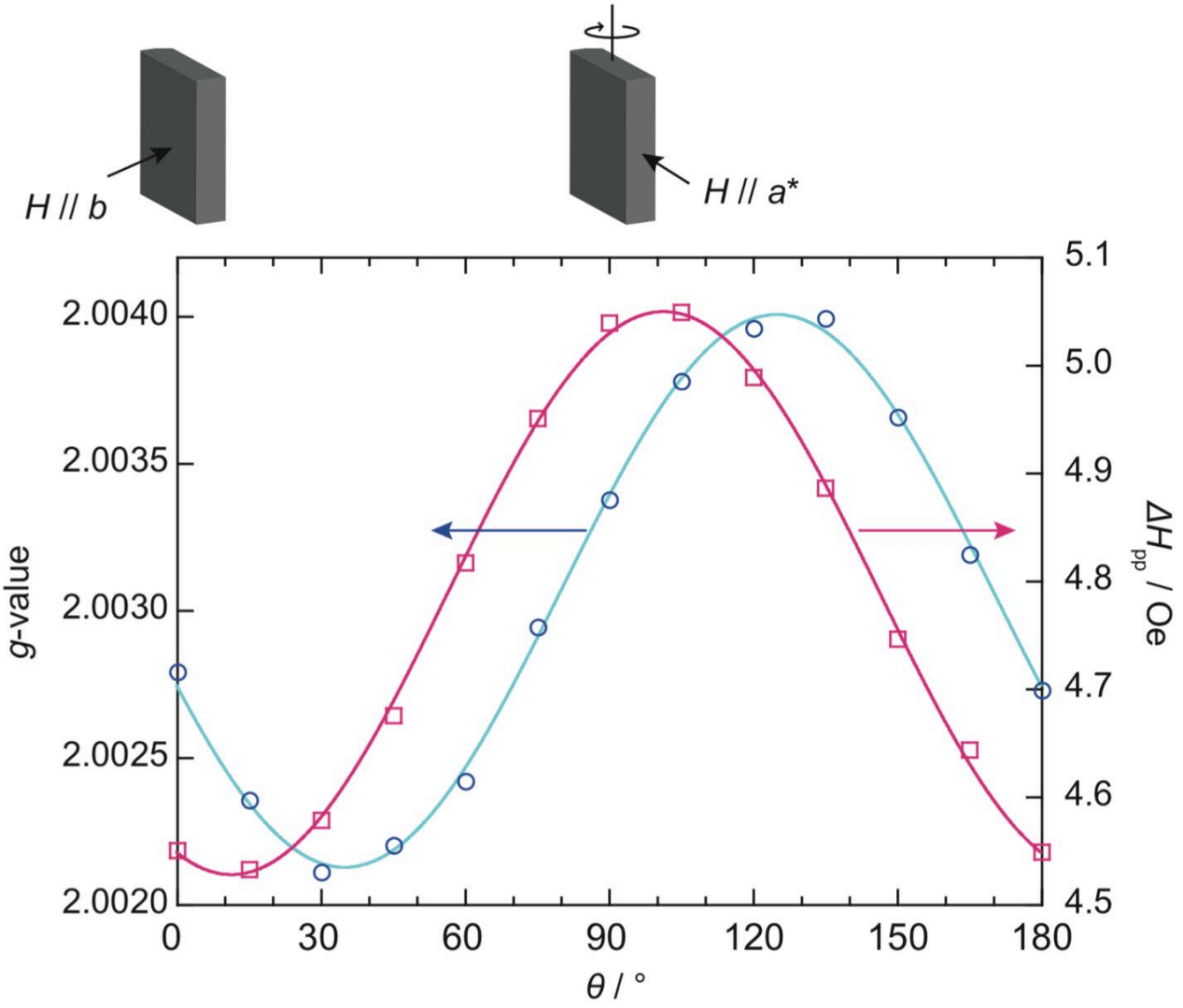

Figure S3. Angle dependence of the ESR line widths (red square) and the *g*-values (blue circle) of $(DMEDO\text{-}TTF)_2PF_6$ at 293 K. Red and blue lines are fitted to the following equations: $\Delta H_{pp} = \Delta H_i \cos^2\theta + \Delta H_j \sin^2\theta$ and $g^2 = g_i^2 \cos^2\theta + g_j^2 \sin^2\theta$.

