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Electronic Supplementary Information

Crystal structure and physical properties of radical cation salt based on 4,5-ethylenedioxy-4'-iodotetrathiafulvalene (EDO-TTF-I) with iodine bonding ability

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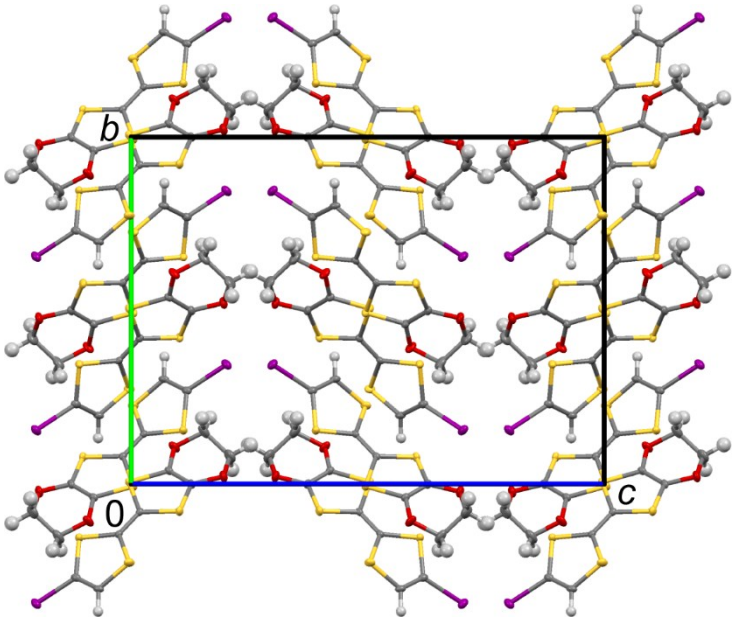
(a)



(b)

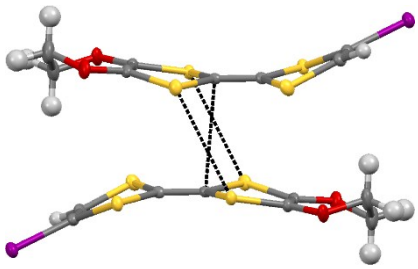


Fig. S1 (a) Crystal and (b) dimer structures of EDO-TTF-I at 100 K.

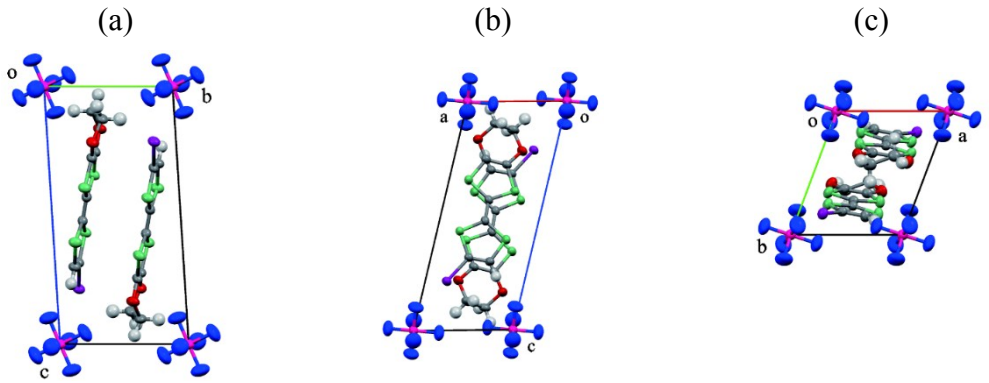


Fig. S2 Crystal structures viewed along (a) *a*, (b) *b*, and (c) *c* axes of $(EDO\text{-}TTF\text{-}I)_2PF_6$ at 300 K.

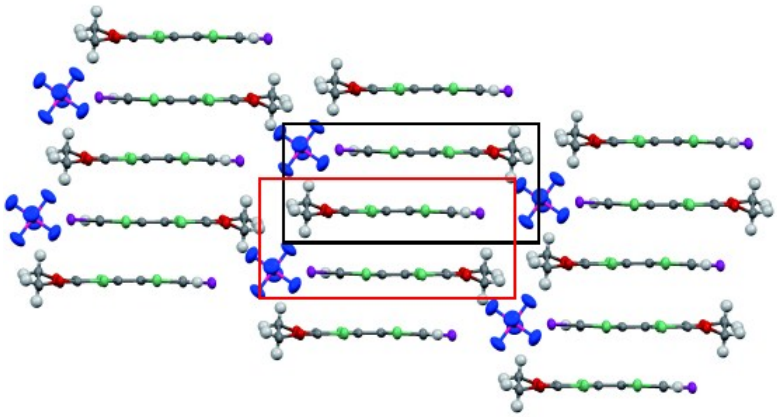


Fig. S3 Molecular packing viewed along molecular short axis in $(EDI\text{-}TTF\text{-}I)_2PF_6$ at 300 K. The boxes in black and red indicate the ring-over-bond and ring-over-atom stacking manners, respectively.

