Zwitterionic π-radical involving EDT-TTF-Imidazole and F_4TCNQ: Redox properties and self-assembled structure by hydrogen-bonds and multiple S···S interactions

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General Information

^{1}H NMR spectra were recorded at 270 MHz, with $CDCl_3$ or DMSO-d_6 as solvent and Me_4Si as an internal standard. Elemental analyses were performed at the Graduate School of Science, Osaka University. EI-Mass spectra were taken at 70 eV by using a Shimadzu QP-5000 mass spectrometer. Infrared spectra were measured on a JASCO FT/IR-660M using KBr plates, and electronic spectra were measured on a Shimadzu UV/Vis-NIR scanning spectrophotometer UV-3100 PC using KBr pellets or THF solution (2×10^{-4} M), respectively. Melting points were measured with a hot-stage apparatus and are uncorrected. ESR measurements of **1** were carried out in a DME solution (6×10^{-4} M) at 300 K and in a powder sample at 298 K on a Bruker E-500 ESR spectrometer. The magnetic susceptibility measurement was performed for the powder sample of **1** on a Quantum Design SQUID magnetometer MPMS-XL with an applied field of 0.1 T in the temperature range of 1.9–298K. The direct current electrical-conductivity measurement of **1** was made on compressed pellets of the powder sample by the conventional two-probe method, using gold paint and gold wire. Electrochemical measurements were made for the powder sample of **1** with an ALS Electrochemical Analyzer Model 612A and were recorded with 3 mm diameter glassy plate carbon and Pt wire counter electrodes in dry DMF (obtained by distillation over CaH_2 under reduced pressure) containing 0.1 M $(Et_4N^+)(ClO_4^-)$ as a supporting electrolyte at room temperature. The experiments employed a $Ag/AgNO_3$ in MeCN reference electrode, and the final results were calibrated with the ferrocene/ferrocenium couple. The concentration of the solution for CV measurement was not determined. X-ray crystallographic measurement was made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71070 Å) at 150 K. Structure was determined by the direct method using SIR-92 and refined by full-matrix least squares on F^2. Non-hydrogen atoms except for C28, C29, C30, C31, and O1 (THF solvent) were refined anisotropically, and all hydrogen atoms were included but not refined.

R_f values on TLC were recorded on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. The plates were sprayed with a solution of 10% phosphomolybdic acid in 95% EtOH and then heated until the spots became clearly visible. Silica gel 60 (100–200 mesh) was used for column chromatography. Recycle preparative gel permeation chromatography (GPC) was performed using tandemly connected two polystyrene gel columns (JAIGEL 1H, Japan Analytical Industry) with $CHCl_3$ as eluant. F_4TCNQ was purchased and purified by sublimation. Ethylenedithio-TTF[1] and $Pd(PPh_3)_4$[2] were prepared according to literature procedure. Solvents were dried (drying agent in parenthesis) and distilled under argon prior to use: THF and DME (Na-benzophenone ketyl); toluene (CaH_2). All reactions requiring anhydrous conditions were conducted under argon atmosphere.

[1] (a) T. K. Hansen, J. Becher, T. Jorgensen, K. S. Varma, R. Khedekar and M. P. Cava, *Org. Synth.*, 1996, **73**, 270. (b) A. J. Moore and M. R. Bryce, *Synthesis*, **1991**, 26. (c) M. Fourmigué, F. C. Krebs and J. Larsen, *Synthesis*, **1993**, 509. (d) A. J. Moore and M. R. Bryce, *Synthesis*, **1997**, 407.

[2] D. R. Coulson, *Inorg. Synth.*, 1971, **13**, 121.

