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Electronic Supplementary information

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Title: Metal-semiconductor structural phase transitions and antiferromagnetic orderings in (Benzo-TTFVO)$_2$•MX$_4$ (M = Fe, Ga; X = Cl, Br) salts

Results on preliminary structure determination at 90 K with cell constants; *a* = 13.00(2), *b* = 13.82(2), *c* = 20.11(3) Å, α = 99.86(5), β = 105.13(6), γ = 89.97(6)°, *U* = 3430(8) Å^3; and four crystallographically independent donor molecules and two $FeBr_4^-$ ions.

Crystal data for 4$_2$•FeBr$_4$ at 90 K. $C_{52}H_{24}S_{24}O4Fe_2Br_8$, *M* = 2233.13, triclinic, *a* = 13.00(2), *b* = 13.82(2), *c* = 20.11(3) Å, α = 99.86(5), β = 105.13(6), γ = 89.97(6)°, *U* = 3430(8) Å^3, *T* = 90 K, space group *P*-1, *Z* = 2, μ(Mo *K*α) 5.872 mm^{-1}, 29328 reflections measured, 14663 unique, of which 4690 were used in all calculations [$F^2 > 2.0\sigma(F^2)$]. The final R_1 and wR_2 were 0.089 and 0.100, respectively.

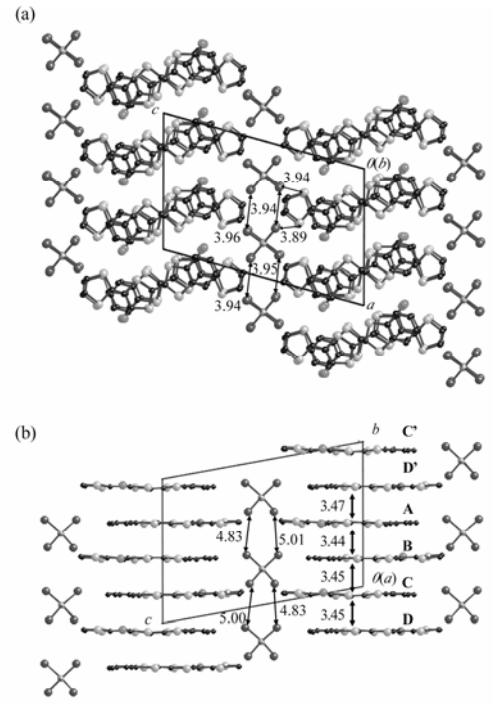

Fig. 1 Projections of the crystal structure of **4**$_2$•FeBr$_4$ at 90 K along the (a) *ac*- and (b) *bc*-planes.

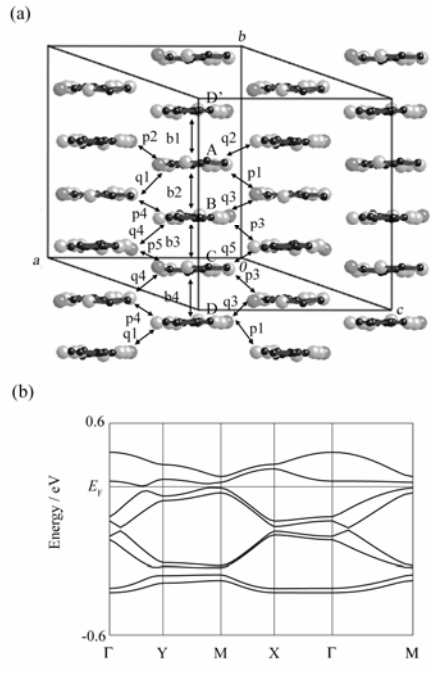

Fig. 2 (a) Donor array in the *ab*-conduction plane and overlap integrals ($\times 10^{-3}$) between neighboring donor molecules in $\mathbf{4}_2$•$FeBr_4$ at 90 K: q1 = 2.56, q2 = 0.78, q3 = –3.47, q4 = –1.21, q5 = 0.63, p1 = 2.64, p2 = 3.99, p3 = –1.72, p4 = –0.38, p5 = 1.77, b1 = –21.7, b2 = 17.5, b3 = 13.8 and b4 = –17.9. (b) Band dispersion of $\mathbf{4}_2$•$FeBr_4$ at 90 K.