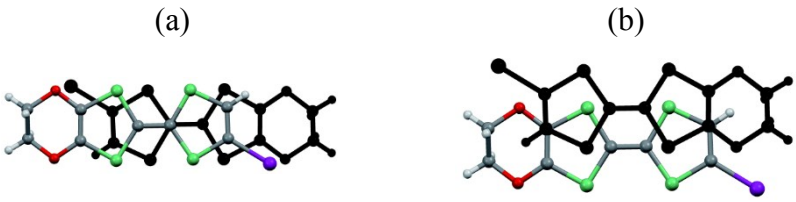


Fig. S4 Stacking manners viewed along stacking axis in $(EDI\text{-}TTF\text{-}I)_2PF_6$ at 300 K. (a) Ring-over-bond and (b) ring-over-atom manners.

Table S1 Overlap integrals (10^{-3}) calculated without and with sulfur 3d orbitals, degree of molecular dimerization ($\Delta s/\langle s\rangle$) and energy gaps between upper and lower bands

	Without sulfur 3d orbitals		With sulfur 3d orbitals	
	300 K	100 K	300 K	100 K
$s1$	11.9	13.2	22.9	25.8
$s2$	7.9	7.5	7.6	6.0
$a1$	1.0	1.4	4.0	5.2
$p1$	5.8	6.9	14.1	15.7
$p2$	2.0	2.1	6.9	7.4
$\Delta s/\langle s\rangle^a$	0.40	0.55	1.00	1.24
E_g / eV	0.002	0.019	0.013	–

[a] $\Delta s/\langle s\rangle = 2(s1 - s2)/(s1 + s2)$.

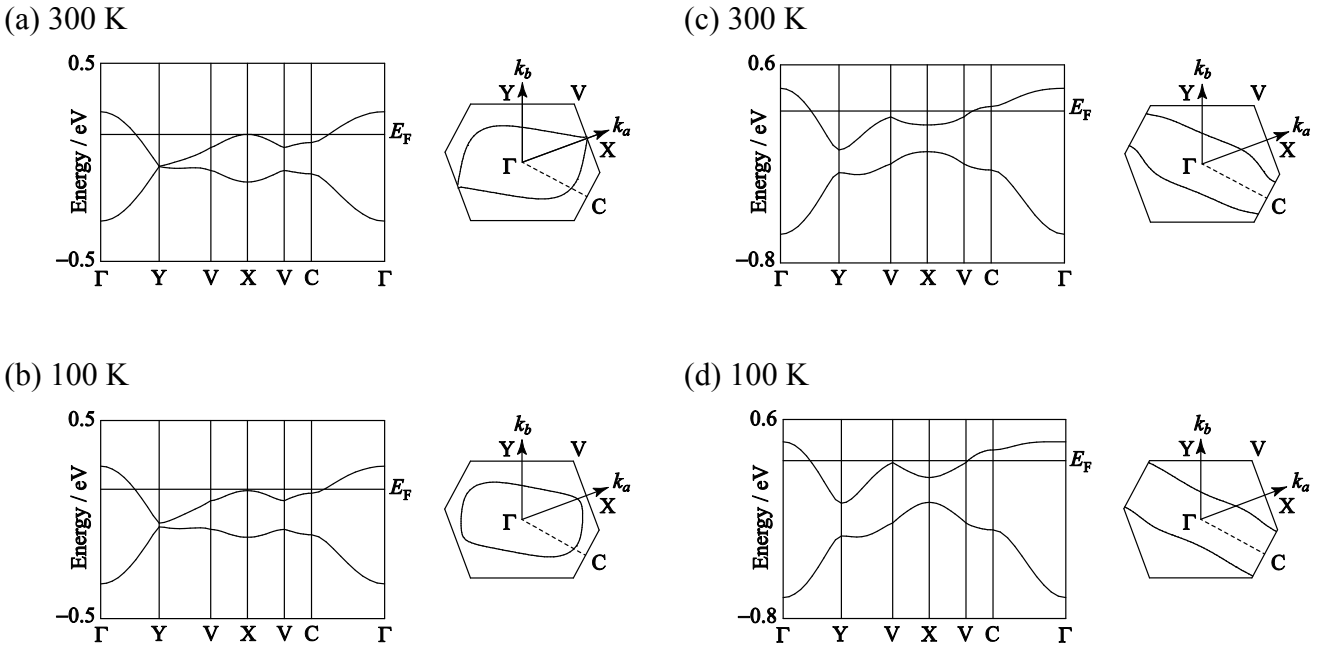


Fig. S5 Energy band structures and Fermi surfaces calculated (a, b) without and (c, d) with sulfur 3d orbitals.

