

The Synthesis of Difluoro and Dimethyl Derivatives of 2,6-Bis(dicyanomethylene)-2,6-dihydro-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophen-4-one (CPDT-TCNQ) and the Conducting Properties of the Metallic Salts Based on the Dimethyl Derivative

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In order to investigate how the sheet-like network along the side-by-side direction constructed by the strong inter-column S...N and O...H atom–atom contacts influences the stability of the metallic state of novel one-dimensional metallic anion radical salts of 2,6-bis(dicyanomethylene)-2,6-dihydro-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (CPDT-TCNQ), the 3,5-difluoro (F₂CPDT-TCNQ) and 3,5-dimethyl (Me₂CPDT-TCNQ) derivatives of CPDT-TCNQ, not possessing hydrogen atoms at the 3,5-positions to construct the inter-column O...H contacts, have been synthesized. The anion radical salts, Me₄X(Me₂CPDT-TCNQ)₂ (X = P and As), showed a metallic temperature dependence of the resistivity from room temperature down to around 240 K and 200 K, respectively, whereas Me₄X(Me₂CPDT-TCNQ)₂ (X = N and Sb) were semiconducting. The metal–insulator transition temperatures (*T*_{MI}) of Me₄X(Me₂CPDT-TCNQ)₂ (X = P and As) are significantly higher than those of MX₄(CPDT-TCNQ)₂ (X = P and As). Moreover, the extent of destabilization of the metallic state is much more significant in Me₄N(Me₂CPDT-TCNQ)₂, since MeN₄(CPDT-TCNQ)₂ is metallic down to 130 K. Although electric conduction can not occur along the side-by-side direction in either salt of CPDT-TCNQ and Me₂CPDT-TCNQ, these facts suggest that the two-dimensional sheet-like molecular network along the *a*-axis may contribute to stabilize the one-dimensional metallic states of the anion radical salts of CPDT-TCNQ.

Since the discovery of one-dimensional metallic behavior of the tetracyano-*p*-quinodimethane (TCNQ)-tetrathiafulvalene (TTF) complex,¹ a great deal of investigation has been devoted towards the synthesis of a variety of π -acceptors and π -donors with the aim of developing novel organic molecular metals or organic superconductors. However, the investigations on the molecular design and synthesis of π -acceptor molecules for organic conductors have been almost limited to those concerning TCNQ, *N,N'*-dicyano-*p*-quinone diimine (DCNQI) and M(dmit)₂ (dmit = 1,3-dithiole-2-thioxo-4,5-dithiolato) families.^{2–4} In recent years, oligothiophene-TCNQs⁵ were synthesized to decrease on-site Coulomb repulsion in the dianion state and were expected to increase intermolecular interactions by means of S...S contacts of the thiophene rings. However, unfortunately, the oligothiophene-TCNQs do not easily form metallic conducting complexes and their electron-accepting abilities are relatively low. On the other hand, heterophene-extended [3]radialene type acceptors gave single crystalline charge-transfer (CT) complexes with tetrathiafulvalene (TTF) and with tetrathiatetracene (TTT) showing metallic properties in which the conducting carrier of the TTF complex was proven to be electrons.⁶ It has also been reported that the dibromo derivative of the thieno[3,2-*b*]thienoquinonoid isologue of *N,N'*-dicyanoquinone diimine (DCNQI) formed a metallic CT complex with TTF.⁷

In 1998, we reported successful synthesis of a novel heterophene-TCNQ type acceptor, namely, 2,6-bis(dicyanomethyl-

ene)-2,6-dihydro-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (CPDT-TCNQ: **1**)⁸ incorporating three electron-accepting groups in one molecule. CPDT-TCNQ has a fairly high electron-accepting ability (*E*₁^{red} = +0.04 V vs SCE in CH₂Cl₂) and was reduced in three reversible one-electron transfer steps to the trianion radical state. The single crystalline anion radical salts of CPDT-TCNQ, namely, Me₄X(CPDT-TCNQ)₂ (X = N, P, and As) exhibited the metallic temperature dependence of the resistivity. In the crystal structures of the three anion radical salts which are isostructural compounds, CPDT-TCNQ molecules stack along the *b*-axis dimerizing weakly in the stacking columns, as shown in Fig. 1(a). The acceptor columns are strongly connected along the side-by-side direction by the four S...N (3.04–2.97 Å) and two O...H (3.25–3.28 Å) atom–atom contacts (Fig. 1(b)), constructing a sheet-like molecular network along the *a*-axis. However, these salts have an extremely one-dimensional metallic electronic structure along the stacking *b*-axis, because the π -electron densities on the peripheral S and O atoms in the LUMO (lowest unoccupied molecular orbital) of the CPDT-TCNQ molecule are very low. In this case, electrical conduction can not occur along the *a*-axis. The one-dimensional metallic salts showed second order type metal–insulator (MI) transitions under ambient pressure at 130, 165, and 185 K accompanied by the superlattice formation of (a, 2b, c), (2a, b, c), and (2a, b, c) for the Me₄N, Me₄P, and Me₄As salts, respectively.⁹ Thus the origins of the metal–insulator transitions have been considered to be the 2*k*_F CDW for the Me₄N

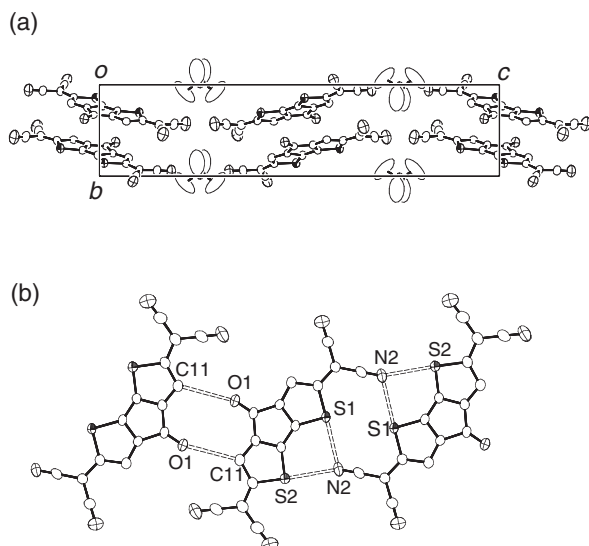


Fig. 1. Crystal structures of $\text{Me}_4\text{N}(\text{CPDT-TCNQ})_2$: (a) projection onto the bc -plane and (b) side-by-side hetero atom contacts among the CPDT-TCNQ molecules.

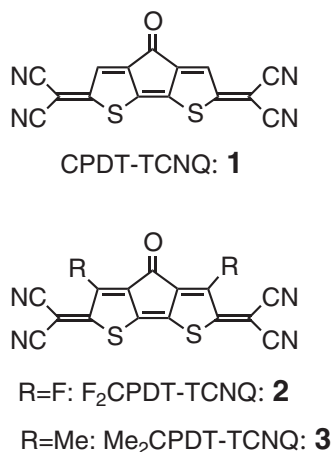


Chart 1. Chemical structural formulas of CPDT-TCNQ, $\text{F}_2\text{CPDT-TCNQ}$, and $\text{Me}_2\text{CPDT-TCNQ}$.

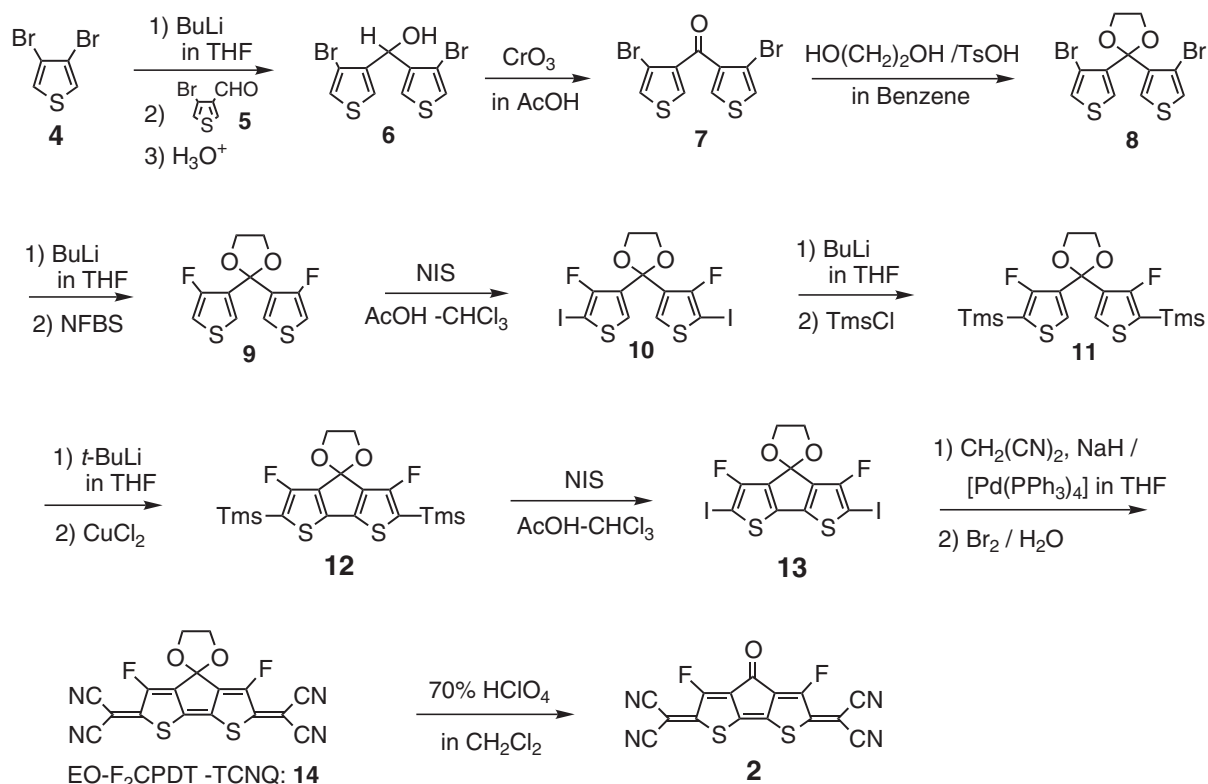
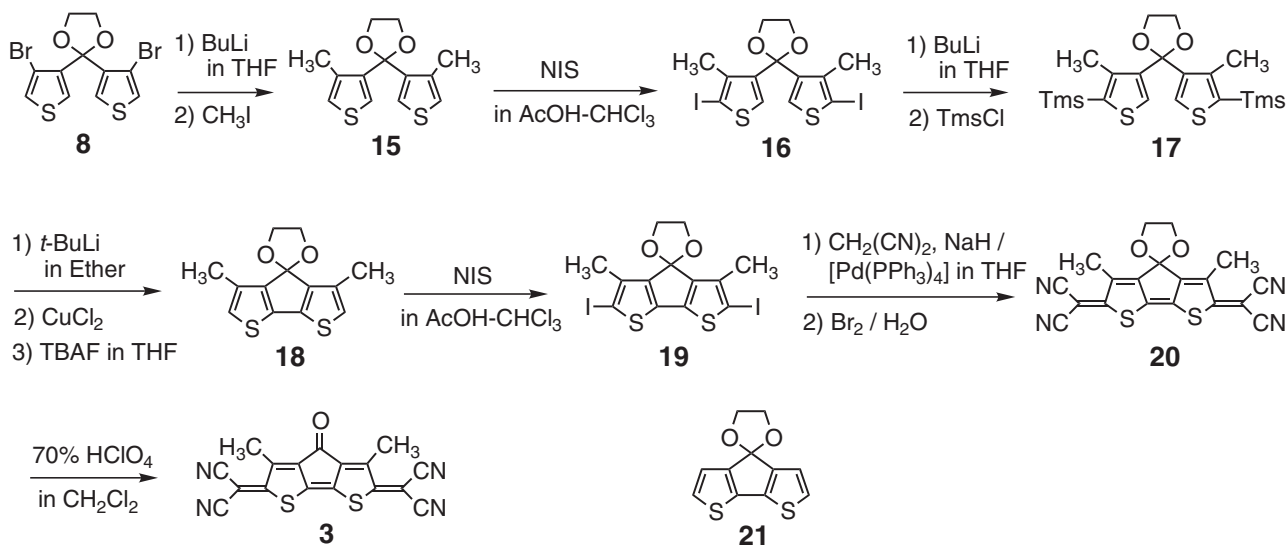
salt, and the $4k_{\text{F}}$ CDW for the Me_4P and Me_4As salts. Although the electrical conduction can not occur along the a -axis, the crystal structure consisting of strong intercolumn $\text{S}\cdots\text{N}$ and $\text{O}\cdots\text{H}$ atom-atom contacts along the a -axis can influence the stability of the one-dimensional metallic state and influence the MI transition temperature of the anion radical salts of CPDT-TCNQ. Therefore, examination into the electric conducting behavior of the anion radical salts of the 3,5-disubstituted derivatives of CPDT-TCNQ appears to be very helpful in evaluating the effect of the structural two-dimensional sheet-like network on the stability of the one-dimensional metallic state of these salts, since the anion radical salts of 3,5-disubstituted CPDT-TCNQs can not construct the sheet-like network along the a -axis due to the lack of the inter-column $\text{O}\cdots\text{H}$ contacts. To this end, we have now synthesized the 3,5-difluoro and 3,5-dimethyl derivatives of CPDT-TCNQ, namely, ($\text{F}_2\text{CPDT-TCNQ}$: **2**) and ($\text{Me}_2\text{CPDT-TCNQ}$: **3**), respectively (Chart 1), and clarified the conducting properties of the anion

