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SYNTHESIS AND PROPERTIES OF A NEW DONOR-ACCEPTOR DIAD COMPOSED OF DT-TTF AND DICYANOMETHYLIDENE GROUP

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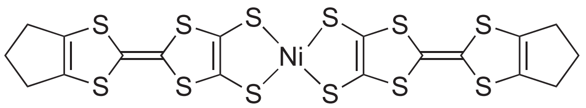
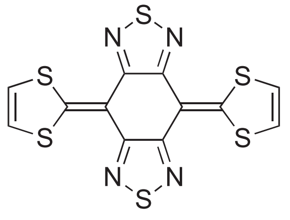
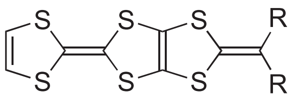
Abstract – Several derivatives of a new donor-acceptor diad **1** composed of DT-TTF and dicyanomethylidene group were synthesized. The IR spectra of **1** demonstrated considerable contribution of a polarized structure. Electronic spectra and molecular orbital calculation suggested that the absorption maximum of **1** was due to NHOMO-LUMO transition. Cyclic voltammetry revealed that the compound **1** exhibited three-stage of oxidation and one-stage of reduction processes. The bis(methylthio)-substitudted derivative **1a** exhibited conductivity of 10^{-6} S cm^{-1} in spite of a single-component material.

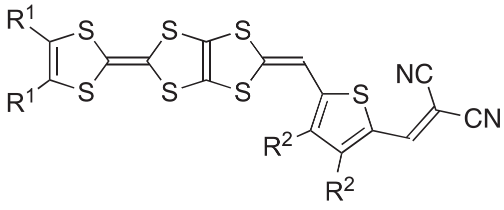
INTRODUCTION

Tetrathiafulvalene (TTF) is a two-stage redox system, which forms one and two aromatic 1,3-dithiolylium cationic structures in the one- and two-electrons oxidized states. TTF and its derivatives have played a leading role for the development of conductive molecular organic materials, because their high planarity in the oxidized states has advantage for the formation of molecular stacks and resulting wide bands.[1] On the other hand, TTF derivatives with strongly electron-withdrawing site have received considerable attention as candidates for electronic materials such as single-component molecular conductors, non-linear optics, field-effect transistors and so on.[2,3] As for development of highly conducting single-component materials, decrease in HOMO-LUMO gap is an indispensable requirement. The strategies for reducing HOMO-LUMO gap are as follows; (i) realization of effective intermolecular overlaps to form a wide band,[3-5] (ii) introduction of electron-accepting unit to lower the LUMO.[4-6] Kobayashi and co-workers reported that a metal complex, Ni(tmdt)$_2$ which has TTF dithiolene as a ligand, showed high electrical conductivity of 400 S cm^{-1} at room temperature and exhibited metallic conducting behavior down to 0.6 K.[4] Stable metallic behavior of Ni(tmdt)$_2$ is derived from the presence of electron-donating TTF moiety and electron-accepting nickel bis(dithiolene) moiety as well as three-dimensional electronic structure of the $Ni(tmdt)_2$ crystal.[4] As for purely organic molecular materials which does not contain any metal atom, the highest conductivity of 3.7 x 10^{-3} S cm^{-1} was observed in a single crystal of BTQBT, which includes thiadiazole rings as acceptor units in an quinoid-extended TTF molecule.[5] In the development of new purely organic single component molecular conductors, 1,3-dithiolo[4,5-*d*]-TTF (DT-TTF)[7,8] is a promising donor unit, because DT-TTF derivatives have many molecular conductors showing metallic conductivity down to low temperature (≤ 4.2 K).[8] In this paper, we report the synthesis and properties of new donor-acceptor (D-A) diads **1a–c**, which have DT-TTF moiety as a donor unit.