1-(*p*-Toluenesulfonyl)-2-iodoimidazole (2). Tosyl-protected imidazole (8.56 g, 38.5 mmol) was placed in a 500-mL Schlenk tube and dissolved with THF (170 mL). To this mixture was added *n*-BuLi (1.6 M hexane solution, 29.0 mL, 46.4 mmol) at –78 °C, and the reaction mixture was stirred at this temperature for 1 h. I_2 (9.87 g, 38.9 mmol) was added to this mixture at one portion at –78 °C, and the reaction mixture was stirred at this temperature for 1 h. After addition of a satd $Na_2S_2O_3$ aqueous solution (200 mL), the resulting mixture was extracted with ethyl acetate (300 mL). The organic layer was washed with a satd NaCl aqueous solution (150 mL × 3) and dried over Na_2SO_4, then filtered and concentrated under reduced pressure. The residual solid was subjected to silica gel column chromatography with a 5:1–3:1 mixture of hexane and ethyl acetate as eluant, to give **2** (5.62 g, 42%) as a pale yellow powder.

mp 140–141 °C; TLC R_f 0.60 (1:3 hexane/ethyl acetate); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.50 (s, 3), 7.05 (d, 1, J = 1.8 Hz), 7.37 (d, 2, J = 8.4 Hz), 7.66 (d, 1, J = 1.6 Hz), 7.90 (d, 2, J = 8.4 Hz); IR (KBr) 3150, 3117, 2922, 1595, 1404, 1381, 1156 cm^{-1}; EI-MS, *m/z* 348 (M^+, 20%), 155 (M^+–$C_3H_2IN_2$, 100%); Anal. Calcd for $C_{10}H_9IN_2O_2S$: C, 34.50; H, 2.61; N, 8.05%. Found: C, 34.52; H, 2.48; N, 8.13%.

2-{4′-[1′′-(*p*-Toluenesulfonyl)imidazol-2′′-yl]-1′,3′-dithiol-2′-ylidene}-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin (3). EDT-TTF (2.01 g, 6.82 mmol) was placed in a 500-mL Schlenk tube and dissolved with THF (200 mL). To this mixture, *n*-BuLi (1.6 M hexane solution, 4.60 mL, 7.36 mmol) was added at –78 °C dropwise for 1 h. Bu_3SnCl (2.20 mL, 7.71 mmol) was added to this mixture, and the reaction mixture was gradually warmed up to room temperature over 1 h. After being poured into pH 7.0 0.1 M phosphate buffer solution (100 mL), the resulting mixture was extracted with ethyl acetate (100 mL × 3). The organic extract was dried over Na_2SO_4, then filtered and concentrated under reduced pressure. The residual oil was dried *in vacuo* at room temperature, to give Bu_3Sn-substituted EDT-TTF (4.89 g) as a vivid reddish orange oil. **2** (2.40 g, 6.89 mmol), Bu_3Sn-substituted EDT-TTF (4.89 g), and $Pd(PPh_3)_4$ (4.09 g, 3.49 mmol) were placed in a 500-mL Schlenk tube and dissolved with toluene (200 mL), and the mixture was degassed by Ar bubbling. To this mixture CuI (141 mg, 0.74 mmol) was added at 100 °C, and the reaction mixture was stirred at the temperature for 18 h. After being cooled to room temperature, the reaction mixture was poured into a satd NaCl aqueous solution (100 mL) and extracted with toluene (100 mL × 3). The organic layer was washed with a 10% ethylenediamine aqueous solution (100 mL × 3) and a satd NaCl aqueous solution (100 mL × 3), and dried over Na_2SO_4, then filtered and concentrated under reduced pressure. The residual oil was subjected to silica gel column chromatography with 20:1–1:3 mixture of hexane and ethyl acetate as eluant. The resulting mixture containing desired compound was subjected to GPC with $CHCl_3$ as eluant. The residual was reprecipitated by THF–hexane, to give **3** (473 mg, 14%) as an orange powder.

mp 156–157 °C; TLC R_f 0.53 (1:1 hexane/ethyl acetate); ^{1}H NMR (DMSO-d_6, rt) δ 2.40 (s, 3), 3.40 (s, 4), 7.21 (d, 1, J = 1.6 Hz), 7.47 (d, 2, J = 8.2 Hz), 7.48 (s, 1), 7.80 (d, 2, J = 8.2 Hz), 7.91 (d, 1, J = 1.6 Hz); IR (KBr) 3154, 3103, 2921, 1583, 1371, 1152 cm^{-1}; EI-MS *m*/*z* 514 (M^+, 88%), 236 ($M^+-C_{12}H_{12}N_2O_2S_2$, 100%); Anal. Calcd for $C_{18}H_{14}N_2O_2S_7$: C, 42.00; H, 2.74; N, 5.44%. Found: C, 42.32; H, 2.82; N, 5.37%.