radical salts of $\text{Me}_2\text{CPDT-TCNQ}$. The substitutional effects of the fluorine and methyl groups on the electron-accepting ability of the new acceptors, $\text{F}_2\text{CPDT-TCNQ}$ and $\text{Me}_2\text{CPDT-TCNQ}$ are also revealed.

Results and Discussion

Synthesis. $\text{F}_2\text{CPDT-TCNQ}$ (**2**) was synthesized through the route depicted in Scheme 1. 3,4-Dibromothiophene (**4**) was first mono-lithiated with butyllithium at -78°C and then allowed to react with 4-bromo-3-thiophenecarbaldehyde (**5**)¹⁰ to give the methanol **6** in 70% yield. The ketone **7**, prepared from **6** by oxidation with chromium trioxide in acetic acid, was allowed to react with ethylene glycol in the presence of a catalytic amount of p -toluenesulfonic acid in benzene to produce the 4,4'-dibromo ketal **8** in 98% yield. The 4,4'-difluoro ketal **9** was prepared by dilithiation of **8** with butyllithium at -78°C in THF and subsequent fluorination of the resulting dilithio derivative with N -fluorobenzenesulfonimide (NFBS) in 49% yield. Iodination of **9** with N -iodosuccinimide (NIS) occurred selectively at the α -positions of the fluorine atoms giving the 5,5'-diiodo derivative **10** in 89% yield. Then, the compound **10** was dilithiated with butyllithium at -78°C , and the resulting 5,5'-dilithio derivative was submitted to the reaction with trimethylsilyl chloride (TmsCl) to give the 5,5'-bis(trimethylsilyl) derivative **11** in 69% yield. The desired cyclopentadithiophene derivative **12** was obtained by the intra-molecular Ullman coupling reaction of the 2,2'-dilithio derivative of **11**, generated by dilithiation of **11** with t -butyllithium at -78°C , with CuCl_2 in THF. Treatment of **12** with NIS in a mixture of acetic acid and chloroform (1:1, v/v) at room temperature afforded the 2,6-diiodo derivative **13** in 91% yield. The compound **13** was then allowed to react with sodium dicyanomethanide, prepared in situ from malononitrile and sodium hydride, in refluxing THF containing a catalytic amount of tetrakis(triphenylphosphine)palladium [$\text{Pd}(\text{PPh}_3)_4$],¹¹ followed by oxidation with aqueous bromine to give 2,6-bis(dicyanomethylene)-4-ethylenedioxy-3,5-difluoro-2,6-dihydro-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (EO- $\text{F}_2\text{CPDT-TCNQ}$: **14**) in 68% yield. When **14** was treated with 70% perchloric acid in dichloromethane, $\text{F}_2\text{CPDT-TCNQ}$ (**2**) was obtained in 19% yield as a violet powder. $\text{F}_2\text{CPDT-TCNQ}$ is air-stable and much more soluble than CPDT-TCNQ (**1**) in polar organic solvents such as dichloromethane and acetonitrile.

$\text{Me}_2\text{CPDT-TCNQ}$ (**3**) was synthesized starting from the 4,4'-dibromo ketal **8** according to the route shown in Scheme 2. The dibromo ketal **8** was dilithiated with 2 molar amounts of butyllithium at -78°C in THF and then allowed to react with excess methyl iodide to give the 4,4'-dimethyl derivative **15** in 99% yield. Direct iodination of **15** was achieved by treatment with NIS at room temperature in a mixture of acetic acid and chloroform (1:1, v/v) to give the 5,5'-diiodo derivative **16** in 78% yield. The diiodo derivative **16** was first dilithiated with butyllithium at -78°C and then treated with trimethylsilyl chloride at -78°C to give **17** in 87% yield. The 2,2'-dilithio derivative of **17**, prepared by lithiation of **17** with t -butyllithium at -78°C , was allowed to react with CuCl_2 to produce the cyclopentadithiophene derivative, which was subsequently desilylated without purification with tetrabutylammonium fluoride (TBAF) in THF to give **18** in 79% yield. The 2,6-diiodo derivative **19**,

Scheme 1. Synthetic route of F₂CPDT-TCNQ: **2**.Scheme 2. Synthetic route of Me₂CPDT-TCNQ: **3**.

prepared by direct iodination of **18** with NIS, was allowed to react with sodium dicyanomethanide in the presence of a catalytic amount of [Pd(PPh₃)₄] in THF,¹¹ followed by oxidation with aqueous bromine to give 2,6-bis(dicyanomethylene)-4-ethylenedioxy-3,5-dimethyl-2,6-dihydro-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (EO-Me₂CPDT-TCNQ: **20**) in 46% yield. Deketalation of **20** was subsequently carried out by a reaction with 70% perchloric acid in dichloromethane to give (Me₂CPDT-TCNQ) (**3**) as a violet powder in 84% yield. Me₂CPDT-TCNQ is stable in the solid state and soluble in

polar solvents such as dichloromethane, acetonitrile, THF, and acetone.

The attempted synthesis of F₂CPDT-TCNQ (**2**) and Me₂CPDT-TCNQ (**3**) starting from 4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**21**) was unsuccessful, since direct or indirect 3,5-difluorination and 3,5-dimethylation of the 2,6-dibromo or the 2,6-bis(trimethylsilyl) derivatives of **21** were unsuccessful.

Electronic Spectra and Redox Properties. The new acceptors, F₂CPDT-TCNQ (**2**) and Me₂CPDT-TCNQ (**3**) exhibit

two intense π - π^* absorption maxima in the visible region similar to the mother CPDT-TCNQ, as shown in Fig. 2. Both the first ($E_1 = 531$ nm ($\log \epsilon = 4.47$)) and the second ($E_2 = 500$ nm ($\log \epsilon = 4.37$)) π - π^* absorptions maxima of Me₂CPDT-TCNQ (**3**) showed bathochromic shifts of 11 nm from those of **1** ($E_1 = 520$ nm ($\log \epsilon = 4.93$), $E_2 = 489$ nm ($\log \epsilon = 4.74$)),^{8b} while the first and the second absorption maxima of F₂CPDT-TCNQ (**2**) ($E_1 = 511$ nm ($\log \epsilon = 4.69$), $E_2 = 483$ nm ($\log \epsilon = 4.50$)) showed hypsochromic shifts of 9 and 6 nm, respectively, from those of **1**. The bathochromic shifts in **3** are reasonable considering that the π -HOMO energy level of **3** is destabilized by the introduction of the two electron-donating methyl groups, resulting in a decrease in the HOMO-LUMO energy splitting. The hypsochromic shift in **2** can be ascribed to the stabilization of the π -HOMO of **2** by the introduction of two electron-withdrawing fluorine atoms, resulting in an increase in the HOMO-LUMO energy splitting. According to MNDO PM-3 calculations, the HOMOs of **2** and **3** lie 0.13 eV lower and 0.15 eV higher in energy than the HOMO of **1**, respectively.¹² The absorption coefficients of the two π - π^* absorptions maxima in the visible region decrease in the order of **1** > **2** > **3**, suggesting that the coplanar conformation may be preferred in this order. However, it is suggested that deviation from the coplanar conformation is not so significant in the 3,5-disubstituted acceptor molecules, **2** and **3**, since even the dimethyl derivative **3** still has large absorption coefficients ($\log \epsilon = 4.47$ (E_1) and 4.37 (E_2)).

The electrochemical reduction of F₂CPDT-TCNQ and Me₂CPDT-TCNQ occurred in three consecutive reversible one-electron transfer processes, as shown in the cyclic voltammograms listed in Fig. 3, affording stable radical anions, dianions, and radical trianions. By considering that both EO-

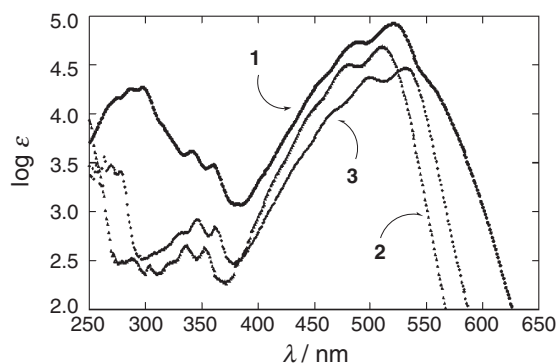


Fig. 2. UV-vis spectra of CPDT-TCNQ: **1**, F₂CPDT-TCNQ: **2**, and Me₂CPDT-TCNQ: **3** in dichloromethane.

