Electronic Supplementary Information

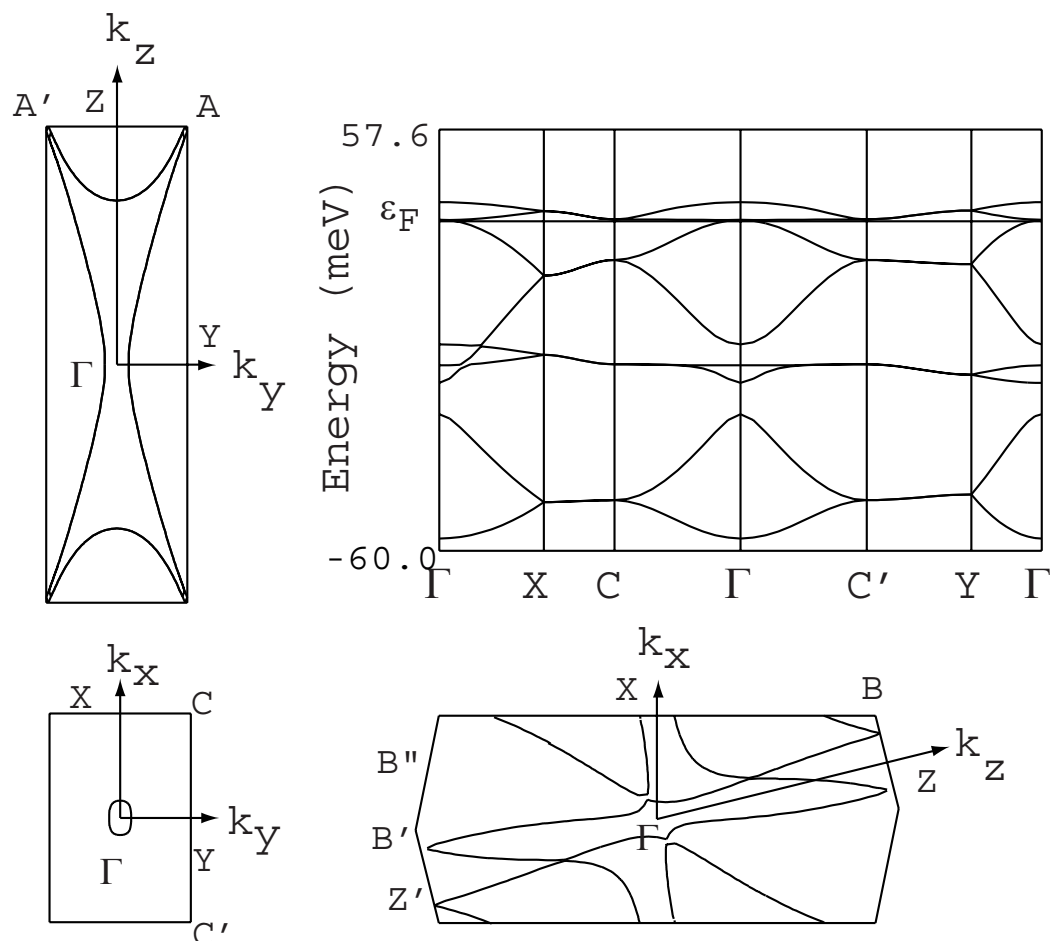

Fig. S1 Calculated electronic band dispersion and the Fermi surface of (TP-EDOT)$_2$PF$_6$. Due to the small band width, the effect of the arithmetic underflows in the calculation procedures caused the unrealistic sensitivity of the Fermi energy and the shape of Fermi surface to the modulation of parameters used. In the calculation, the