3. Extended Hückel parameters

Table S2. Semiempirical parameters for Slater-type orbitals

orbitals	ζ	I_P / Ryd
S 3s	2.122	−1.47
S 3p	1.827	−0.808
S 3d	1.5	−0.40
O 2s	2.275	−2.375
O 2p	2.275	−1.088
C 2s	1.625	−1.573
C 2p	1.625	−0.838
H 1s	1.00	−1.0

4. Crystal destruction during MM transition of $(DMEDO\text{-}TTF)_2PF_6$

Movie S1. Rapid cooling of the crystals of $(DMEDO\text{-}TTF)_2PF_6$.

5. DSC measurement of the AsF_6 salt

DSC of $(DMEDO\text{-}TTF)_2AsF_6$ was performed on a Seiko Instruments Inc. DSC 6200 with scan rate of 10 K min^{-1}.

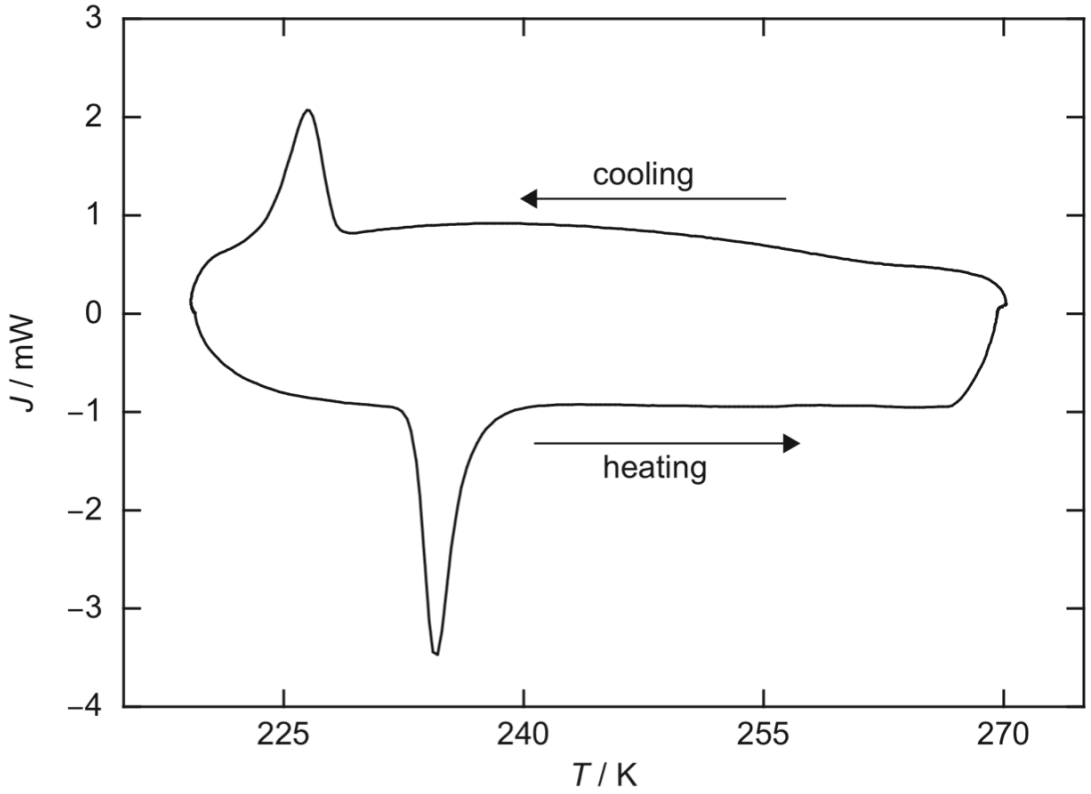

Figure S4. DSC of $(DMEDO\text{-}TTF)_2AsF_6$.