F₂CPDT-TCNQ (**14**) and EO-Me₂CPDT-TCNQ (**20**) are reduced in a two-step one-electron transfer process affording the radical anions and dianions, the third one-electron transfer at -1.27 and -1.43 V in F₂CPDT-TCNQ and Me₂CPDT-TCNQ, respectively, should correspond to the reduction of the carbonyl group at the central five-membered ring. The reduction potentials are listed in Table 1. The first half-wave reduction potential E_1^{red} of EO-F₂CPDT-TCNQ is more positive by 0.11 V than that of EO-CPDT-TCNQ. The same trend is observed in the E_1^{red} of 2,5-difluorotetracyano-*p*-quinodimethane (F₂TCNQ) ($E_1^{\text{red}} = 0.300$ V vs SCE in MeCN),¹³ which is 0.16 V more positive than the E_1^{red} of TCNQ ($E_1^{\text{red}} = 0.17$ V vs SCE in MeCN).¹⁴ This fact indicates that the two fluorine atoms in EO-F₂CPDT-TCNQ contribute to the increase in the electron-accepting ability of the terminal dicyanomethylene groups. On the other hand, the E_1^{red} of F₂CPDT-TCNQ is more negative by 0.08 V than that of CPDT-TCNQ, while the third

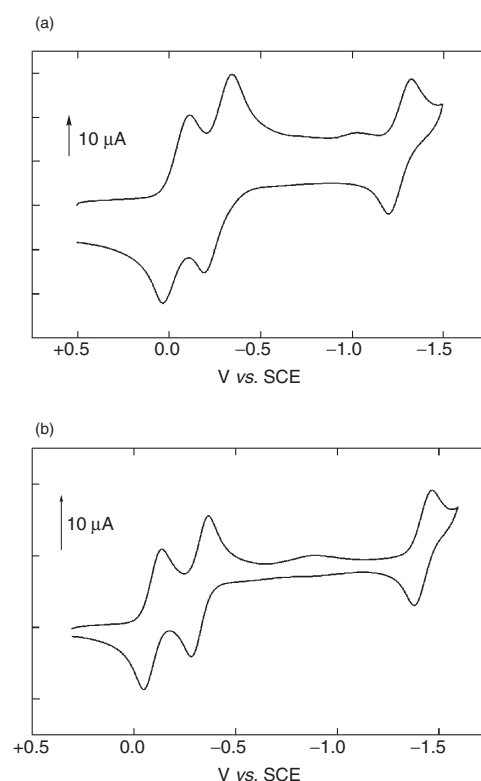


Fig. 3. Cyclic voltammograms of (a) F₂CPDT-TCNQ and (b) Me₂CPDT-TCNQ (1.0 mM solution with 0.1 M TBAP in dichloromethane under argon at room temperature in scan rate: 50 mV s⁻¹).

Table 1. Reduction Potentials^{a)} and Related Electrochemical Data of Acceptors

Compound	E_1^{red}	E_2^{red}	E_3^{red}	ΔE ($E_1^{\text{red}} - E_2^{\text{red}}$)	$\log K_{\text{sem}}$
CPDT-TCNQ	+0.04	-0.27	-1.43	0.31	5.26
F ₂ CPDT-TCNQ	-0.04	-0.27	-1.27	0.23	3.90
Me ₂ CPDT-TCNQ	-0.10	-0.33	-1.43	0.23	3.90
EO-CPDT-TCNQ	-0.14	-0.37	—	0.23	3.90
EO-F ₂ CPDT-TCNQ	-0.03	-0.24	—	0.21	3.56
EO-Me ₂ CPDT-TCNQ	-0.25	-0.36	—	0.11	1.87

a) V vs SCE, 50 mV s⁻¹, 1.0 mM in CH₂Cl₂.

Table 2. Galvanostatic Electrochemical Reduction in Acetone and Conducting Properties of Anion Radical Salts of Me₂CPDT-TCNQ

Electrolyte	Current /μA	Period /day	Cation	Form	C:A ^{a)}	ν_{CN} /cm ⁻¹	ν_{CO} /cm ⁻¹	$\sigma_{\text{r.t.}}^{\text{b)}$ /S cm ⁻¹	$\sigma_{\text{max}}^{\text{b)}$ /S cm ⁻¹	$T_{\sigma\text{max}}^{\text{c)}$ /K	$T_{\text{MI}}^{\text{d)}$ /K
Me ₄ NBF ₄	0.3	11	Me ₄ N	Needle	1:2	2179	1707	0.27	—	—	—
Me ₄ PClO ₄	0.3	11	Me ₄ P	Needle	1:2	2193	1711	12.5	13.0	281	ca. 240
Me ₄ AsClO ₄	0.3	11	Me ₄ As	Needle	1:2	2193	1711	84.3	88.1	254	ca. 185
Me ₄ SbClO ₄	0.3	11	Me ₄ Sb	Needle	1:2	2189	1711	71.8	—	—	—
			Neutral			2212	1720				

a) Determined by the elemental analysis. b) Measured by the four probe method on a polycrystalline solid. c) The temperature showing the maximum conductivity. d) The metal–insulator transition temperature.

half-wave reduction potential E_3^{red} of F₂CPDT-TCNQ is more positive by 0.16 V than that of CPDT-TCNQ. This evidence indicates that the two fluorine atoms of F₂CPDT-TCNQ contribute to the increase in the electron-accepting ability of the central carbonyl group rather than the terminal dicyanomethylene groups. This may be reasonable since the fluorine atoms are located at the β -positions of the α,β -unsaturated carbonyl group. The first reduction potentials of Me₂CPDT-TCNQ and EO-Me₂CPDT-TCNQ are more negative by 0.14 and 0.11 V than those of CPDT-TCNQ and EO-CPDT-TCNQ, respectively. This can be ascribed to the destabilization of the energy levels of the π -LUMOs of Me₂CPDT-TCNQ and EO-Me₂CPDT-TCNQ by the introduction of the electron donating 3,5-dimethyl groups. The steric hindrance of the two methyl groups in EO-Me₂CPDT-TCNQ appears to be significant since the ΔE ($E_1^{\text{red}} - E_2^{\text{red}}$) value as well as the $\log K_{\text{sem}}$ value¹⁵ of EO-Me₂CPDT-TCNQ is remarkably small, as shown in Table 1. Indeed, the ΔE ($E_1^{\text{red}} - E_2^{\text{red}}$) value (0.31) as well as the $\log K_{\text{sem}}$ value (5.26) of CPDT-TCNQ is very large, indicating that the anion radical of CPDT-TCNQ is thermodynamically very stable due to the widespread delocalization of the unpaired electron over all of the extremely planar molecule.⁸ The ΔE ($E_1^{\text{red}} - E_2^{\text{red}}$) values as well as the $\log K_{\text{sem}}$ values of F₂CPDT-TCNQ and Me₂CPDT-TCNQ are relatively small when compared with those of CPDT-TCNQ, indicating that the extent of the delocalization of the unpaired electron is less in the anion radicals of the 3,5-disubstituted derivatives than in the anion radical of unsubstituted CPDT-TCNQ, probably due to the less planar conformations of the 3,5-disubstituted derivatives. However, the deviation from the coplanarity in F₂CPDT-TCNQ and Me₂CPDT-TCNQ seems to not be so significant as that in EO-Me₂CPDT-TCNQ, since the $\log K_{\text{sem}}$ values of F₂CPDT-TCNQ (3.90) and Me₂CPDT-TCNQ (3.90) are more than twice as large as that of EO-Me₂CPDT-TCNQ (1.87).

Conducting Properties of Anion Radical Salts.

Me₂CPDT-TCNQ formed anion radical salts on conventional electrochemical crystallization in acetone in the presence of an electrolyte under a constant current by using an H-type cell. The conditions of the electrochemical crystallization are shown in Table 2. We have obtained four anion radical salts with the molecular formula Me₄X(Me₂CPDT-TCNQ)₂ (X = N, P, As, and Sb). The stoichiometries and room temperature conductivities as well as the ν_{CN} and ν_{CO} frequencies of the salts are also summarized in Table 2. In spite of many efforts to find out the conditions to grow single crystals of good quality, we have not succeeded in preparing large size single crystals for crystallographic analysis, but rather have obtained polycrystalline solids

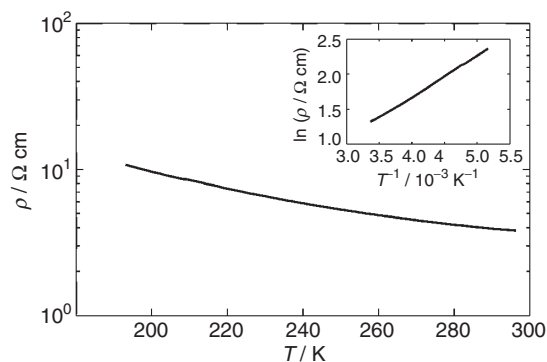


Fig. 4. Temperature dependence of the resistivity for Me₄N(Me₂CPDT-TCNQ)₂.

consisting of a bundle of several needles. As a consequence, the conductivities were measured by the four probe method on the polycrystalline solids.

As shown in Table 2, the Me₄P, Me₄As, and Me₄Sb salts showed fairly high room temperature conductivities, although the conductivity of the Me₄N salt is not so high. The ν_{CN} frequencies of the four salts appeared at 2179–2193 cm⁻¹, which are lower wavenumber by 33–19 cm⁻¹ than that of neutral Me₂CPDT-TCNQ (2212 cm⁻¹). The ν_{CO} frequencies of the salts also appeared at a lower wavenumber region than that of neutral Me₂CPDT-TCNQ (1720 cm⁻¹). Although we have no data on the ν_{CN} and ν_{CO} frequencies of the fully ionic Me₂CPDT-TCNQ dianion, the Me₄P and Me₄As salts should at least exist in a partial CT state, since these salts showed metallic behavior as described below.

The resistivity of the polycrystalline Me₄N salt showed a semiconducting temperature dependence from room temperature down to 193 K, as shown in Fig. 4. However, the activation energy obtained by the Arrhenius plot ($E_a = 51$ meV in the temperature region) is fairly small.

On the other hand, as described above, the resistivity of Me₄P(Me₂CPDT-TCNQ)₂ showed a metallic temperature dependence from room temperature down to around 283 K, and the conductivity reached a maximum value of 13.0 S cm⁻¹ at $T_{\sigma\text{max}} = 281$ K, as shown in Fig. 5. After passing through the maximum, the metallic state became unstable and transferred to the first semiconducting phase with $E_{a1} = 18$ meV in the temperature region from 230 K down to 170 K, and then transferred to the second semiconducting phase with $E_{a2} = 67$ meV in the temperature region from 120 K down to 85 K. The activation energies were obtained from the Arrhenius plots of the temperature dependence of the resistivity, as shown in Fig. 6.

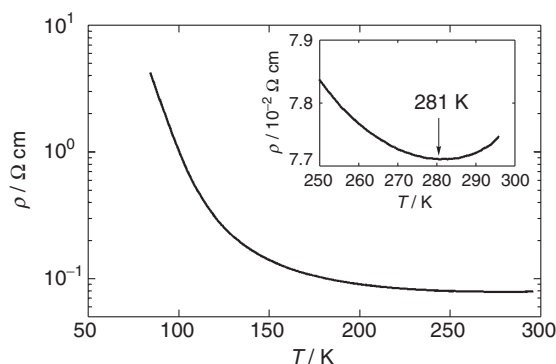


Fig. 5. Temperature dependence of the resistivity for $\text{Me}_4\text{P}(\text{Me}_2\text{CPDT-TCNQ})_2$.

