A novel metal-insulator phase transition observed in $(EDO\text{-}TTF)_2PF_6$

The data of the Raman spectra for $(EDO\text{-}TTF)_2PF_6$, $(EDO\text{-}TTF)_2AsF_6$

The peaks derived from the C=C stretching of ethylenedioxy ring (ν_1), 1,3-dithiole ring without ethylenedioxy group (ν_2), and central C=C bond (ν_3) are shown in Table for each donor molecule. Assuming the linear relationship between the charge on a donor molecule and the Raman shifts, the charge distribution in the donor molecules in the LT phase is estimated. The details of the optical spectra of $(EDO\text{-}TTF)_2PF_6$ will be published separately: O. Drozdova, K. Yakushi, A. Ota, H. Yamochi, G. Saito, submitted to Synth. Met.

Table

		ν_1 / cm^{-1}	ν_2 / cm^{-1}	ν_3 / cm^{-1}	Charge
Neutral EDO-TTF		1650	1538	1510	0
$(EDO\text{-}TTF)_2PF_6$ at RT		Very week	1515	1472	+0.5
$(EDO\text{-}TTF)_2AsF_6$ at RT		Very week	1515	1469	+0.5
$(EDO\text{-}TTF)IBr_2$		1560	1480	1408	+1
$(EDO\text{-}TTF)_2PF_6$ at 4.2K	B	1649	1539	1499	< +0.1 (estimated)
	F	1572	1484	1412	> +0.9 (estimated)
$(EDO\text{-}TTF)_2AsF_6$ at 4.2K	B	1647	1538	1497	< +0.1 (estimated)
	F	1570	1483	1412	> +0.9 (estimated)

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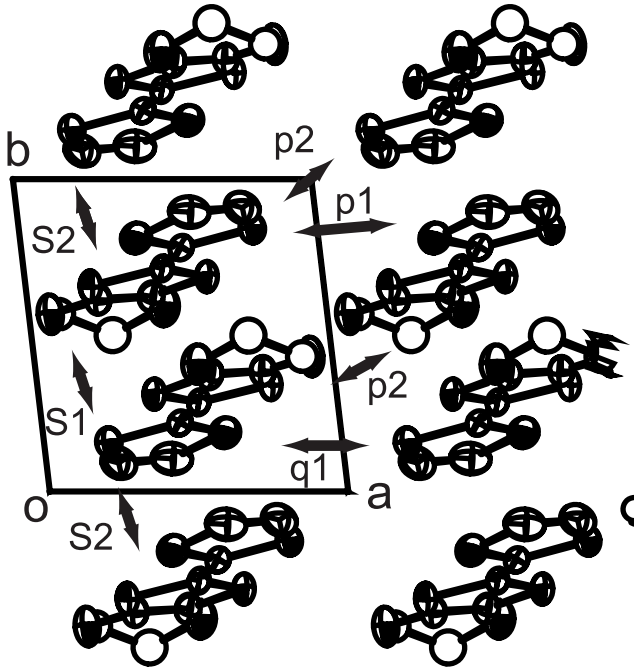
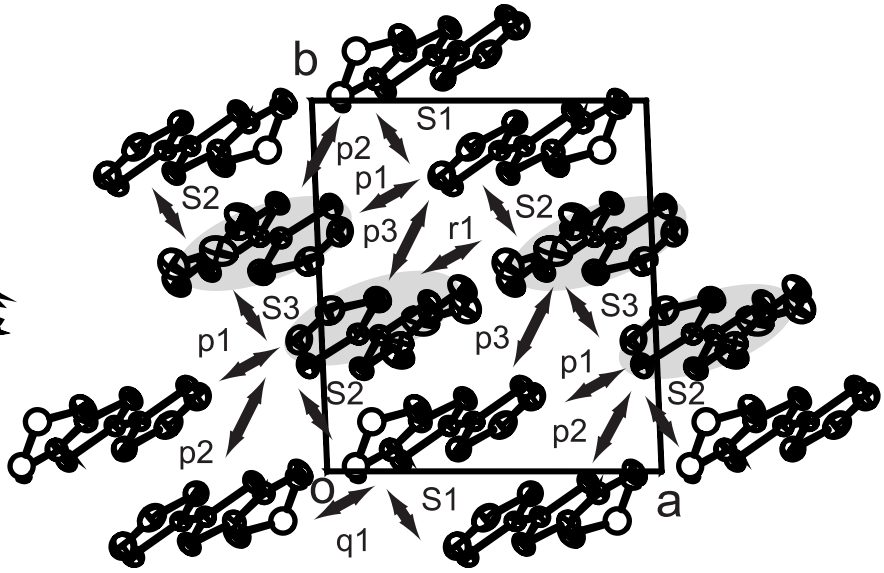
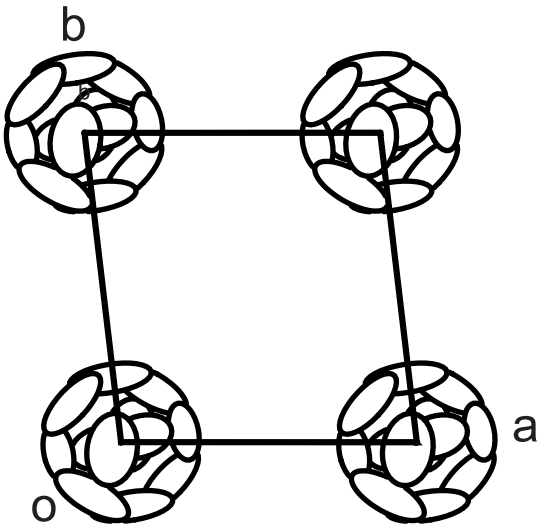


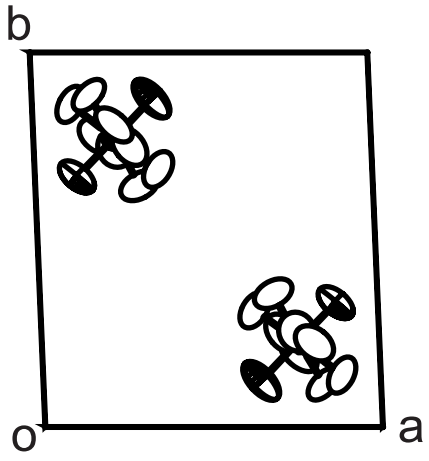
(RT-a) s1 = 27.4, s2 = 23.3, p1 = 2.3, p2 = -6.3, q1 = 1.6×10^{-3}



(LT-a) s1 = 44.2, s2 = -23.0, s3 = 13.0, p1 = -0.9, p2 = 3.3, p3 = 8.1, q1 = 0.4, r1 = 1.6×10^{-3}



(RT-b)



(LT-b)

Supporting Information: The crystal structures of $(EDO\text{-}TTF)_2PF_6$ at room temperature (RT) and at 260 K. (RT-a) and (LT-a) depict the c-axis projection of donor layers in RT and low temperature (LT) phases along with the calculated overlap integrals, respectively. For the donor molecules in RT phase and the flat shaped ones in LT phase, both of the two orientations of the terminal ethylene group obtained by the structural analysis afforded the same intermolecular overlap integrals and hence the band structure. In (LT-a), the bent donor molecules, which are assigned to be less charged than the flat ones, are shaded. (RT-b) and (LT-b) depict the anion layers in RT and LT phases, respectively. The a- and b-axes for the LT phase correspond to those of (a+b) and (a-b) in RT phase, respectively. In all cases, the atoms, of which site occupancy factors are less than unity are depicted by open ellipsoids.