6. Complete entry of reference 27

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr. J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; "Gaussian 03, Revision C.02", Gaussian, Inc., Wallingford, CT, 2004.

7. Reflectivity and the optical conductivity spectra of $(DMEDO\text{-}TTF)_2PF_6$

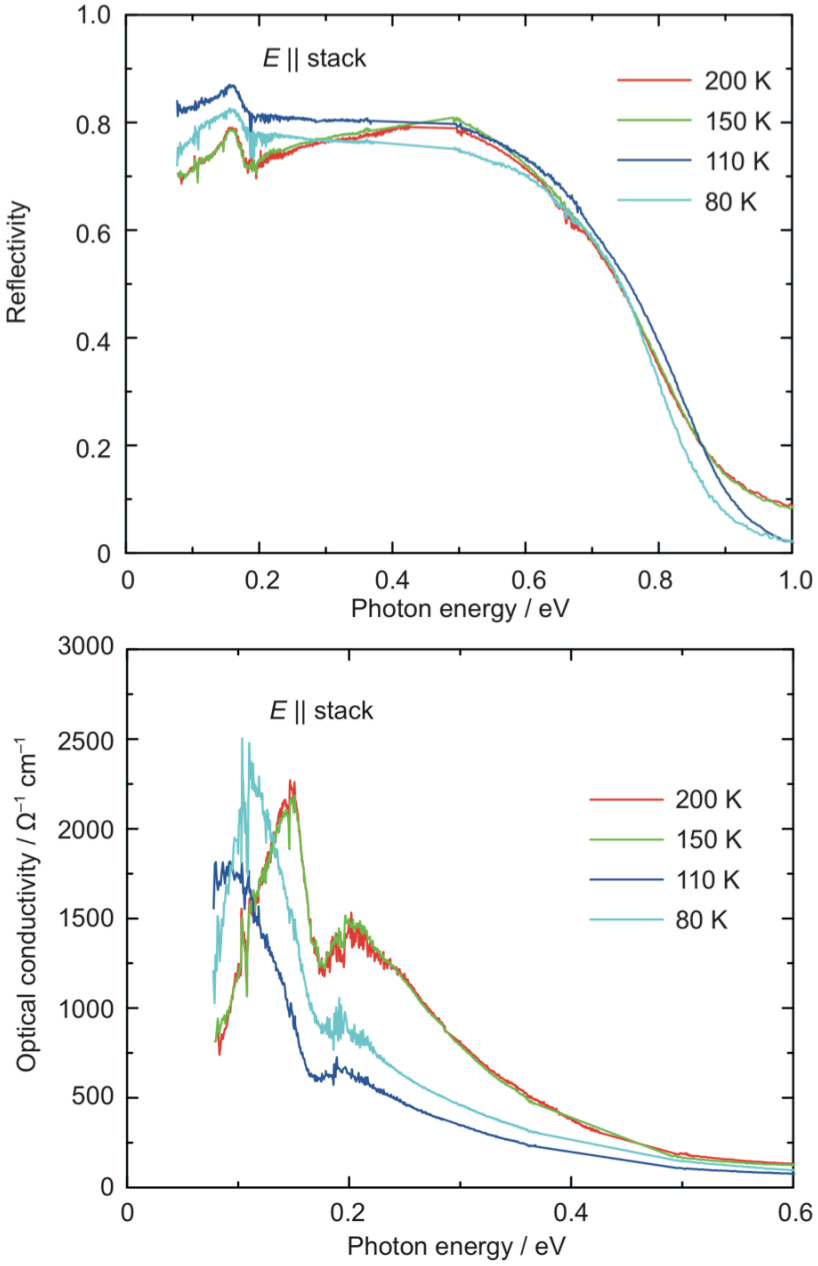

Figure S5. (a) Reflectivity spectra of $(DMEDO\text{-}TTF)_2PF_6$ with the linear polarized light E || stack at various temperature. (b) The optical conductivity spectra of $(DMEDO\text{-}TTF)_2PF_6$ deduced from the reflectivity spectra using Kramers-Kronig transformation.