2-{4′-(Imidazol-2′′-yl)-1′,3′-dithiol-2′-ylidene}-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin (EDT-TTF-Im). **3** (496 mg, 0.96 mmol) was dissolved with CH_2Cl_2 (45 mL) and MeOH (90 mL) in a 200-mL round bottomed flask. To this mixture was added KOH (14 M aqueous solution, 15 mL, 210 mmol) at room temperature, and the reaction mixture was stirred at this temperature for 2 h. The reaction mixture was neutralized with 2 M HCl aqueous solution, then concentrated under reduced pressure to remove CH_2Cl_2 and MeOH. The residual precipitate was collected by filtration and washed with water, to give EDT-TTF-Im (330 mg, 95%) as an orange powder.

mp 154–155 °C; TLC R_f 0.53 (1:3 hexane/ethyl acetate); ^{1}H NMR (DMSO-d_6, rt) δ 3.38 (s, 4), 6.94 (brs, 1), 7.14 (s, 1), 7.26 (brs, 1), 12.71 (brs, 1); IR (KBr) 3400–2200, 1594, 1528 cm^{-1}; UV (KBr) 310 nm; EI-MS *m*/*z* 360 (M$^+$, 15%), 124 (M$^+$–$C_6H_6S_5$, 100%); Anal. Calcd for $C_{11}H_8N_2S_6$: C, 36.64; H, 2.28; N, 7.77%. Found: C, 36.89; H, 2.28; N, 7.64%.

EDT-TTF-Im$^{\bullet+}$–F_4TCNQ$^-$ (1).

Diffusion method. EDT-TTF-Im (2.0 mg, 5.6 μmol) and F_4TCNQ (2.0 mg, 7.6 μmol) were placed at the bottom of each side of an H-shaped tube. Diffusion of them in a 10 mL of 5:1 mixture of MeCN and THF at room temperature for 2 months afforded deep green crystals of **1** suitable for X-ray analysis. Due to the highly efflorescence and hygroscopic nature, the elemental analysis did not give the appropriate value.

IR (KBr) 3200–2800, 2185, 2144, 1646, 1628, 1533, 1485 cm^{-1}; UV (KBr) 332, 444, 894 nm; UV (THF) 336, 390, 468, 866 nm; Anal. Calcd for $C_{23}H_7F_4N_6S_6$: C, 43.45; H, 1.11; N, 13.22%. Found: C, 43.53; H, 1.83; N, 13.01%.

Mixing method. EDT-TTF-Im (34.1 mg, 0.095 mmol) was dissolved with THF (5 mL) in a 100-mL round bottomed flask. A solution of F_4TCNQ (29.0 mg, 0.105 mmol) in MeCN (5 mL) was added to this mixture. The mixture was stirred at room temperature for 0.5 h. The resulting precipitate was collected by filtration, then washed with MeCN (3 mL × 3) to give the adduct **1** (29.9 mg, 56%) as a dark green powder. Due to the highly efflorescence and hygroscopic nature, the elemental analysis did not give the appropriate value.

mp 168–172 °C (dec.); IR (KBr) 3200–2800, 2184, 2146, 1645, 1627, 1532, 1483 cm^{-1}; UV (KBr) 334, 394, 464(sh), 886 nm; UV (THF) 286, 336, 416, 444, 864 nm; Anal. Calcd for $(C_{23}H_7F_4N_6S_6)(H_2O)_{1.7}$: C, 41.46; H, 1.57; N, 12.61%. Found: C, 41.42; H, 1.63; N, 12.61%.