intermolecular overlap integral of $s3$ was ignored. The results indicated here are based on the assumption that the Fermi energy (ε_F) is 31.92 meV which corresponds to the 3/4-filling of the band in the calculation of the Fermi surface at $k_z = 0$.
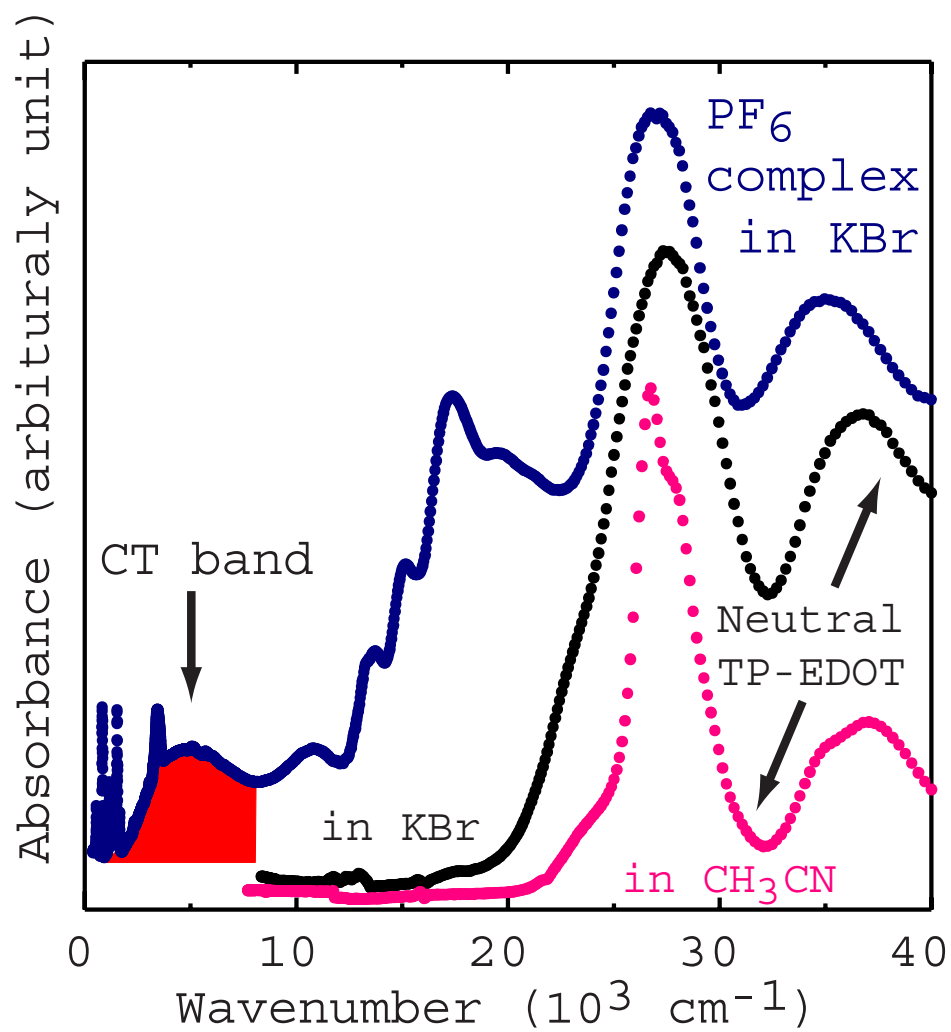
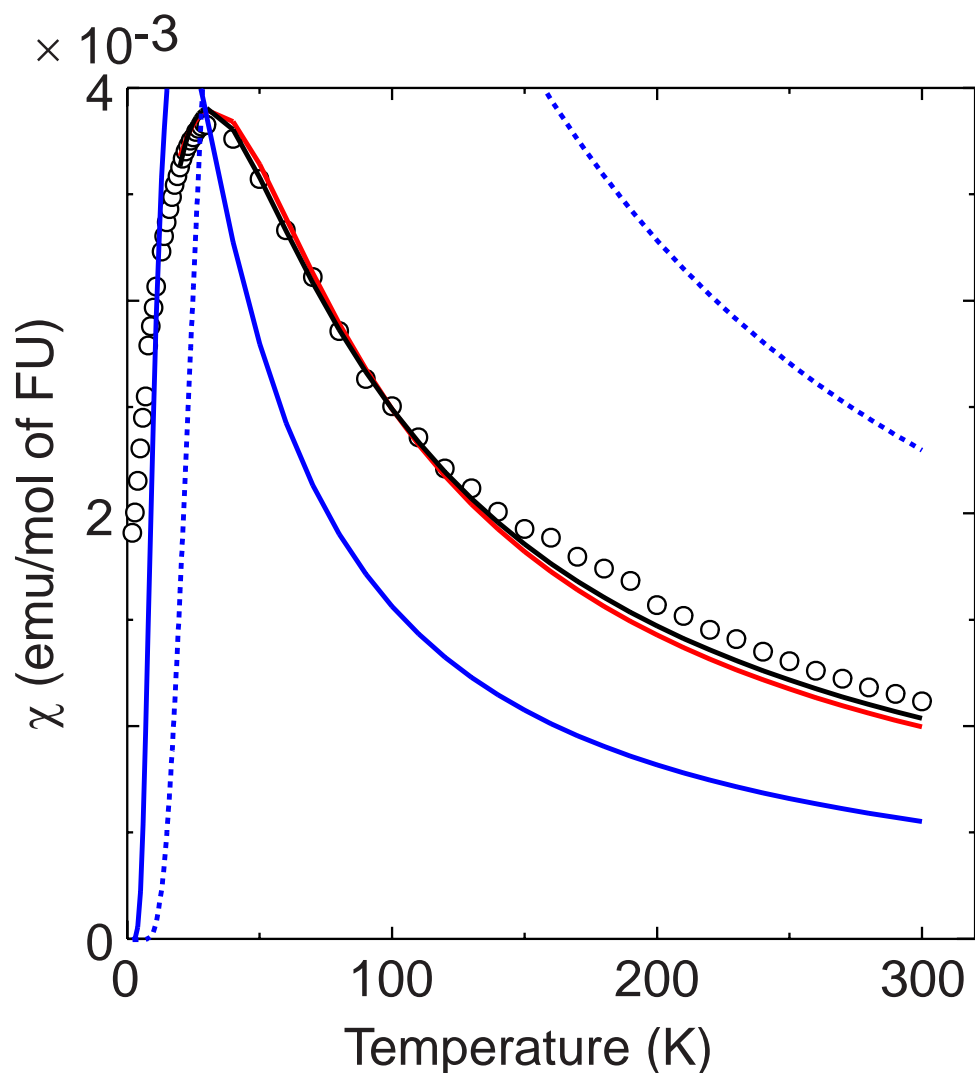Fig. S2 Optical Absorption spectra of TP-EDOT and (TP-EDOT)$_2$PF$_6$