8. Temperature dependence of the lattice parameters of $(DMEDO\text{-}TTF)_2AsF_6$

Temperature dependence of the lattice parameters for the AsF_6 salt was measured on a Rigaku AFC7R four-circle diffractometer.

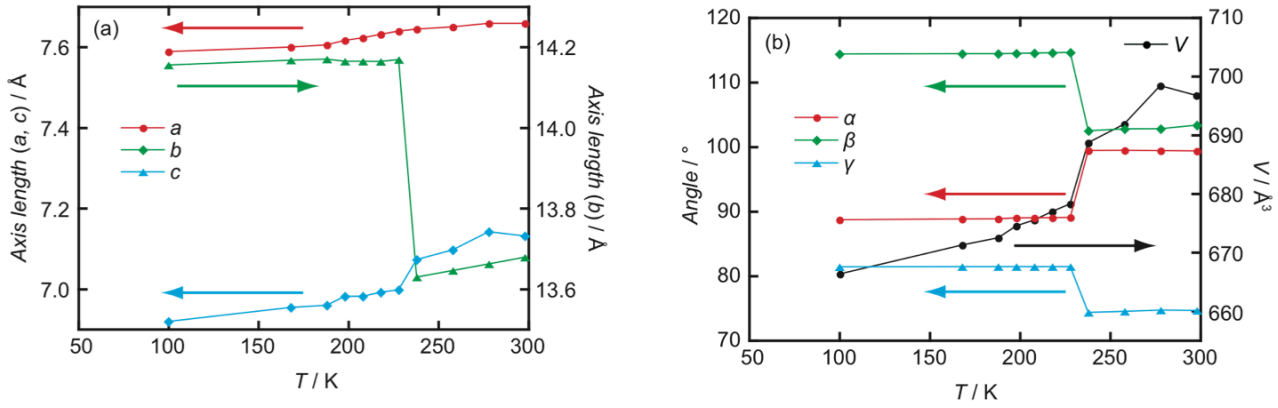

Figure S6. Temperature dependence of the lattice parameters for $(DMEDO\text{-}TTF)_2AsF_6$.

9. Definition of geometrical parameters

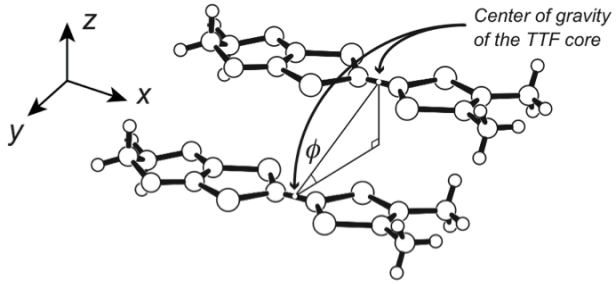

Figure S7. Definition of geometrical parameters: *x* and *y* are the slip distance along the molecular long and short axes, respectively; *z* is the interplaner distance between the molecular plane; ϕ is an angle of the intermolecular vector from the molecular plane, where $\phi = \tan^{-1} z/y$. The intermolecular vector is calculated based on the center of gravity of the TTF core of the unsymmetrical DMEDO-TTF molecule.