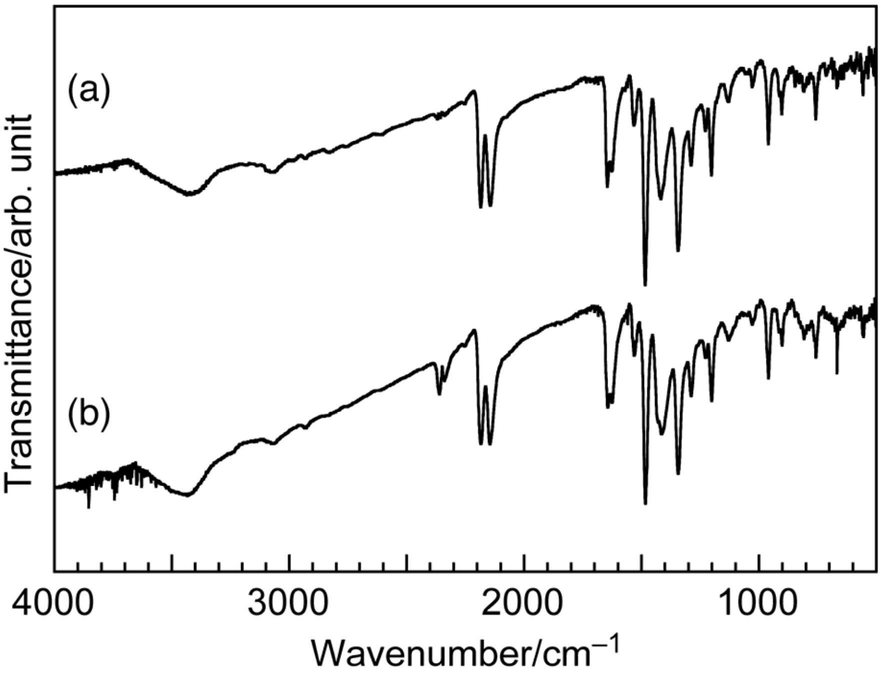


Figure S1. IR spectra of **1** in KBr pellets in the range of 4000–500 cm^{-1}. (a) Crystal sample and (b) powder sample. These IR spectra show identification of the two samples obtained by the diffusion method and by the mixing method.