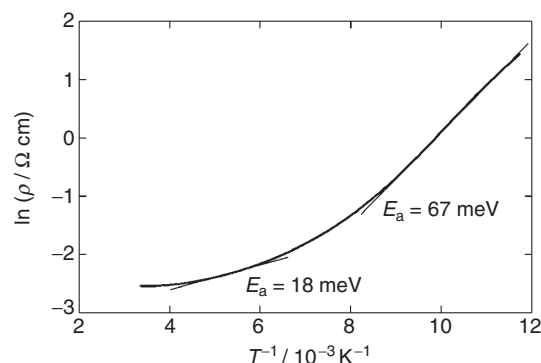


Fig. 6. Arrhenius plot of the temperature dependence of the resistivity for $\text{Me}_4\text{P}(\text{Me}_2\text{CPDT-TCNQ})_2$.

The temperature dependence of the resistivity of $\text{Me}_4\text{As}(\text{Me}_2\text{CPDT-TCNQ})_2$ is shown in Fig. 7. It is also metallic from room temperature down to around 240 K, and the conductivity reached a maximum value of 88.1 S cm^{-1} at $T_{\sigma\text{max}} = 254 \text{ K}$. The activation energy of the first semiconducting phase obtained by the Arrhenius plot was $E_{a1} = 21 \text{ meV}$ in the temperature region from 210 K down to 180 K. The activation energy of the second semiconducting phase is $E_{a2} = 81 \text{ meV}$ in the temperature region from 150 K down to 100 K, as shown in Fig. 8.

The resistivity of $\text{Me}_4\text{Sb}(\text{Me}_2\text{CPDT-TCNQ})_2$ exhibited a semiconducting temperature dependence from room temperature down to 85 K, as shown in Fig. 9. The activation energy obtained by the Arrhenius plot was $E_a = 72 \text{ meV}$ in the temperature region from room temperature down to 110 K.

$\text{Me}_4\text{X}(\text{CPDT-TCNQ})_2$ ($\text{X} = \text{P}$ and As) also have the first insulating phase, adjacent to the metallic phase, with a small activation energy, and the second insulating phase with a relatively large activation energy at lower temperature regions.¹⁶ Therefore, the profiles of the existence of the first and second insulating phases, and the small and large activation energies of the respective phases in $\text{Me}_4\text{X}(\text{Me}_2\text{CPDT-TCNQ})_2$ ($\text{X} = \text{P}$ and As) closely resemble the cases of $\text{Me}_4\text{X}(\text{CPDT-TCNQ})_2$ ($\text{X} = \text{P}$ and As). Moreover, it has already been proven that the CPDT-TCNQ molecule has a very strong tendency to maintain its characteristic molecular packing motif shown in Fig. 1 in the crystal structure of anion radical salts, even when the size or structure of the cation changes.¹⁷ Moreover, πAO coeffi-

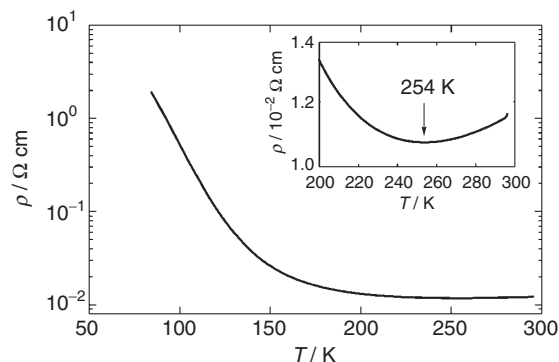


Fig. 7. Temperature dependence of the resistivity for $\text{Me}_4\text{As}(\text{Me}_2\text{CPDT-TCNQ})_2$.

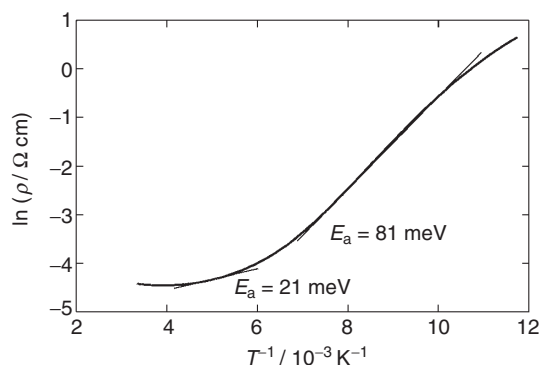


Fig. 8. Arrhenius plot of the temperature dependence of the resistivity for $\text{Me}_4\text{As}(\text{Me}_2\text{CPDT-TCNQ})_2$.

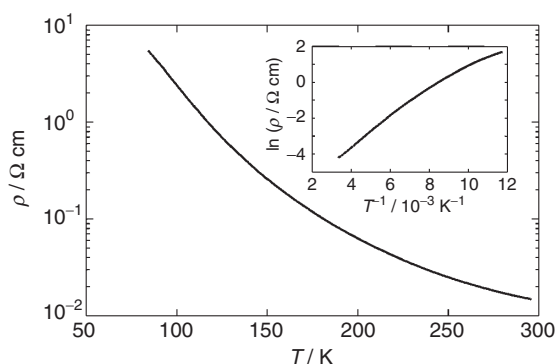


Fig. 9. Temperature dependence of the resistivity for $\text{Me}_4\text{Sb}(\text{Me}_2\text{CPDT-TCNQ})_2$.

cients as well as the bonding and antibonding orbital symmetry in the LUMO of $\text{Me}_2\text{CPDT-TCNQ}$ obtained from MNDO PM-3 calculations closely resemble those of CPDT-TCNQ. Therefore, although the crystal structures of $\text{Me}_4\text{X}(\text{Me}_2\text{CPDT-TCNQ})_2$ ($\text{X} = \text{N}$, P , As , and Sb) have not been determined, we can speculate that these salts may have a similar molecular packing motif as those of $\text{Me}_4\text{X}(\text{CPDT-TCNQ})_2$ ($\text{X} = \text{N}$, P , As , and Sb), respectively, except for the sheet-like network along the side-by-side direction, which should disappear in the salts of the 3,5-dimethyl derivative due to the lack of the inter-column O...H contacts.

The resistivity of $\text{Me}_4\text{N}(\text{Me}_2\text{CPDT-TCNQ})_2$ showed a semiconducting temperature dependence from room temperature,

even though $\text{Me}_4\text{N}(\text{CPDT-TCNQ})_2$ is metallic down to 130 K. Therefore, the metallic state of $\text{Me}_4\text{N}(\text{Me}_2\text{CPDT-TCNQ})_2$ is significantly destabilized compared with that of $\text{Me}_4\text{N}(\text{CPDT-TCNQ})_2$. On the other hand, the destabilization of the metallic state is not so significant in $\text{Me}_4\text{P}(\text{Me}_2\text{CPDT-TCNQ})_2$ and $\text{Me}_4\text{As}(\text{Me}_2\text{CPDT-TCNQ})_2$, since the conductivity of both of these salts showed a metallic temperature dependence, although the $T_{\sigma\text{max}}$ of $\text{Me}_4\text{P}(\text{Me}_2\text{CPDT-TCNQ})_2$ was higher by 61 K than that of $\text{Me}_4\text{P}(\text{CPDT-TCNQ})_2$ and the $T_{\sigma\text{max}}$ of $\text{Me}_4\text{As}(\text{Me}_2\text{CPDT-TCNQ})_2$ was higher by 79 K than that of $\text{Me}_4\text{As}(\text{CPDT-TCNQ})_2$. It seems difficult to explain why the metallic state of $\text{Me}_4\text{N}(\text{Me}_2\text{CPDT-TCNQ})_2$ is significantly more destabilized than the metallic states of $\text{Me}_4\text{X}(\text{Me}_2\text{CPDT-TCNQ})_2$ ($\text{X} = \text{P}$ and As) only based on the difference in the quality of the crystals, since all three of these polycrystalline samples of the $\text{Me}_2\text{CPDT-TCNQ}$ salts exhibit a metallic luster and are similar in shape under a microscope. The MI transition mechanisms have been proven to be a $2k_{\text{F}}$ CDW instability for $\text{Me}_4\text{N}(\text{CPDT-TCNQ})_2$ and $4k_{\text{F}}$ CDW instabilities for $\text{Me}_4\text{X}(\text{CPDT-TCNQ})_2$ ($\text{X} = \text{P}$ and As).⁹ The parameter for determining either the $2k_{\text{F}}$ or $4k_{\text{F}}$ CDW drawings for the CPDT-TCNQ salts has been ascribed to the degree of dimerization, since strong dimerization enhances the effect of the Coulomb interaction, which enhances the $4k_{\text{F}}$ CDW instability. Therefore, from the fact that the metallic state of the Me_4N salt is significantly less stable than the metallic states of the Me_4P and Me_4As salts, it may be possible to speculate that the origin of the MI transition in $\text{Me}_4\text{N}(\text{Me}_2\text{CPDT-TCNQ})_2$ may be $2k_{\text{F}}$ CDW instability, which occurred at around room temperature, and the origins of the MI transitions in $\text{Me}_4\text{X}(\text{Me}_2\text{CPDT-TCNQ})_2$ ($\text{X} = \text{P}$ and As) may be $4k_{\text{F}}$ CDW, because the $4k_{\text{F}}$ CDW instability is generally much less common than the $2k_{\text{F}}$ CDW instability. Although we cannot deduce any critical conclusions at this stage due to the lack of crystal structural data of $\text{Me}_4\text{X}(\text{Me}_2\text{CPDT-TCNQ})_2$ ($\text{X} = \text{N}$, P , and As), the conducting properties of $\text{Me}_4\text{X}(\text{Me}_2\text{CPDT-TCNQ})_2$ ($\text{X} = \text{N}$, P , and As) suggest that these salts may have a similar molecular packing motif as those of $\text{Me}_4\text{X}(\text{CPDT-TCNQ})_2$ ($\text{X} = \text{N}$, P , and As), and the one-dimensional metallic states may be destabilized by the lack of the inter-column sheet-like network along the side-by-side direction. In this case, the extent of the destabilization would be much more significant in $\text{Me}_4\text{N}(\text{Me}_2\text{CPDT-TCNQ})_2$, if the origin of the MI transition of the Me_4N salt is a $2k_{\text{F}}$ CDW instability. Preparations of single crystals in good quality and determination of the crystal structures are in progress.

Experimental

General. All synthetic reactions were carried out under an argon atmosphere. All chemicals and solvents were dried well and solvents were freshly distilled before use. Column chromatography was carried out with silica gel (150–425 μm). Melting points were determined with a Yanagimoto micro melting point apparatus MP-J3, and are not corrected. Elemental analyses were performed at the Instrumental Analysis Center for Chemistry, Tohoku University. ^1H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AC-200P spectrometer or AM-600 spectrometer and chemical shifts are recorded in δ relative to tetramethylsilane as an internal standard. Chemical shift assignments were confirmed through spin

decoupling and two-dimensional carbon–proton chemical shift correlation experiments. FT-IR spectra were recorded on a HORIBA FT-300 spectrometer with a KBr disk method. Mass spectra were recorded on a JEOL HX-100 or a HITACHI M-2500S spectrometer. Electronic absorption spectra were recorded on a HITACHI U-3210 spectrometer. The cyclic voltammograms were taken on a BAS CV-50W under argon atmosphere at room temperature. The conductivities of the anion radical salts were measured by the four-probe method on using a YOKOGAWA 7651 programmable direct current source and a KEITHLEY 2001 digital multimeter unit on a polycrystalline solid. Gold wires (10 or 15 μm diameter) were attached to the polycrystalline solid with carbon paste.