10. Calculated Fermi surfaces of (DMEDO-TTF)$_2$*X*F$_6$ (*X* = P, As, and Sb)

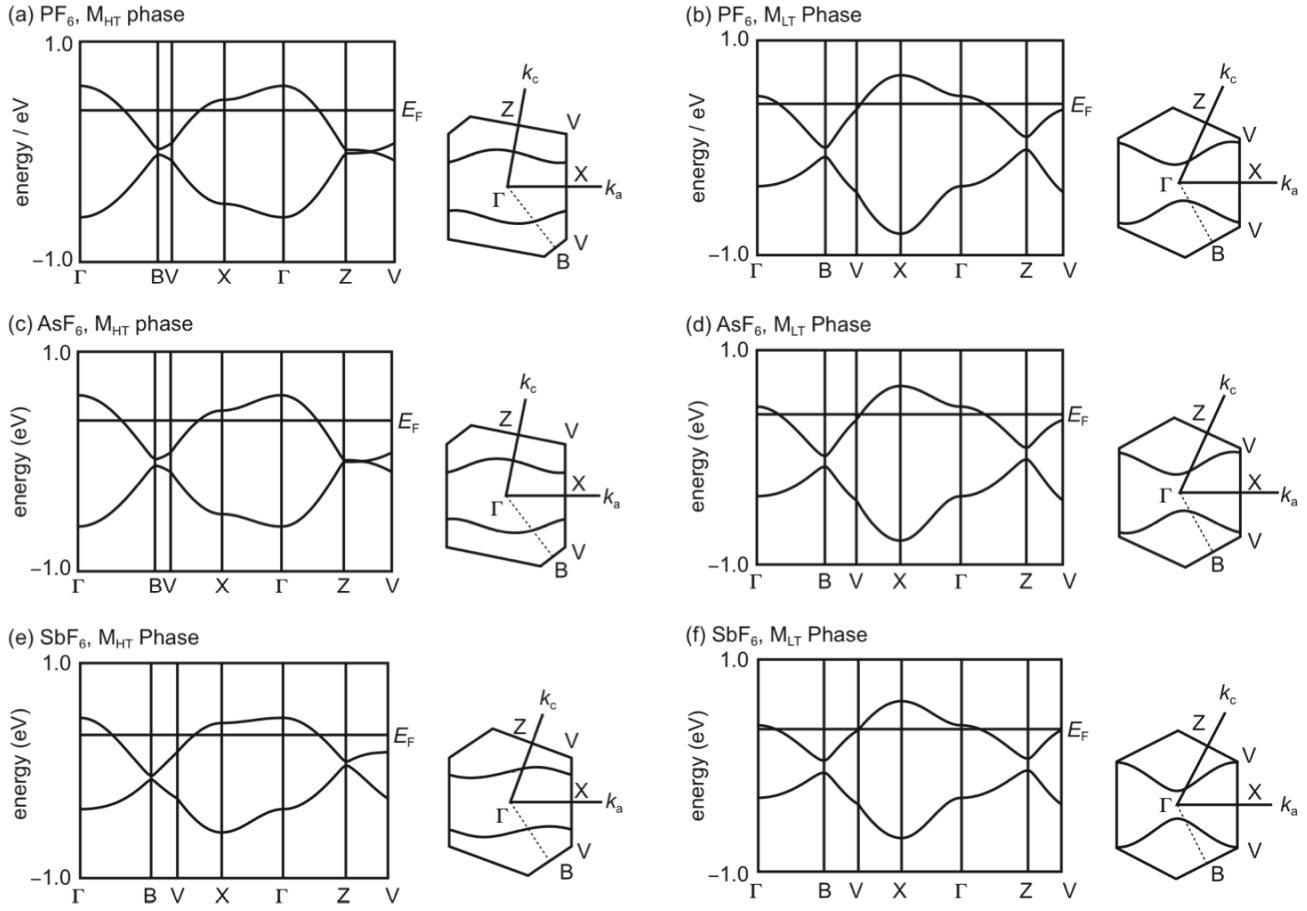

Figure S8. Calculated Fermi surfaces of (DMEDO-TTF)$_2$*X*F$_6$; (a) *X* = P, M$_{HT}$ phase; (b) *X* = P, M$_{LT}$ phase; (c) *X* = As, M$_{HT}$ phase; (d) *X* = As, M$_{LT}$ phase; (e) *X* = Sb, M$_{HT}$ phase; (f) *X* = Sb, M$_{LT}$ phase.