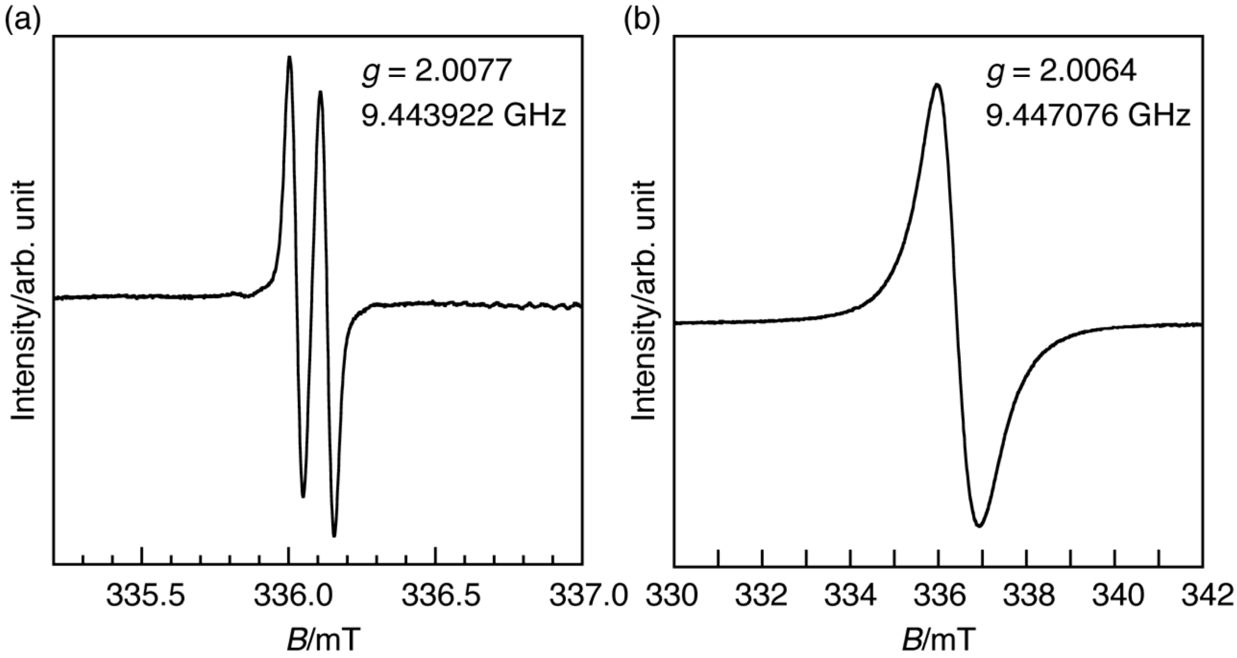


Figure S2. ESR spectra of **1** (a) in a DME solution (6×10^{-4} M) at 300 K and (b) in a powder sample at 298 K.

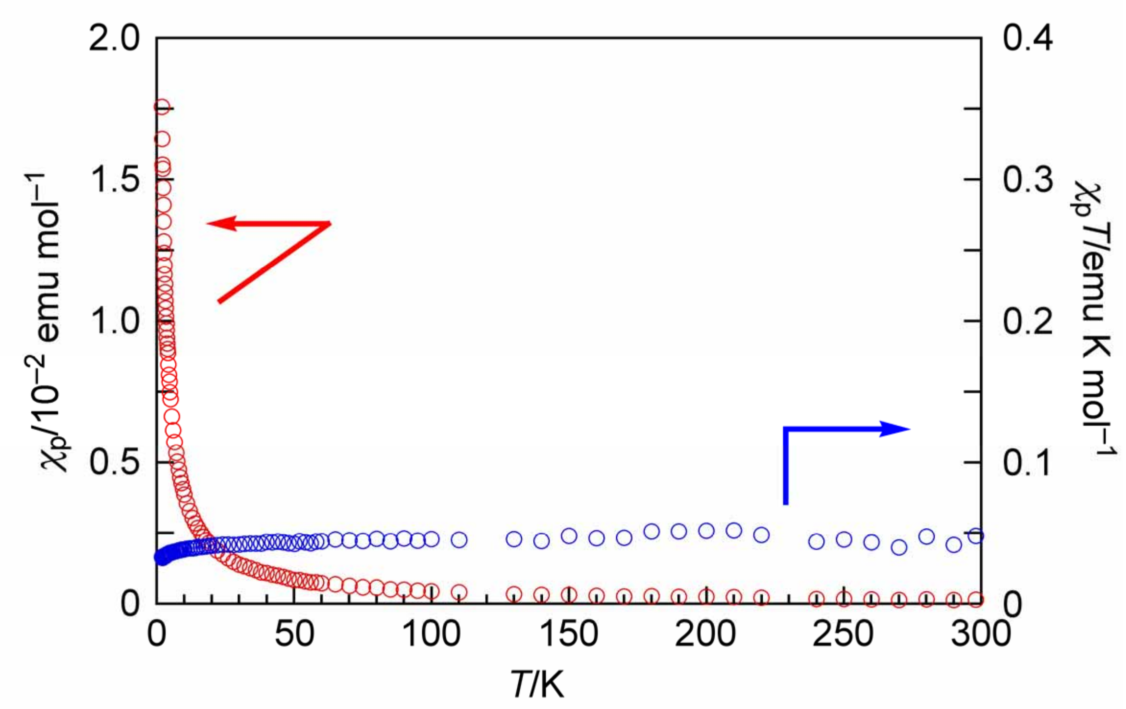


Figure S3. Temperature dependence of paramagnetic susceptibility (χ_p, red and χ_pT, blue) for the powder sample of **1**.