Bis(4-bromo-3-thienyl)methanol (6). To a hexane solution of butyllithium (1.66 M (1 M = 1 mol dm^{-3}) solution, 4.40 mL, 7.30 mmol) cooled at -78°C , a solution of 3,4-dibromothiophene (**4**) (1.72 g, 7.11 mmol) in anhydrous ether (12 mL) was added dropwise with stirring at -78°C over a period of 1 min and this reaction mixture was stirred for 30 min at -78°C under argon atmosphere. To this was added dropwise a solution of 4-bromo-3-thiophenecarbaldehyde (**5**)¹⁰ (1.43 g, 7.46 mmol) in anhydrous ether (6 mL) with stirring at -78°C over a period of 5 min, and this reaction mixture was stirred for 30 min at -78°C . After being warmed to room temperature, the reaction mixture was poured into 1 M hydrochloric acid and extracted with ether. The ether extract was washed with water and then brine, and was then dried over Na_2SO_4 . Solvent evaporation from the extract gave a residue (2.59 g), which was chromatographed on basic alumina by eluting with ether to give a yellow oil (5.23 g, 4.79 mmol, 70%): ^1H NMR (CDCl_3 , 200 MHz) δ 7.31 (2H, d, $J_{2,5} = 3.5$ Hz, H-5), 7.18 (2H, dd, $J_{2,5} = 3.5$ Hz, $J_{2,\text{CHOH}} = 0.7$ Hz, H-2), 5.95 (1H, dd, $J_{\text{CH,OH}} = 4.3$ Hz, $J_{2,\text{CHOH}} = 0.7$ Hz, CHOH), 2.50 (1H, d, $J_{\text{CH,OH}} = 4.3$ Hz, OH); ^{13}C NMR (CDCl_3 , 150 MHz) δ 141.5 (C-3), 124.1 (C-2), 124.0 (C-5), 110.4 (C-4), 67.5 (CHOH); IR (neat) 3564, 3320, 3111, 2925, 2875, 1518, 1425, 1377, 1352, 1284, 1261, 1157, 1041, 1003, 962, 881, 852, 802, 768, 714, 658 cm^{-1} ; HRMS (EI, 110 eV) m/z 351.8232 (M^+) (Calcd for $\text{C}_9\text{H}_6\text{Br}_2\text{OS}_2$: 351.8227). Found: C, 30.44; H, 1.98; Br, 44.95%. Calcd for $\text{C}_9\text{H}_6\text{Br}_2\text{OS}_2$: C, 30.53; H, 1.71; Br, 45.13%.

Bis(4-bromo-3-thienyl) Ketone (7). To a solution of **6** (1.94 g, 5.47 mmol) in acetic acid (20 mL) was added dropwise a solution of chromium trioxide (547 mg, 5.47 mmol) dissolved in the mixture of acetic acid (10 mL) and water (4 mL) with stirring at room temperature over a period of 30 min. Then the reaction mixture was stirred for 6 h at room temperature. The reaction mixture was extracted with ether. The ether extract was washed successively with an aqueous NaHCO_3 solution, water, and then brine, and was then dried over Na_2SO_4 . Solvent evaporation from the extract gave a dark yellow oil (1.85 g), which was chromatographed on silica gel by eluting with toluene to give bis(4-bromo-3-thienyl) ketone (**7**) (1.76 g, 5.00 mmol, 92%) as pale yellow plates: mp $84\text{--}85^\circ\text{C}$; ^1H NMR (CDCl_3 , 200 MHz) δ 7.77 (2H, d, $J_{2,5} = 3.5$ Hz, H-2), 7.38 (2H, d, $J_{5,2} = 3.5$ Hz, H-5); ^{13}C NMR (CDCl_3 , 150 MHz) δ 182.3 (CO), 139.3 (C-3), 134.1 (C-2), 125.5 (C-5), 110.6 (C-4); IR (KBr) 3097, 1672, 1637, 1485, 1415, 1365, 1340, 1257, 1219, 1134, 1038, 957, 879, 854, 808, 766, 688, 648 cm^{-1} ; MS (DEI, 70 eV) m/z (rel intensity) 354 ($\text{M}^+ + 4$, 34.48), 352 ($\text{M}^+ + 2$, 60.97), 350 (M^+ , 30.40), 273 ($\text{M}^+ + 2 - \text{Br}$, 71.42), 271 ($\text{M}^+ - \text{Br}$, 64.86), 192 ($\text{M}^+ - 2\text{Br}$, 45.19), 191 ($\text{C}_5\text{H}_2\text{BrOS} + 2$, 100), 189 ($\text{C}_5\text{H}_2\text{BrOS}$, 97.7); HRMS m/z 349.8068 (M^+) (Calcd for $\text{C}_9\text{H}_4\text{Br}_2\text{OS}_2$: 349.8070). Found: C, 31.11; H, 1.42; Br, 45.07%. Calcd for $\text{C}_9\text{H}_4\text{Br}_2\text{OS}_2$: C, 30.70; H,

1.15; Br, 45.39%.

2,2-Bis(4-bromo-3-thienyl)-1,3-dioxolane (8). A solution of **7** (1.65 g, 4.67 mmol), *p*-toluenesulfonic acid (89 mg, 0.47 mmol), and ethylene glycol (2.60 mL, 46.6 mmol) in benzene (50 mL) was heated to reflux under a Dean–Stark head for 5 days under argon atmosphere. After being cooled to room temperature, the reaction mixture was poured into aqueous NaHCO₃ and extracted with benzene. The benzene extract was washed with water and then brine, and was then dried over Na₂SO₄. Solvent evaporation from the extract gave a crude product, which was chromatographed on basic alumina by eluting with toluene to give pure 2,2-bis(4-bromo-3-thienyl)-1,3-dioxolane (**8**) (1.81 g, 4.57 mmol, 98%) as colorless prisms: mp 170.0–170.5 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.51 (2H, d, $J_{2,5}$ = 3.70 Hz, H-2), 7.27 (2H, d, $J_{5,2}$ = 3.70 Hz, H-5), 4.16 (4H, s, OCH₂CH₂O); ¹³C NMR (CDCl₃, 150 MHz) δ 138.5 (C-3), 126.8 (C-2), 125.2 (C-5), 109.1 (C-4), 105.4 (OCO), 65.3 (OCH₂CH₂O); IR (KBr) 3107, 2981, 2937, 2881, 2852, 1545, 1510, 1466, 1408, 1192, 1159, 1092, 1043, 1007, 951, 885, 858, 806, 727, 658 cm⁻¹; UV (MeCN) λ /nm (log ϵ) 250.1 (sh, 3.89), 245.4 (3.96), 227.6 (sh, 3.82); MS (DEI, 70 eV) m/z (rel intensity) 398 (M⁺ + 4, 17.77), 396 (M⁺ + 2, 29.25), 394 (M⁺, 15.04), 317 (M⁺ + 2 – Br, 7.15), 315 (M⁺ – Br, 7.15), 191 (C₅H₂BrOS + 2, 100), 189 (C₅H₂BrOS, 87); HRMS m/z 393.8329 (M⁺) (Calcd for C₁₁H₈Br₂O₂S₂: 393.8332). Found: C, 33.31; H, 2.13; S, 16.00; Br, 40.22%. Calcd for C₁₁H₈Br₂O₂S₂: C, 33.35; H, 2.04; S, 16.19; Br, 40.34%.

2,2-Bis(4-fluoro-3-thienyl)-1,3-dioxolane (9). To a solution of **8** (300 mg, 0.757 mmol) in anhydrous THF (5 mL) was added dropwise a hexane solution of butyllithium (1.66 M solution, 1.00 mL, 1.66 mmol) with stirring at –78 °C under argon atmosphere, and this reaction mixture was stirred for 30 min at –78 °C. To this was added dropwise a solution of *N*-fluorobenzenesulfonimide (NFBS) (573 g, 1.82 mmol) in anhydrous THF (6 mL) at –78 °C over a period of 10 min, and then this reaction mixture was stirred for 1 h at –78 °C. After a mixture of water (1 mL) and THF (1 mL) was added to the reaction mixture at –78 °C, this resulting reaction mixture was warmed to room temperature, then poured into aqueous Na₂SO₃, and then extracted with ether. The ether extract was washed with water and then brine, and was then dried over Na₂SO₄. Solvent evaporation from the extract gave a crude product (243 mg), which was chromatographed on silica gel by eluting with toluene to give colorless crystals (161 mg, 78%). Further recrystallization from ethanol gave 2,2-bis(4-fluoro-3-thienyl)-1,3-dioxolane (**9**) as colorless plates (89 mg, 43%): mp 107–108 °C; ¹⁹F NMR (CDCl₃, 188 MHz) δ –129.4 (br.d, $J_{\text{H,F}}$ = 3.2 Hz); ¹H NMR (CDCl₃, 200 MHz) δ 7.29 (2H, dd, $J_{\text{H,H}}$ = 3.8 Hz, $J_{\text{H,F}}$ = 3.8 Hz, H-2), 6.72 (2H, dd, $J_{\text{H,H}}$ = 3.8 Hz, $J_{\text{H,F}}$ = 1.0 Hz, H-5), 4.14 (4H, s, OCH₂CH₂O); ¹³C NMR (CDCl₃, 150 MHz) δ 155.0 (C-4), 130.5 (C-3), 123.3 (C-2), 105.1 (C-5), 104.0 (OCO), 65.5 (OCH₂CH₂O); IR (KBr) 3113, 3068, 1562, 1456, 1410, 1203, 1144, 1086, 1055, 1028, 1003, 947, 928, 827, 742, 690, 633, 592, 565 cm⁻¹; UV (MeCN) λ /nm (log ϵ) 238.8 (4.02), 226.0 (sh, 3.99); HRMS (EI, 110 eV) m/z 273.9933 (M⁺) (Calcd for C₁₁H₈F₂O₂S₂: 273.9934). Found: C, 47.89; H, 3.10%. Calcd for C₁₁H₈F₂O₂S₂: C, 48.16; H, 2.94%.

