

Supplementary Information for

An Organic Superconductor, (TEA)(HEDO-TTF-dc)₂·2(H₂C₂O₄), Coupled with Strong Hydrogen-Bonding Interactions

Yuto Morimachi,^{‡a} Mizuki Urai,^{‡b} Ryota Nakajima,^{ac} Hajime Kamebuchi,^a Kazuya Miyagawa,^b Kazushi Kanoda,^{*b} and Biao Zhou^{*a}

^a Department of Chemistry, College of Humanities and Sciences, Nihon University, Sakurajosui 3-25-40 Setagaya-Ku, Tokyo 156-8550, Japan. Email: zhou.biao@nihon-u.ac.jp

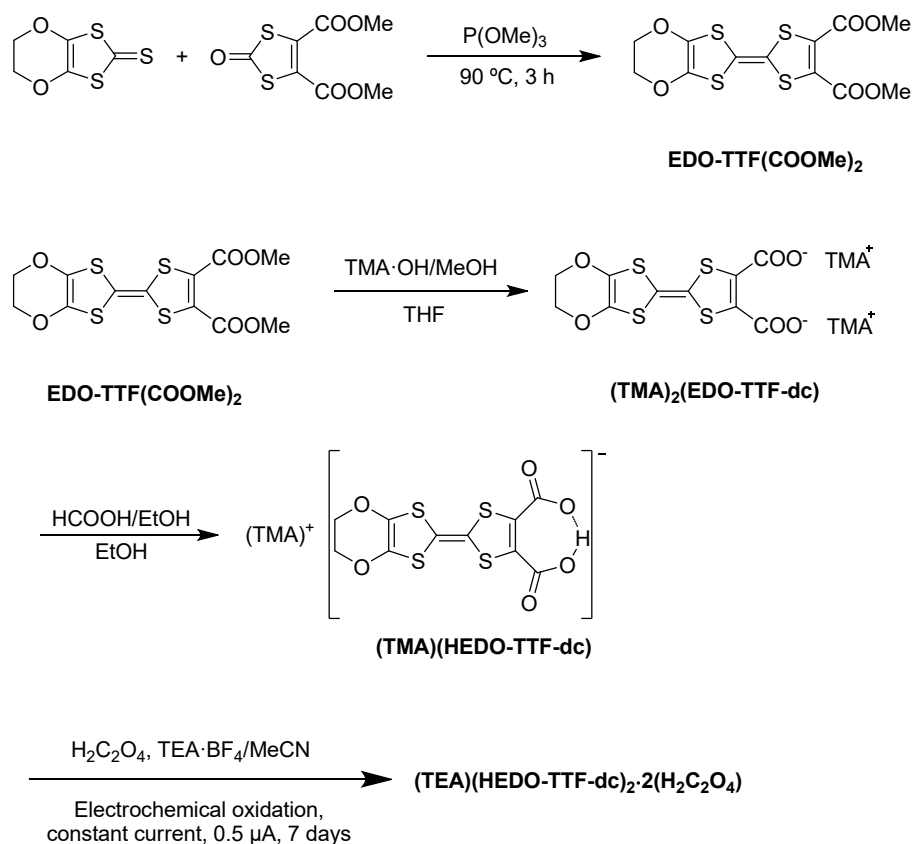
^b Department of Applied Physics, The University of Tokyo, Hongo 7-3-1 Bunkyo-ku, Tokyo 113-8656, Japan. Email: kanoda@ap.t.u-tokyo.ac.jp

^c Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan.

[‡] These authors contributed equally to this work.

Experimental detail

Scheme of synthesis



Synthesis of $EDO-TTF(COOMe)_2$

$EDO-TTF(COOMe)_2$ was synthesized by a coupling reaction with $C_5H_4O_2S_3$ (5,6-Dihydro-1,3-dithiolo[4,5-b][1,4]dioxin-2-thione) and $C_7H_6O_5S_2$ (4,5-Dimethyl 2-oxo-1,3-dithiole-4,5-dicarboxylate), using a method similar to that reported in reference 1-4.