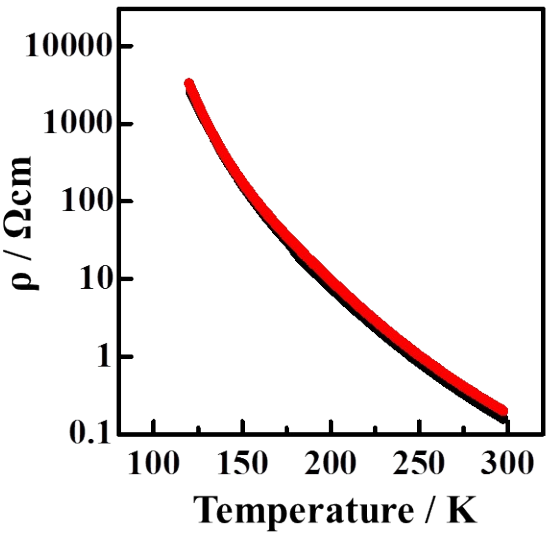


Fig. S6 Sample dependence on electrical resistivity measured along *b* axis in (EDI-TTF-I)$_2$PF$_6$. Two samples showed almost the same behavior.

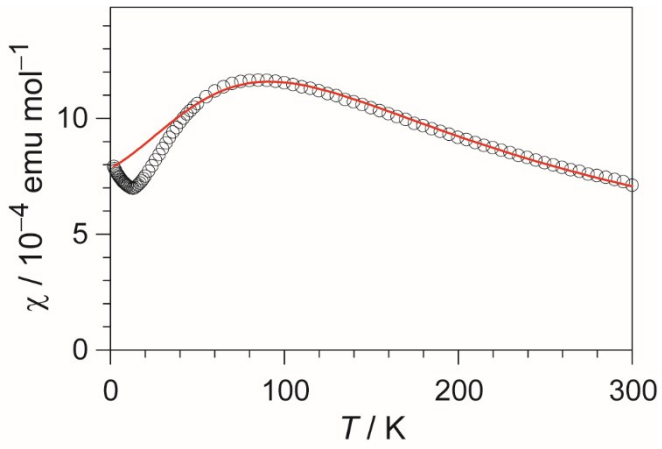


Fig. S7 Temperature dependence of the magnetic susceptibility (χ) of (EDO-TTF-I)$_2$PF$_6$. The solid curve represents the best fit to the Bonner−Fisher model.

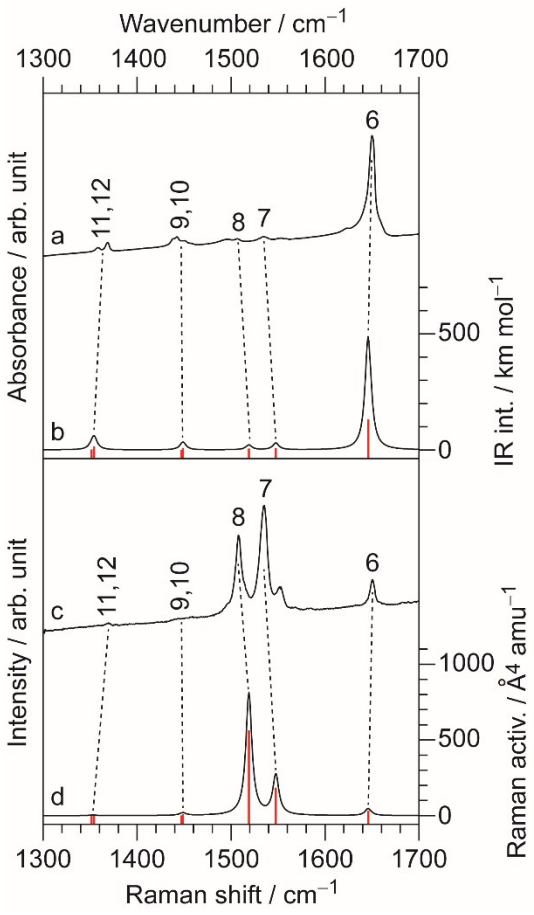


Fig. S8 (a) Observed infrared spectra of neutral EDO-TTF-I dispersed in KBr at room temperature. (c) Observed Raman spectra of neutral EDO-TTF-I excited by a 633-nm laser at 300 K. (b) Infrared spectra and (d) Raman spectra EDO-TTF-I^0 molecule calculated at the B3LYP/Aug-cc-pVTZ(-PP). The numbering *j* denotes the v_j mode. The frequency scaling factor is 0.969.

Table S2 Observed and calculated frequencies (cm^{-1}) of EDO-TTF-I

ν	Infrared	Raman	Calc.[a]	Assignment
6	1650	1650	1646	C=C stretching
7	1535	1535	1548	C=C stretching
8	1507	1508	1519	C=C stretching
9	1464	1463	1449	CH_2 scissoring
	1451	1454		
10	1443	1445	1447	CH_2 scissoring
11	1369	1369	1354	CH_2 wagging
12	1366	1365	1352	CH_2 wagging

[a] B3LYP/Aug-cc-pVTZ(-PP), frequency scaling factor = 0.969.