2,2-Bis(4-fluoro-5-iodo-3-thienyl)-1,3-dioxolane (10). To a solution of **9** (250 mg, 0.91 mmol) in a mixture of chloroform (10 mL) and acetic acid (10 mL) was added NIS (450 mg, 2.00 mmol) with stirring at room temperature under argon atmosphere. Then, this resulting reaction mixture was stirred for 2 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into aqueous NaHCO₃, and the resulting solution was extracted

with chloroform. The chloroform extract was washed successively with aqueous Na₂SO₃, water, and then brine, and was then dried over Na₂SO₄. Solvent evaporation from the extract gave a crude product (469 mg), which was chromatographed on silica gel by eluting with toluene to give 2,2-bis(4-fluoro-5-iodo-3-thienyl)-1,3-dioxolane (**10**) as colorless plates (428 mg, 89%): mp 117–118 °C; ¹⁹F NMR (CDCl₃, 188 MHz) δ –119.7 (d, $J_{\text{H,F}}$ = 4.1 Hz); ¹H NMR (CDCl₃, 600 MHz) δ 7.52 (2H, d, $J_{\text{H,F}}$ = 5.0 Hz, H-2), 4.14 (4H, s, OCH₂CH₂O); ¹³C NMR (CDCl₃, 150 MHz) δ 157.3 (C-4), 130.2 (C-3), 128.3 (C-2), 102.9 (OCO), 65.7 (OCH₂CH₂O), 55.5 (C-5); IR (KBr) 3132, 2956, 2887, 1556, 1450, 1398, 1203 1178, 1153, 1059, 1030, 1007, 964, 945, 850, 787, 768, 737, 708 cm⁻¹; HRMS (EI, 110 eV) m/z 525.7864 (M⁺) (Calcd for C₁₁H₄F₂I₂O₂S₂: 525.7867). Found: C, 24.98; H, 0.91; I, 48.18%. Calcd for C₁₁H₄F₂I₂O₂S₂: C, 25.21; H, 0.77; I, 48.43%.

2,2-Bis(4-fluoro-5-trimethylsilyl-3-thienyl)-1,3-dioxolane (11). To a solution of **10** (424 mg, 0.806 mmol) in anhydrous THF (25 mL) was added dropwise a hexane solution of butyllithium (1.59 M solution, 1.05 mL, 1.67 mmol) with stirring at –78 °C under argon atmosphere. Then this reaction mixture was stirred at –78 °C for 30 min. To this was added dropwise trimethylsilyl chloride (0.410 mL, 3.22 mmol) at –78 °C, and this resulting reaction mixture was stirred at –78 °C for 1 h. After warming to room temperature, the reaction mixture was poured into aqueous NaHCO₃ and extracted with ether. The ether extract was washed successively with water and then brine, and was then dried over Na₂SO₄. Solvent evaporation from the dried extract gave a residue, which was chromatographed on silica gel by eluting with a mixture of toluene–hexane (1:1, v/v) to give pure 2,2-bis(4-fluoro-5-trimethylsilyl-3-thienyl)-1,3-dioxolane (**11**) as colorless plates (232 mg, 69%): mp 72–73 °C; ¹⁹F NMR (CDCl₃, 188 MHz) δ –120.1 (d, $J_{\text{H,F}}$ = 3.4 Hz); ¹H NMR (CDCl₃, 200 MHz) δ 7.42 (2H, d, $J_{\text{H,F}}$ = 3.5 Hz, H-2), 4.13 (4H, s, OCH₂CH₂O), 0.31 (18H, s, SiMe₃); IR (KBr) 3114, 2956, 2893, 1549, 1439, 1400, 1252, 1192, 1171, 1066, 984, 947, 872, 841, 758, 719, 694, 638, 613, 513 cm⁻¹; MS (DEI, 70 eV) m/z (rel intensity) 420 (M⁺ + 2, 5.49), 419 (M⁺ + 1, 8.22), 418 (M⁺, 27.29), 403 (M⁺ – Me, 15.25), 245 (M⁺ – C₄HFSSiMe₃, 100); HRMS (EI, 110 eV) m/z 418.0739 (M⁺) (Calcd for C₁₇H₂₄F₂O₂S₂Si₂: 418.0724). Found: C, 48.52; H, 5.99%. Calcd for C₁₇H₂₄F₂O₂S₂Si₂: C, 48.77; H, 5.78%.

4-Ethylenedioxy-3,5-difluoro-2,6-bis(trimethylsilyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (12). To an anhydrous THF (8 mL) solution of **11** (125 mg, 0.299 mmol) was added dropwise *t*-butyllithium (1.64 M pentane solution, 0.44 mL, 0.656 mmol) with stirring at –78 °C under argon atmosphere. After the reaction mixture was stirred for 30 min at –78 °C under argon atmosphere, copper(II) chloride (212 mg, 1.58 mmol) was added and then the reaction mixture was stirred for another 30 min at –78 °C. After being warmed to room temperature, the reaction mixture was stirred for 3 h at room temperature. The inorganic precipitate was removed by filtration through a glass disk and the filtrate was poured into aqueous NaHCO₃ and then extracted with ether. The ether extract was washed with water and then brine, and then was dried over Na₂SO₄. Solvent evaporation gave a residue (123 mg), which was chromatographed on silica gel by eluting with a mixture of toluene–hexane (1:2, v/v) to give **12** as colorless plates (51 mg, 41%): mp 146–147 °C; ¹⁹F NMR (CDCl₃, 188 MHz) δ –124.5 (s); ¹H NMR (CDCl₃, 200 MHz) δ 0.32 (18H, s, SiMe₃), 4.28 (4H, s, OCH₂CH₂O); IR (KBr) 2956, 2895, 1506, 1460, 1396, 1250, 1221, 1182, 1105, 1012, 991, 974, 949, 845, 760 cm⁻¹; MS

(DEI, 70 eV) m/z (rel intensity) 419 ($M^+ + 3$, 5.05), 418 ($M^+ + 2$, 19.78), 417 ($M^+ + 1$, 29.35), 416 (M^+ , 100); HRMS (EI, 110 eV) m/z 416.0564 (M^+) (Calcd for $C_{17}H_{22}F_2O_2S_2Si_2$: 416.0568). Found: C, 48.78; H, 5.42%. Calcd for $C_{17}H_{22}F_2O_2S_2Si_2$: C, 49.01; H, 5.32%.

4-Ethylenedioxy-3,5-difluoro-2,6-diiodo-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (13). To a solution of **12** (120 mg, 0.288 mmol) in a mixture of anhydrous chloroform (6 mL) and acetic acid (6 mL) was added NIS (143 mg, 0.636 mmol) with stirring at room temperature under argon atmosphere. Then, this resulting reaction mixture was stirred for 2 h at room temperature, and was then poured into aqueous Na_2SO_3 . The resulting mixture was extracted with chloroform. The chloroform extract was washed successively with aqueous $NaHCO_3$, water, and then brine, and was then dried over Na_2SO_4 . Solvent evaporation gave a crude product, which was chromatographed on silica gel by eluting with a mixture of toluene–hexane (1:1, v/v) to give pure 4-ethylenedioxy-3,5-difluoro-2,6-diiodo-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**13**) as yellow needles (141 mg, 93.4%): mp 258–259 °C (decomp); ^{19}F NMR ($CDCl_3$, 188 MHz) δ –124.0 (s); 1H NMR ($CDCl_3$, 200 MHz) δ 4.27 (4H, s, OCH_2CH_2O); IR (KBr) 1527, 1452, 1240, 1213, 1092, 1028, 999, 945, 916, 843, 573, 544 cm^{-1} ; HRMS (EI, 110 eV) m/z 523.7705 (M^+) (Calcd for $C_{11}H_4F_2I_2O_2S_2$: 523.7711). Found: C, 24.92; H, 0.96; I, 48.22%. Calcd for $C_{11}H_4F_2I_2O_2S_2$: C, 25.21; H, 0.77; I, 48.43%.

2,6-Bis(dicyanomethylene)-4-ethylenedioxy-3,5-difluoro-2,6-dihydro-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (EO- F_2 CPDT-TCNQ: **14).** To a suspension of sodium hydride (60 wt %, 18.0 mg, 0.450 mmol) in anhydrous THF (1 mL) was added dropwise a solution of malononitrile (15.0 mg, 0.227 mmol) in anhydrous THF (1 mL) at room temperature under argon atmosphere. Then, this reaction mixture was stirred for 10 min at room temperature. To this were added successively a solution of **13** (30.0 mg, 0.0572 mmol) in anhydrous THF (1 mL) and $[Pd(PPh_3)_4]$ (13.0 mg, 0.0112 mmol). This reaction mixture was heated at reflux for 4 h and then cooled to room temperature with stirring. The reaction mixture was poured into a mixture of bromine (0.2 mL) and water (20 mL). Then, this resulting mixture was poured into aqueous Na_2SO_3 water and extracted with dichloromethane. The dichloromethane extract was washed successively with aqueous $NaHCO_3$, water, and then brine, and was then dried over Na_2SO_4 . Solvent evaporation from the dried extract gave a crude product, which was chromatographed on silica gel by eluting with dichloromethane to give pure 2,6-bis(dicyanomethylene)-4-ethylenedioxy-3,5-difluoro-2,6-dihydro-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (EO- F_2 CPDT-TCNQ: **14**) as a violet powder (15.6 mg, 68%): mp > 300 °C; ^{19}F NMR ($CDCl_3$, 188 MHz) δ –123.9 (s); 1H NMR ($CDCl_3$, 200 MHz) δ 4.37 (4H, s, OCH_2CH_2O); IR (KBr) 2222, 1693, 1639, 1514, 1383, 1288, 1211, 1182, 1032, 997, 941 cm^{-1} ; MS (DEI, 70 eV) m/z (rel intensity) 400 ($M^+ + 2$, 12.18), 399 ($M^+ + 1$, 22.12), 398 (M^+ , 100), 354 (F_2 CPDT-TCNQ $^+$, 17.87); HRMS (EI, 110 eV) m/z 397.9749 (M^+) (Calcd for $C_{17}H_4F_2N_4O_2S_2$: 397.9744). Found: C, 51.08; H, 1.24; N, 13.83%. Calcd for $C_{17}H_4F_2N_4O_2S_2$: C, 51.26; H, 1.01; N, 14.06%.

2,6-Bis(dicyanomethylene)-3,5-difluoro-2,6-dihydro-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (F_2 CPDT-TCNQ: **2).** To a solution of **14** (12.0 mg, 0.0301 mmol) in dichloromethane (4 mL) was added 70% perchloric acid (1 mL) at 0 °C. After vigorous stirring at room temperature for 6 h, the reaction mixture was poured into ice-water. The resulting mixture was extracted with dichloromethane. The dichloromethane extract was washed with aqueous $NaHCO_3$, water, and then brine, and was then dried over

Na_2SO_4 . Solvent evaporation from the extract gave a crude product (9.3 mg), which was chromatographed on silica gel by eluting with dichloromethane to give 2,6-bis(dicyanomethylene)-3,5-difluoro-2,6-dihydro-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (F_2 CPDT-TCNQ: **2**) as a violet powder (4.0 mg, 37.6%): mp > 300 °C; ^{19}F NMR ($CDCl_3$, 188 MHz) δ –112.7 (s); IR (KBr) 2216, 1722, 1576, 1510, 1460, 1342, 1286, 1221, 1142, 1078, 1016, 889 cm^{-1} ; UV–vis (CH_2Cl_2) λ/nm (log ϵ) 511 (4.69), 483 (4.50), 448 (sh, 4.03), 353 (2.62), 337 (2.65), 304 (2.46), 288 (2.52); HRMS (EI, 110 eV) m/z 353.9487 (M^+) (Calcd for $C_{15}F_2N_4OS_2$: 353.9481). Found: C, 50.77; N, 15.97%. Calcd for $C_{15}F_2N_4OS_2$: C, 50.85; N, 15.81%.