$Ni(tmdt)_2$


BTQBT

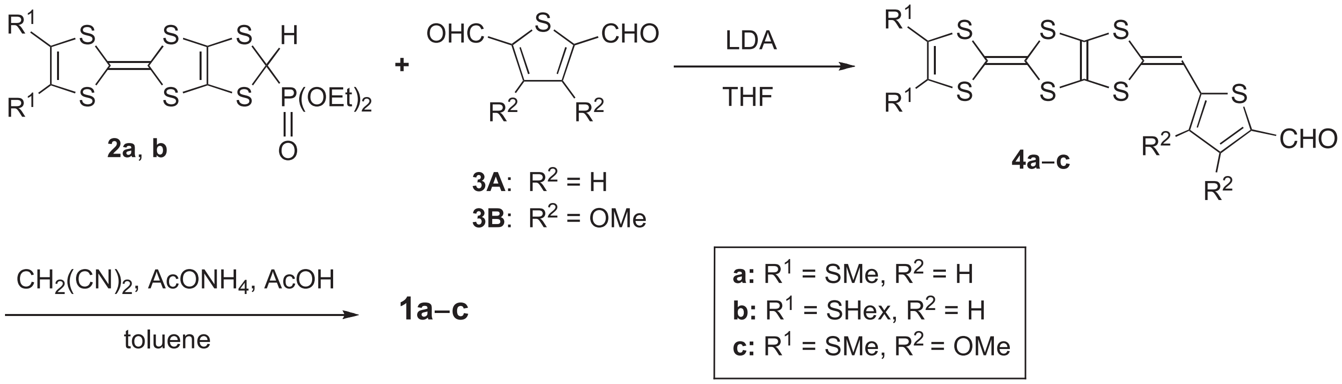

DT-TTF



1a: R^1 = SMe, R^2 = H
1b: R^1 = SHex, R^2 = H
1c: R^1 = SMe, R^2 = OMe

RESULTS AND DISCUSSION

The synthesis of new D-A diads was carried out according to Scheme 1. Phosphonates with TTF core (**2a**, **b**)[9] were treated with thiophene dicarboaldehyde derivatives (**3A**, **B**) in the presence of LDA to give the mono adducts **4a–c** in 66–89% yields. In this reaction, an excess amount (1.5 equiv. mol) of **3** was



a: R^1 = SMe, R^2 = H
b: R^1 = SHex, R^2 = H
c: R^1 = SMe, R^2 = OMe

Scheme 1

used so as to avoid the formation of the bis-adducts. The reaction of **4a–c** with an excess of malononitrile in the presence of ammonium acetate and acetic acid in refluxing toluene[10] gave the target molecules **1a–c** in 86–95% yields.

In the IR spectra, all the derivatives of **1** exhibited the cyano stretching band at 2210-2211 cm^{-1}, which is lower by 14-15 cm^{-1} than that of TCNQ (2225 cm^{-1}), and is higher by 27 cm^{-1} than that of $TCNQ^{\bullet}$ (2183 cm^{-1}). This result indicates considerable contribution of a polarized structure as shown in Figure 1, in other words, the molecule **1** is situated in an intramolecular charge-transfer (ICT) state. The degree of charge-transfer was estimated to be about 0.3 on the basis of comparison of the wavenumber of the cyano stretching absorption band according to the Chapell's equation.[11]

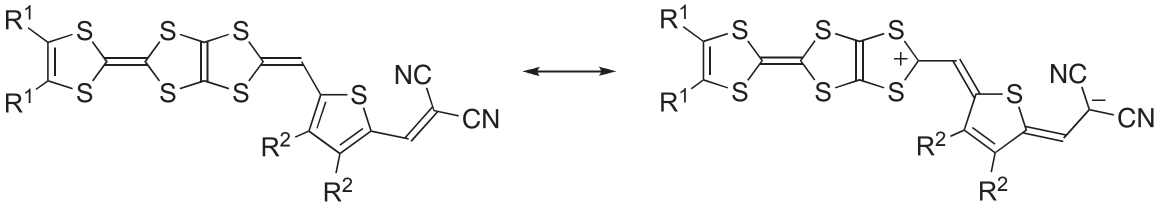


Figure 1. Plausible resonance structures of **1**

Figure 2 shows electronic spectra of **1a** and **1c** measured in dicholoromethane together with their related compounds. Both compounds exhibited three absorption maxima at 568, 460 and 322 nm for **1a**, 584, 489 and 324 nm for **1c**, respectively. The absorption maximum at the longest wavelength region of **1c** slightly shifted by 10 nm to the longer wavelength region than **1a**. This result suggests that introduction of electron-donating methoxy groups might not be effective for enhancement of the occupied molecular orbitals. The absorption maximum at the longest wavelength region of **1a** was longer by 175 nm than that of **5**[12] due to the presence of strongly electron-withdrawing dicyanomethylidene moiety. In contrast, the red-shift of the absorption maximum at the longest wavelength region of **1a** was only 21 nm compared to **6**[10] in spite of the presence of strongly electron-donating TTF moiety.