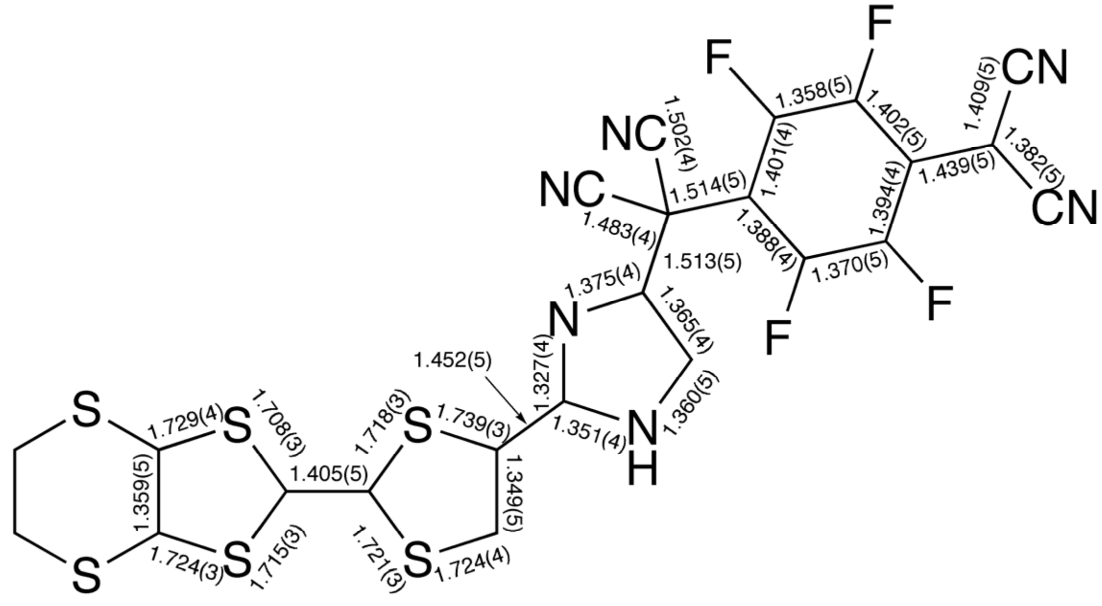
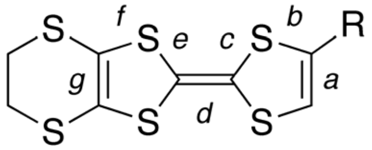


Figure S4. Intramolecular bond lengths (Å) of **1**.

Table S1. Intramolecular bond lengths of EDT-TTF and F_4TCNQ together with related compounds.

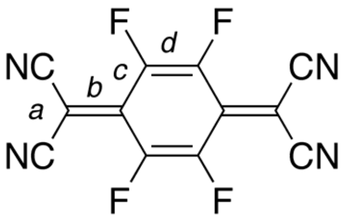


		a/Å	*b*/Å	*c*/Å	*d*/Å	*e*/Å	*f*/Å	*g*/Å
EDT-TTF-Im[3]		1.338(3)	1.767(2)	1.765(2)	1.347(3)	1.751(2)	1.767(2)	1.341(3)
			1.731(2)	1.764(2)		1.763(2)	1.765(2)	
EDT-TTF[4]		1.317(6)	1.743(4)	1.756(4)	1.335(4)	1.759(3)	1.757(3)	1.339(7)
(EDT-TTF$^{\bullet+}$)(I_3^-)[5]	I	1.34(1)	1.724(9)	1.719(8)	1.40(1)	1.712(8)	1.743(7)	1.34(1)
			1.718(9)	1.717(8)		1.715(8)	1.744(7)	
	II	1.33(1)	1.721(6)	1.721(6)	1.397(8)	1.728(5)	1.716(5)	1.359(8)
			1.712(6)	1.716(6)		1.721(6)	1.721(6)	

[3] T. Murata, Y. Morita, Y. Nishimura, Y. Yakiyama and K. Nakasuji, in *Multifunctional Conducting Molecular Materials*, ed. by G. Saito, F. Wudl, R. C. Haddon, K. Tanigaki, T. Enoki, H. E. Katz and M. Maesato, Royal Society of Chemistry, London, 2007, pp. 135–138.