2,2-Bis(4-methyl-3-thienyl)-1,3-dioxolane (15). To a solution of **8** (500 mg, 1.262 mmol) in anhydrous THF (20 mL) was added dropwise a hexane solution of butyllithium (1.54 M solution, 1.72 mL, 2.649 mmol) with stirring at –78 °C under argon atmosphere. Then this reaction mixture was stirred for 30 min at –78 °C. To this was added dropwise methyl iodide (0.39 mL, 889 mg, 6.265 mmol) at –78 °C, and this reaction mixture was stirred for 1 h at –78 °C. After a mixture of water (1 mL) and THF (2 mL) was added to the reaction mixture at –78 °C, the reaction mixture was warmed to room temperature, then poured into aqueous Na_2SO_3 and extracted with ether. The ether extract was washed with aqueous $NaHCO_3$, water, and then brine, and was then dried over Na_2SO_4 . Solvent evaporation from the dried extract gave colorless fine crystals (358 mg), which were chromatographed on silica gel by eluting with toluene to give 2,2-bis(4-methyl-3-thienyl)-1,3-dioxolane (**15**) as colorless plates (333 mg, 99%): mp 141–142 °C; 1H NMR ($CDCl_3$, 600 MHz) δ 7.27 (2H, d, $J_{2,5} = 3.3$ Hz, H-2), 6.88 (2H, dq, $J_{5,2} = 3.3$ Hz, $J_{5,Me} = 1.0$ Hz, H-5), 4.07 (4H, s, OCH_2CH_2O), 2.12 (6H, d, $J_{Me,5} = 1.0$ Hz, Me); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 140.4 (C-4), 136.7 (C-3), 125.0 (C-2), 122.8 (C-5), 107.0 (OCO), 64.7 (OCH_2CH_2O), 15.3 (Me); IR (KBr) 3122, 3097, 2931, 2883, 1456, 1375, 1205, 1171, 1146, 1049, 984, 949, 922, 864, 822, 700 cm^{-1} ; UV (MeCN) λ/nm (log ϵ) 241.8 (4.02); MS (DEI, 110 eV) m/z (rel intensity) 268 ($M^+ + 2$, 5.95), 267 ($M^+ + 1$, 8.91), 266 (M^+ , 52.06), 169 ($M^+ - C_5H_5S$, 100); HRMS (EI, 110 eV) m/z 266.0435 (M^+) (Calcd for $C_{13}H_{14}O_2S_2$: 266.0435). Found: C, 58.60; H, 5.25%. Calcd for $C_{13}H_{14}O_2S_2$: C, 58.62; H, 5.30%.

2,2-Bis(5-iodo-4-methyl-3-thienyl)-1,3-dioxolane (16). To a solution of **15** (1000 mg, 3.754 mmol) in a mixture of chloroform (40 mL) and acetic acid (40 mL) was added NIS (1860 mg, 8.267 mmol) with stirring at room temperature under argon atmosphere. Then this reaction mixture was stirred for 3 h at room temperature. The reaction mixture was then poured into aqueous Na_2SO_3 , and the resulting solution was extracted with chloroform. The chloroform extract was washed successively with aqueous $NaHCO_3$, water, and brine, and was then dried over Na_2SO_4 . Solvent evaporation from the dried extract gave a reddish oil (1944 mg), which was chromatographed on silica gel by eluting with a mixture of toluene and hexane (1:1, v/v) to give 2,2-bis(5-iodo-4-methyl-3-thienyl)-1,3-dioxolane (**16**) as colorless plates (1557 mg, 80%): mp 121–122 °C; 1H NMR ($CDCl_3$, 600 MHz) δ 7.45 (2H, s, H-2), 4.06 (4H, s, OCH_2CH_2O), 2.08 (6H, s, Me); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 140.8 (C-3), 139.7 (C-4), 129.8 (C-2), 105.8 (OCO), 77.6 (C-5), 64.8 (OCH_2CH_2O), 17.5 (Me); IR (KBr) 3101, 2885, 1535, 1448, 1429, 1375, 1190, 1167, 1147, 1053, 1024, 987, 947, 914, 843, 781, 706 cm^{-1} ; UV (MeCN) λ/nm (log ϵ) 247.8 (4.25); MS (DEI, 110 eV) m/z (rel intensity) 520 ($M^+ + 2$, 4.02), 519 ($M^+ + 1$, 7.65), 518 (M^+ , 45.27), 295 ($M^+ - C_5H_4IS$, 100); HRMS (EI, 110 eV) m/z 517.8367 (M^+) (Calcd for

$C_{13}H_{12}I_2O_2S_2$: 517.8369). Found: C, 29.97; H, 2.57; I, 48.71%. Calcd for $C_{13}H_{12}I_2O_2S_2$: C, 30.13; H, 2.33; I, 48.98%.

2,2-Bis(4-methyl-5-trimethylsilyl-3-thienyl)-1,3-dioxolane (17). To a solution of **16** (1500 mg, 2.895 mmol) in anhydrous THF (60 mL) was added dropwise a hexane solution of butyllithium (1.54 M hexane solution, 4.25 mL, 6.375 mmol) with stirring at -78°C under argon atmosphere. Then this reaction mixture was stirred at -78°C for 30 min. To this was added dropwise trimethylsilyl chloride (1.47 mL, 1258 mg, 11.582 mmol) at -78°C , and then this reaction mixture was stirred at -78°C for 30 min. After warming to room temperature, the reaction mixture was poured into aqueous Na_2SO_3 and was then extracted with ether. The ether extract was washed successively with aqueous NaHCO_3 , water and then brine, and was then dried over Na_2SO_4 . Solvent evaporation from the dried extract gave pale yellow crystals (1228 mg), which were chromatographed on silica gel by eluting with a mixture of toluene–hexane (1:1, v/v) to give pure 2,2-bis(4-methyl-5-trimethylsilyl-3-thienyl)-1,3-dioxolane (**17**) as colorless plates (1052 mg, 88%): mp $130\text{--}131^\circ\text{C}$; $^1\text{H NMR}$ (CDCl_3 , 200 MHz) δ 7.41 (2H, s, H-2), 4.07 (4H, s, $\text{OCH}_2\text{CH}_2\text{O}$), 2.21 (6H, s, Me), 0.32 (18H, s, SiMe_3); IR (KBr) 3120, 2954, 2893, 2879, 1525, 1452, 1406, 1375, 1360, 1250, 1184, 1159, 1063, 1041, 968, 837, 781, 752, 710, 688, 629 cm^{-1} ; MS (DEI, 70 eV) m/z (rel intensity) 412 ($\text{M}^+ + 2$, 6.84), 411 ($\text{M}^+ + 1$, 11.04), 410 (M^+ , 31.23), 395 ($\text{M}^+ - \text{Me}$, 13.40), 241 ($\text{M}^+ - \text{C}_8\text{H}_{13}\text{SSi}$, 100); HRMS (EI, 110 eV) m/z 410.1214 (M^+) (Calcd for $\text{C}_{19}\text{H}_{30}\text{O}_2\text{S}_2\text{Si}_2$: 410.1226). Found: C, 55.34; H, 7.61%. Calcd for $\text{C}_{19}\text{H}_{30}\text{O}_2\text{S}_2\text{Si}_2$: C, 55.56; H, 7.36%.

4-Ethylenedioxy-3,5-dimethyl-4H-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene (18). To a solution of **17** (700 mg, 1.704 mmol) in anhydrous ether (70 mL) was added dropwise *t*-butyllithium (1.47 M pentane solution, 2.55 mL, 3.749 mmol) with stirring at -78°C under argon atmosphere. After the reaction mixture was stirred for 30 min at -78°C under argon atmosphere, copper(II) chloride (1833 mg, 13.633 mmol) was added, and then this reaction mixture was stirred for another 30 min at -78°C . After being warmed to room temperature, the reaction mixture was stirred for 3 h at room temperature. The inorganic precipitate was removed by filtration through a glass disk. Then the filtrate was poured into water and extracted with ether. The ether extract was washed successively with aqueous NaHCO_3 , water, and then brine, and was then dried over Na_2SO_4 . Solvent evaporation from the dried extract gave crude 4-ethylenedioxy-3,5-dimethyl-2,6-bis(trimethylsilyl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene as a reddish oil (638 mg), which was used in the following reaction without further purification. To an anhydrous THF (40 mL) solution of crude 4-ethylenedioxy-3,5-dimethyl-2,6-bis(trimethylsilyl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene (638 mg, ca. 1.56 mmol) was added dropwise a THF solution of tetrabutylammonium fluoride (TBAF: 1.0 M THF solution containing 5% water, 3.12 mL). After stirring for 2 h at room temperature, the reaction mixture was poured into aqueous NaHCO_3 and then extracted with ether. The ether extract was washed with water and then brine, and was then dried over Na_2SO_4 . Solvent evaporation from the dried extract gave a crude product (450 mg), which was chromatographed on silica gel by eluting with toluene to give pure 4-ethylenedioxy-3,5-dimethyl-4H-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene (**18**) as colorless needles (309 mg, 75%): mp $138\text{--}139^\circ\text{C}$ (decomp); $^1\text{H NMR}$ (CDCl_3 , 200 MHz) δ 6.67 (2H, q, $J_{2,\text{Me}} = J_{5,\text{Me}} = 1.0$ Hz, H-2, 6), 4.33 (4H, s, $\text{OCH}_2\text{CH}_2\text{O}$), 2.25 (6H, d, $J_{2,\text{Me}} = J_{5,\text{Me}} = 1.0$ Hz, Me); IR (KBr) 3095, 2952, 2891, 1522, 1435, 1383, 1325, 1211, 1165, 1076, 1020, 980, 949, 843, 715 cm^{-1} ; MS (DEI, 110 eV) m/z

(rel intensity) 266 ($\text{M}^+ + 2$, 12.14), 265 ($\text{M}^+ + 1$, 16.78), 264 (M^+ , 100); HRMS (EI, 110 eV) m/z 264.0287 (M^+) (Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}_2$: 264.0279). Found: C, 58.83; H, 4.66%. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}_2$: C, 59.06; H, 4.58%.