1. R. R. Schumaker and E. M. Engler, *Journal of the American Chemical Society*, 1980, **102**, 6651-6652.
2. T. Mori, H. Inokuchi, A. M. Kini and J. M. Williams, *Chemistry Letters*, 1990, **19**, 1279-1282.
3. P. Blanchard, M. Sallé, G. Duguay, M. Jubault and A. Gorgues, *Tetrahedron Letters*, 1992, **33**, 2685-2688.
4. H.-H. Lin, Z.-M. Yan, J. Dai, D.-Q. Zhang, J.-L. Zuo, Q.-Y. Zhu and D.-X. Jia, *New Journal of Chemistry*, 2005, **29**, 509-513.

Synthesis of (TMA)₂(EDO-TTF-dc)

EDO-TTF(COOMe)₂ (98mg, 0.26 mmol) was hydrolyzed with a 25 wt% MeOH solution of TMA·OH (TMA = tetramethylammonium) (362 mg; 1.0 mmol) in THF (tetrahydrofuran) at room temperature. The solution was stirred for 10 min, and an orange precipitate was obtained as the reaction proceeded. The precipitate was collected by filtration and washed with THF and dried in vacuo as dianionic species (TMA)₂(EDO-TTF-dc).

Synthesis of (TMA)(HEDO-TTF-dc)

Dark-red rod-shaped crystals of monoanionic species (TMA)(HEDO-TTF-dc) were obtained by vapor diffusion method from an ethanol of (TMA)₂(EDO-TTF-dc) with an ethanol solution of formic acid. (yield 63 mg, 57% based on EDO-TTF(COOMe)₂)

Electrochemical Synthesis of (TEA)(HEDO-TTF-dc)₂·2(H₂C₂O₄) (**1**)

A mixture of (TMA)(HEDO-TTF-dc) (10 mg, 0.024 mmol), TEA·BF₄ (TEA = tetraethylammonium) (100 mg, 0.46 mmol) and anhydrous oxalic acid (20 mg, 0.22 mmol) were weighed into an H-shaped glass cells containing Pt electrodes and dissolved in dehydrated acetonitrile (20.0 mL). When a constant current of 0.5 μA was applied at room temperature, black plate-like crystals of **1** were obtained on the platinum anode over approximately one week.

Crystal Structure Determinations

The single-crystal X-ray diffraction data for **1** and (TMA)(HEDO-TTF-dc) were collected on a Rigaku Micro7HFM-VariMax Saturn 724R CCD system equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a confocal X-ray mirror. The crystal structures were solved using direct methods (SHELXT) [5] and refined by full-matrix least-squares (SHELXL) [6] under the Olex2 graphical interface [7]. Anisotropic temperature factors were applied for the non-hydrogen atoms. The calculated positions of the hydrogen atoms were not refined but included in the final calculations. The finally reported crystal structures are refined by crystallography reviewer.

5. G. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112-122.
6. G. Sheldrick, *Acta Crystallographica Section C*, 2015, **71**, 3-8.
7. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Journal of Applied Crystallography*, 2009, **42**, 339-341.

First-principles DFT calculations

Molecular orbital (MO), band structure, and density of state (DOS) calculations were performed by density functional theory (DFT) and the general gradient approximation (GGA) method using the DMol³ module [8,9] as implemented in Materials Studio v5.5 (Accelrys, San Diego, CA, USA).

Becke-Lee-Yang-Parr (BLYP) functional [10] and double numeric plus polarization (DNP) basis set were used in the calculations.

8. B. Delley, *The Journal of Chemical Physics*, 1990, **92**, 508-517.
9. B. Delley, *The Journal of Chemical Physics*, 2000, **113**, 7756-7764.
10. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865-3868.