Fig. S3 The results of least-squares fittings of the temperature dependence of χ of (TP-EDOT)$_2$PF$_6$ to theoretical models. Open circles indicate the observed data. Red solid line shows the best fit with Bonner-Fisher model. In this case, the g-value was also refined as a fitting parameter along with the interaction parameter J. This treatment resulted in the unrealistic value of $g = 1.883$ and $J = 50.0$ K. Black solid line corresponds to the result with QLAF model, in which g and J were refined to give the final values of $g = 1.928$ and $J = 33.5$ K. Blue solid and dotted lines indicate the best results fitted with the singlet-triplet model, in which g-value is refined and fixed, respectively. The former resulted in the values of $g = 0.956$ and $J = -32.0$ K, while the latter afforded the value of $J = -89.7$ K for fixed g-value of 2.000. For the last model, see pp. 251-257 of the reference 17.

Table S1 The averaged bond lengths (Å) of TP-EDOT under the assumption of *C2v* symmetry.

	a	b	c	d	e	f	g	h
in PF$_6$ complex								
	1.717(9)	1.34(1)	1.44(1)	1.373(7)	1.744(7)	1.739(8)	1.329(8)	1.36(1)
in Sb$_2$F$_{11}$ complex*								
D1	1.71(1)	1.36(1)	1.40(1)	1.42(2)	1.718(7)	1.731(9)	1.33(2)	1.36(1)
D2	1.75(1)	1.32(1)	1.43(1)	1.40(2)	1.710(6)	1.718(9)	1.33(2)	1.36(1)
D3	1.77(1)	1.30(1)	1.45(1)	1.40(2)	1.757(7)	1.732(8)	1.33(2)	1.37(1)

*: In the unit cell of the Sb$_2$F$_{11}$ complex, D1, D2, and D3 correspond to those in Fig. 6, respectively. The notations of bonds are indicated in the right;
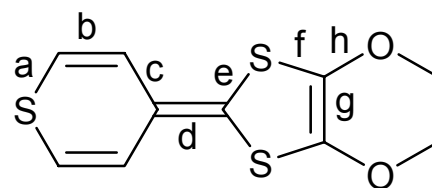
Table S2 Variation of the intermolecular overlap integrals by 0.1 Å displacements of the donor molecules in $(BEDO-TTF)_5(HCTMM)(benzonitrile)_2$.