4-Ethylenedioxy-2,6-diiodo-3,5-dimethyl-4H-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene (19). To a solution of **18** (590 mg, 2.232 mmol) in a mixture of anhydrous chloroform (30 mL) and acetic acid (30 mL) was added NIS (1105 mg, 4.911 mmol) with stirring at room temperature under argon atmosphere. Then, this reaction mixture was stirred for 2 h at room temperature, and then was poured into aqueous Na_2SO_3 . The resulting mixture was extracted with chloroform. The chloroform extract was washed successively with aqueous NaHCO_3 , water, and brine, and was then dried over Na_2SO_4 . Solvent evaporation from the dried extract gave a crude product, which was chromatographed on silica gel by eluting with toluene to give pure 4-ethylenedioxy-2,6-diiodo-3,5-dimethyl-4H-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene (**19**) as yellow needles (878 mg, 76.2%): mp $184\text{--}185^\circ\text{C}$ (decomp); $^1\text{H NMR}$ (CDCl_3 , 200 MHz) δ 4.36 (4H, s, $\text{OCH}_2\text{CH}_2\text{O}$), 2.18 (6H, s, Me); IR (KBr) 2891, 1718, 1512, 1417, 1373, 1315, 1196, 1149, 1082, 1026, 980, 951, 795, 737, 596 cm^{-1} ; MS (DEI, 110 eV) m/z (rel intensity) 518 ($\text{M}^+ + 2$, 12.09), 517 ($\text{M}^+ + 1$, 16.51), 516 (M^+ , 100); HRMS (EI, 110 eV) m/z 515.8214 (M^+) (Calcd for $\text{C}_{13}\text{H}_{10}\text{I}_2\text{O}_2\text{S}_2$: 515.8212). Found: C, 30.19; H, 2.17; I, 48.94%. Calcd for $\text{C}_{13}\text{H}_{10}\text{I}_2\text{O}_2\text{S}_2$: C, 30.25; H, 1.95; I, 49.17%.

2,6-Bis(dicyanomethylene)-4-ethylenedioxy-3,5-dimethyl-2,6-dihydro-4H-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene (EO-Me₂-CPDT-TCNQ: 20). To a suspension of sodium hydride (60 wt %, 62.0 mg, 0.450 mmol) in anhydrous THF (5 mL) was added dropwise a solution of malononitrile (51.0 mg, 0.772 mmol) in anhydrous THF (5 mL) at room temperature under argon atmosphere. Then, the reaction mixture was stirred for 10 min at room temperature. To this were added successively a solution of **19** (100.0 mg, 0.194 mmol) in anhydrous THF (5 mL) and $[\text{Pd}(\text{PPh}_3)_4]$ (45.0 mg, 0.0389 mmol). The reaction mixture was stirred at 50°C for 2 h, and then stirred for 2 h at the refluxing temperature. After cooling to room temperature, the reaction mixture was poured into a mixture of bromine (0.5 mL) and water (20 mL). Then, the resulting mixture was poured into aqueous Na_2SO_3 and extracted with dichloromethane. The dichloromethane extract was washed with aqueous NaHCO_3 , water, and brine, and was then dried over Na_2SO_4 . Solvent evaporation from the dried extract gave a crude product, which was chromatographed on silica gel by eluting with dichloromethane to give pure 2,6-bis(dicyanomethylene)-4-ethylenedioxy-3,5-dimethyl-2,6-dihydro-4H-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene (EO-Me₂CPDT-TCNQ: **20**) as a violet powder (34.8 mg, 45.8%): mp $> 300^\circ\text{C}$; $^1\text{H NMR}$ (CDCl_3 , 200 MHz) δ 4.46 (4H, s, $\text{OCH}_2\text{CH}_2\text{O}$), 2.49 (6H, s, Me); IR (KBr) 2214, 1496, 1439, 1383, 1346, 1269, 1244, 1174, 1066, 1034, 1009, 989, 951, 874 cm^{-1} ; HRMS (EI, 110 eV) m/z 390.0251 (M^+) (Calcd for $\text{C}_{19}\text{H}_{10}\text{N}_4\text{O}_2\text{S}_2$: 390.0245). Found: C, 58.52; H, 2.44; N, 14.19%. Calcd for $\text{C}_{19}\text{H}_{10}\text{N}_4\text{O}_2\text{S}_2$: C, 58.45; H, 2.58; N, 14.35%.

2,6-Bis(dicyanomethylene)-3,5-dimethyl-2,6-dihydro-4H-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophen-4-one (Me₂CPDT-TCNQ: 3). To a solution of **20** (35.0 mg, 0.0896 mmol) in dichloromethane (70 mL) was added 70% perchloric acid (35 mL) with stirring at 10°C . The reaction mixture was warmed to 20°C , and then stirred at 20°C for 24 h. The reaction mixture was poured into ice-water, and then was extracted with dichloromethane. The dichloromethane extract was washed with aqueous NaHCO_3 , water, and then brine, and was then dried over Na_2SO_4 . Solvent evaporation from the dried extract gave a crude product (29.7 mg), which was chro-

matographed on silica gel by eluting with dichloromethane to give pure 2,6-bis(dicyanomethylene)-3,5-dimethyl-2,6-dihydro-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (Me₂CPDT-TCNQ: **3**) as a violet powder (26.2 mg, 84.4%): mp > 300 °C; ¹H NMR (CDCl₃, 200 MHz) δ 2.75 (6H, s, Me); IR (KBr) 2958, 2922, 2854, 2362, 2212, 1720, 1496, 1377, 1329, 1263, 1200, 1101, 1022, 874 cm⁻¹; UV-vis (CH₂Cl₂) λ/nm (log ε) 531 (4.47), 500 (4.37), 476 (sh, 4.10), 362 (2.84), 346 (2.92), 278 (3.41), 269 (3.47); HRMS (EI, 110 eV) *m/z* 345.9986 (M⁺) (Calcd for C₁₇H₆N₄O₂: 345.9983). Found: C, 58.77; H, 1.87; N, 15.89%. Calcd for C₁₇H₆N₄O₂: C, 58.95; H, 1.75; N, 16.17%.

Me₄N(Me₂CPDT-TCNQ)₂. Black needles, mp > 300 °C; IR (KBr) 2179, 1707, 1460, 1419, 1379, 1313, 1215, 1161, 1149 1083 cm⁻¹. Found: C, 59.33; H, 3.37; N, 16.27%. Calcd for C₃₈H₂₄N₉O₂S₄: C, 59.51; H, 3.15; N, 16.44%.

Me₄P(Me₂CPDT-TCNQ)₂. Black needles, mp > 300 °C; IR (KBr) 2193, 2175, 1711, 1462, 1421, 1379, 1321 (br), 1275, 1213, 1122 (br), 1080, 982 cm⁻¹. Found: C, 58.08; H, 3.35; N, 13.96%. Calcd for C₃₈H₂₄N₈O₂S₄P: C, 58.22; H, 3.09; N, 14.29%.

Me₄As(Me₂CPDT-TCNQ)₂. Black needles, mp > 300 °C; IR (KBr) 2193, 2173, 1711, 1462, 1421, 1379, 1321 (br), 1273, 1211, 1115 (br), 1076, 930 cm⁻¹. Found: C, 54.95; H, 3.21; N, 13.28%. Calcd for C₃₈H₂₄N₈O₂S₄As: C, 55.13; H, 2.92; N, 13.54%.

Me₄Sb(Me₂CPDT-TCNQ)₂. Black needles, mp > 300 °C; IR (KBr) 2189, 2168, 1711, 1460, 1415, 1379, 1317, 1277, 1211, 1167, 1132 (br), 1115 (br), 1078, 993, 908, 866 cm⁻¹. Found: C, 51.91; H, 3.02; N, 12.57%. Calcd for C₃₈H₂₄N₈O₂S₄Sb: C, 52.18; H, 2.77; N, 12.81%.

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References

- 1 J. Ferraris, D. O. Cowan, V. J. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).
- 2 R. C. Wheland, *J. Am. Chem. Soc.*, **98**, 3926 (1979); R. C. Wheland and J. L. Gilson, *J. Am. Chem. Soc.*, **98**, 3916 (1976); A. Andrieux, P. M. Chaikin, C. Duroire, D. Je'rome, C. Weyl, K. Bechgaard, and J. R. Anderson, *J. Phys.*, **40**, 1199 (1979); H. Urayama and G. Sato, *Synth. Met.*, **19**, 469 (1987).
- 3 A. Aumüller, P. Erk, G. Klebe, S. Hünig, J. U. von Schütz, and H.-P. Werner, *Angew. Chem., Int. Ed. Engl.*, **25**, 740 (1986); S. Hünig and P. Erk, *Adv. Mater.*, **3**, 225 (1991).
- 4 T. Otsuka, A. Kobayashi, Y. Miyamoto, J. Kiuchi, N. Wada, E. Ojima, H. Fujiwara, and H. Kobayashi, *Chem. Lett.*, **2000**, 732; T. Otsuka, A. Kobayashi, Y. Miyamoto, J. Kikuchi, S. Nakamura, N. Wada, E. Fujiwara, H. Fujiwara, and H. Kobayashi, *J. Solid State Chem.*, **159**, 407 (2001); R. Kato, *Kotai Butsuri*, **28**, 141 (1993).
- 5 K. Yui, Y. Aso, T. Otsubo, and F. Ogura, *J. Chem. Soc., Chem. Commun.*, **1987**, 1816; K. Yui, Y. Aso, T. Otsubo, and F. Ogura, *Bull. Chem. Soc. Jpn.*, **62**, 1539 (1989).
- 6 K. Takahashi and S. Tarutani, *J. Chem. Soc., Chem. Commun.*, **1994**, 519; K. Takahashi and S. Tarutani, *Adv. Mater.*, **1995**, 639; K. Takahashi and S. Tarutani, *Synth. Met.*, **70**, 1165 (1995); S. Tarutani, T. Mori, H. Mori, S. Tanaka, and K. Takahashi, *Chem. Lett.*, **1997**, 627.
- 7 E. Günther, S. Hünig, K. Peters, H. Rieder, H. G. von Schnering, J.-U. von Schütz, S. Söderholm, H.-P. Werner, and H. C. Wolf, *Angew. Chem., Int. Ed. Engl.*, **29**, 204 (1990).
- 8 a) K. Takahashi and S. Tarutani, *Chem. Commun.*, **1998**, 1233. b) S. Tarutani and K. Takahashi, *Bull. Chem. Soc. Jpn.*, **77**, 463 (2004).
- 9 J. Yamaura, R. Kato, H. Tajima, S. Tarutani, and K. Takahashi, *Synth. Met.*, **103**, 2212 (1999).
- 10 S. Gronowitz, P. Moses, A.-B. Hörnfeldt, and R. Hakansson, *Ark. Kemi*, **17**, 165 (1961).
- 11 M. Uno, K. Seto, and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, **1984**, 932; M. Uno, K. Seto, M. Sasuda, W. Ueda, and S. Takahashi, *Tetrahedron Lett.*, **26**, 1553 (1985).
- 12 The destabilization extent of the LUMO level of **3** is about a half of the destabilization extent of the HOMO level of **3**. However, the half-wave reduction potentials obtained by cyclic voltammetry are much more reliable to know the energy levels of the LUMOs.
- 13 G. Saito and J. P. Ferraris, *J. Chem. Soc., Chem. Commun.*, **1979**, 1027.
- 14 R. C. Wheland and J. L. Gilson, *J. Am. Chem. Soc.*, **98**, 3916 (1976); R. C. Wheland, *J. Am. Chem. Soc.*, **98**, 3926 (1976).
- 15 K. Deuchert and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, **17**, 875 (1978); S. Hünig, *Pure Appl. Chem.*, **62**, 395 (1990); M. Horner and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, **16**, 410 (1977).
- 16 S. Tarutani, J. Yamaura, K. Takahashi, and R. Kato, *Solid State Commun.*, **123**, 251 (2002).
- 17 J. Yamaura, M. Fujiwara, R. Kato, T. Chonan, and K. Takahashi, *Synth. Met.*, **120**, 913 (2001).