Magnetic Susceptibility Measurements

The *dc* magnetic susceptibility measurements of **1** (5.74 mg; 5.69×10^{-3} mmol) were performed by a Quantum Design MPMS-7XL SQUID magnetometer in the temperature range from 1.8 to 300 K. The samples were wrapped with a clean aluminum foil whose magnetic susceptibility was separately measured and subtracted. The diamagnetic contribution was calculated from Pascal's constants ($\chi_{\text{dia}} = -3.9 \times 10^{-4}$ emu·mol⁻¹). The *ac* magnetic susceptibility measurements were performed on a Quantum Design MPMS-5S using a polycrystalline sample with a mass of 1.302 mg (1.29×10^{-3} mmol). The frequency of the *ac* magnetic field was 10 Hz with amplitudes of 0.01 and 0.1 Oe, and the static magnetic field was set to zero.

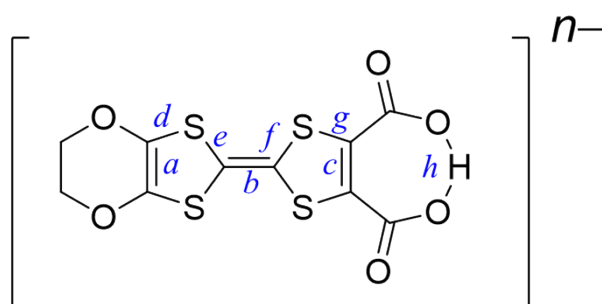
Electrical Resistivity Measurements

Electrical resistivity measurements were performed on single crystal of **1**, along an arbitrary direction within the *bc*-plane in the 1.9–300 K temperature range using the conventional four-probe method at ambient pressure by use of a KEITHLEY 2400 source meter and a KEITHLEY 2182 nanovoltmeter. Annealed gold wires (15 μm in diameter) bonded to a single crystal by carbon paint were used as leads.

Table S1. X-ray Crystallographic Data of 1 and (TMA)(HEDO-TTF-dc)

	1	(TMA)(HEDO-TTF-dc)
CCDC No.	2196210	219621
Empirical Formula	C ₁₆ H ₁₇ N _{0.5} O ₁₀ S ₄	C ₁₄ H ₁₇ NO ₆ S ₄
Formula Weight	504.54	423.52
Temperature (K)	223	173
Crystal System	monoclinic	orthorhombic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Lattice Parameters		
<i>a</i> (Å)	22.5852(5)	6.8601(2)
<i>b</i>	12.2019(3)	13.4801(4)
<i>c</i>	7.3075(2)	19.2445(5)
<i>α</i> (°)	90	90
<i>β</i>	99.150(2)	90
<i>γ</i>	90	90
<i>V</i> (Å ³)	1988.19(9)	1779.63(9)
Z value	4	4
<i>D</i> _{calc} (g/cm ³)	1.686	1.581
<i>μ</i> (Mo Kα) (mm ⁻¹)	0.533	0.565
Diffractometer	Rigaku Saturn724	
Radiation	Mo Kα (λ = 0.71073 Å)	
No. of Reflections Measured		
Total	33387	15035
Unique	4923	3630
No. Observations (I>2σ)	4133	3358
No. Variables	331	286
R _{int}	0.0270	0.0496
Residuals: <i>R</i> ₁ (I>2σ)	0.0292	0.0293
Residuals: <i>wR</i> ₂ (I>2σ)	0.0757	0.0718
Goodness-of-fit on F ²	1.007	1.032
Largest diff. peak/hole (e/Å ³)	0.341/-0.205	0.300/-0.190

Table S2. The change in bond lengths of HEDO-TTF-dc anion donor of 1 and (TMA)(HEDO-TTF-dc)



		1	(TMA)(HEDO-TTF-dc)	
		($n = 0.5$)	($n = 1$)	δ (Å)
$d_{(C=C)}$ (Å)	<i>a</i>	1.348(2)	1.323(4)	0.025
	<i>b</i>	1.369(2)	1.343(3)	0.026
	<i>c</i>	1.358(2)	1.348(4)	0.010
$d_{(C-S)}$ (Å)	<i>d</i>	1.735(1)/1.740(1)	1.751(3)/1.753(3)	-0.014(avg.)
	<i>e</i>	1.737(1)/1.738(1)	1.760(2)/1.762(2)	-0.023(avg.)
	<i>f</i>	1.737(1)/1.739(1)	1.752(2)/1.754(2)	-0.015(avg.)
	<i>g</i>	1.737(1)/1.742(1)	1.745(3)/1.745(3)	-0.005(avg.)
$d_{(O\cdots H\cdots O)}$ (Å)	<i>h</i>	2.423	2.415	0.008

Figure S1. TEA cation is disordered from tetrahedral to cube geometry.