[4] B. Garreau, D. De Montauzon, P. Cassoux, J.-P. Legros, J.-M. Fabre, K. Saoud and S. Chakroune, *New J. Chem.*, 1995, **19**, 161.

[5] A. Hountas, A. Terzis, G. C. Papavassiliou, B. Hilti and J. Pfeiffer, *Acta Crystallogr., Sect. C,* 1990, **46**, 220.



	a/Å	*b*/Å	*c*/Å	*d*/Å
F_4TCNQ[6]	1.435(2), 1.439(2)	1.372(2)	1.436(2), 1.438(2)	1.334(2)
(Bu_4N^+)(F_4TCNQ$^{\bullet-}$)[7]	1.426, 1.425	1.418, 1.418	1.415, 1.416	1.357, 1.357
	1.425, 1.426		1.418, 1.419	

[6] T. J. Emge, M. Maxfield, D. O. Cowan and T. J. Kistenmacher, *Mol. Cryst. Liq. Cryst.*, 1981, **65**, 161.

[7] S. A. O'Kane, R. Clérac, H. Zhao, X. Ouyang, J. R. Galán-Mascarós, R. Heintz and K. R. Dunbar,

J. Solid State Chem., 2000, **152**, 159.

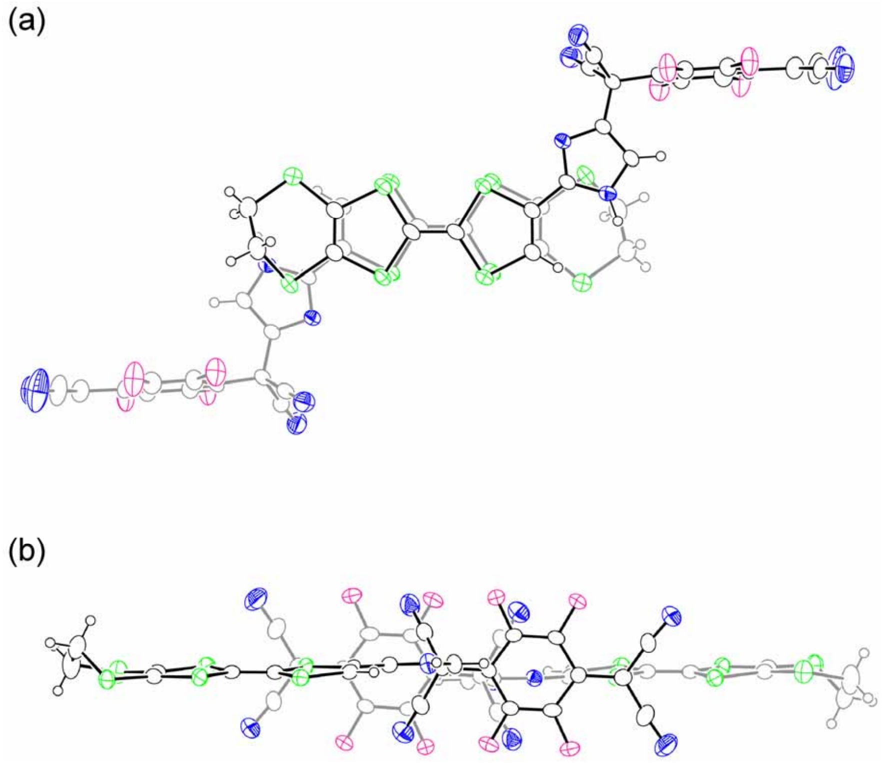


Figure S5. Overlap patterns in the crystal structure of **1**. (a) Face-to-face dimer of EDT-TTF$^{\bullet+}$ moiety. (b) Overlapping at F$_4$TCNQ$^-$ moiety.