displacement[a]	s (ratio)[b]	s' (ratio)[b]	p (ratio)[b]	p' (ratio)[b]	q (ratio)[b]	q' (ratio)[b]
none	-5.82		3.99		-10.93	
longitudinal (+)	-5.77 (-0.8%)	-4.98 (-14.5%)	3.75 (-5.9%)	4.32 (8.3%)	-10.27 (-6.0%)	-12.11 (10.8%)
longitudinal (-)	-4.98 (-14.5%)	-5.77 (-0.8%)	4.32 (8.3%)	3.75 (-5.9%)	-12.11 (10.8%)	-10.27 (-6.0%)
lateral (+)	-6.35 (9.2%)	-6.00 (3.1%)	5.93 (48.8%)	2.66 (-33.2%)	-11.65 (6.6%)	-10.02 (-8.3%)
lateral (-)	-6.00 (3.1%)	-6.35 (9.2%)	2.66 (-33.2%)	5.93 (48.8%)	-10.02 (-8.3%)	-11.65 (6.6%)
stack (+)	-4.66 (-19.8%)	-7.10 (22.0%)	5.40 (35.4%)	2.74 (-31.3%)	-8.47 (-22.5%)	-13.49 (23.4%)
stack (-)	-7.10 (22.0%)	-4.66 (-19.8%)	2.74 (-31.3%)	5.40 (35.4%)	-13.49 (23.4%)	-8.47 (-22.5%)

a: Intermolecular overlap integrals were calculated for the donor arrangements in which they were displaced along the molecular longitudinal, stack, and lateral directions. The translations correspond to the motions along the crystallographic ($5b-2a$), ($a+2c$), and ($3a+c$) directions, respectively. In cases of (+), the donor molecule at the body center in a unit cell was translated along the indicated direction, while the other donor molecules were moved in the reverse direction. For the cases of (-), the relation were reversed.

b: The overlap integrals were calculated between the donor molecules as depicted in Fig. S4 and given in the unit of 10^{-3}. The overlap integrals of s (s'), p (p'), q (q') correspond to the intermolecular interaction along the 60, 0, and 30º directions, respectively. The ratio is defined as {(overlap integral after translation) - (overlap integral before translation) } / (overlap integral before translation) × 100.
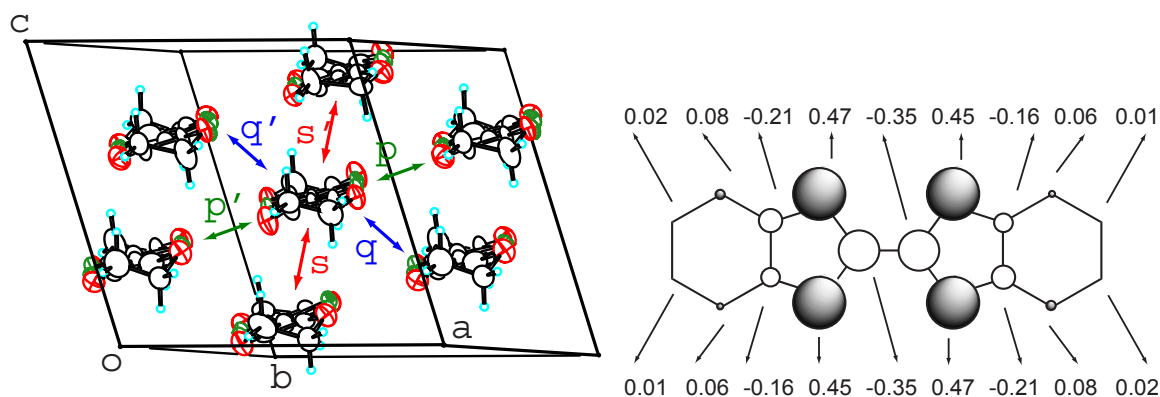

Fig. S4   (left) Molecular longitudinal axis projection of the donor layer in $(BEDO-TTF)_5$ $(HCTMM)(benzonitrile)_2$, and (right) the p_z orbital coefficients in the HOMO of BEDO-TTF. Sulfur 3d orbitals were not included in all the calculations. The intermolecular overlap integrals defined in the left figure are listed in Table S2 along with the variation of them by the slight displacements of the donor molecules. Since the donor molecule at the body center of the unit cell is located on a center of inversion, the overlap integrals of s, p, q are equal to s', p', q', respectively, in the original crystal structure, while they are independent to each other when the molecular displacements are assumed as indicated in Table S2.