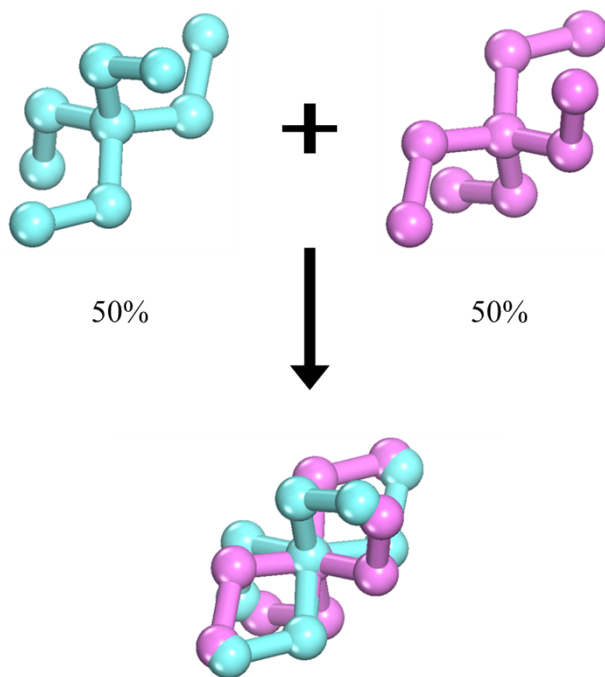


Figure S1. TEA cation is disordered from tetrahedral to cubic geometry at the lattice site.

Figure S2. HOMO of HEDO-TTF-dc anion.

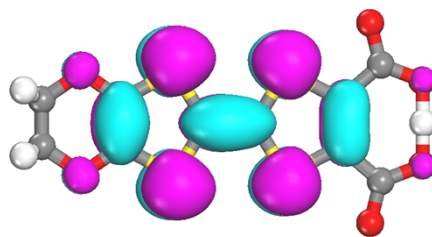


Figure S2. HOMO (the highest occupied molecular orbital) of HEDO-TTF-dc anion, which is very similar to those of reported TTF-type donor.

Figure S3. The band energy dispersion surface.

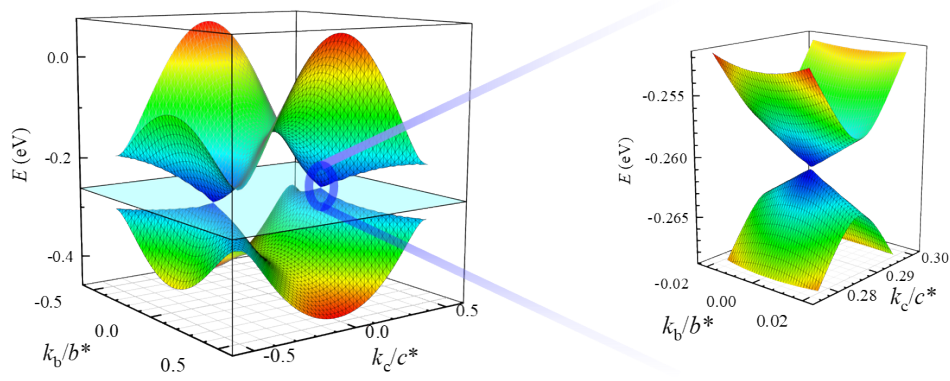


Figure S3. The band energy dispersion surface of the second and the third band of **1** in the first Brillouin zone, where $k_a = 0$. A pair of cone-like dispersions (Dirac cones) appear with the apexes of $(b^*, c^*) = (0, \pm 0.288)$ on the b^* - c^* plane.