The molecular orbital calculation of unsubstituted derivative **1A** and its related compounds **5A** and **6A** was carried out based on the density functional theory (DFT) using B3LYP/6–31+G method.[13] Figure 3 shows an optimized structure of **1A**. The 1,3-dithiole ring fused with the TTF moiety, thiophene ring, and the dicyanomethylidene moiety have high planarity, indicating effective conjugation between the donor and the acceptor moieties. However, the DT-TTF moiety is a little bent with a dihedral angle of 21.3°. As shown in Figure 4, the HOMO of **1A** mainly distributed on the DT-TTF moiety. On the other hand, the second highest occupied orbital (NHOMO) spread over the whole molecule, although the molecular orbital coefficients of the sulfur atoms in the 1,3-dithiole ring fused with **6A** was smaller than those of the others. The LUMO distributed on only the moiety of **6A**, while the TTF moiety mainly contributed to the

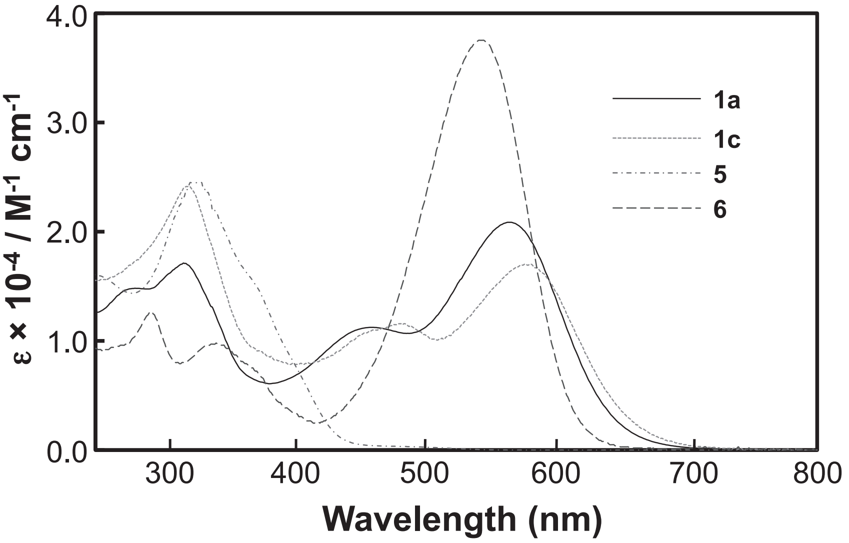
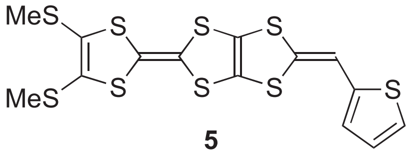
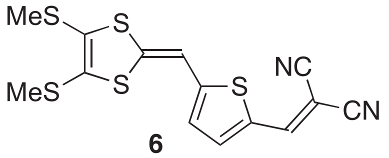


Figure 2. UV-Vis spectra of **1a**, **c** and the related compounds **5** and **6**

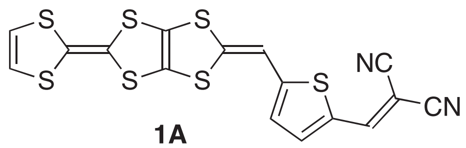


5

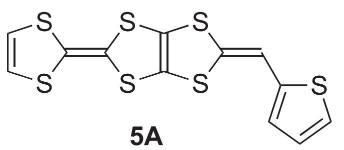


6

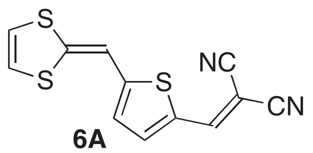
second lowest unoccupied molecular orbital (NLUMO). The shape of the HOMO, NHOMO, and NLUMO in the DT-TTF unit is close to those of **5A**. In contrast, NHOMO and LUMO of **1A** in the unit of **6A** resembled to HOMO and LUMO of **6A**. The energy levels of the HOMO and LUMO of **1A** were -5.141 and -2.856 eV, respectively (see Table 1). The energy gap of HOMO-LUMO in **6A** (2.720 eV) is



1A



5A



6A

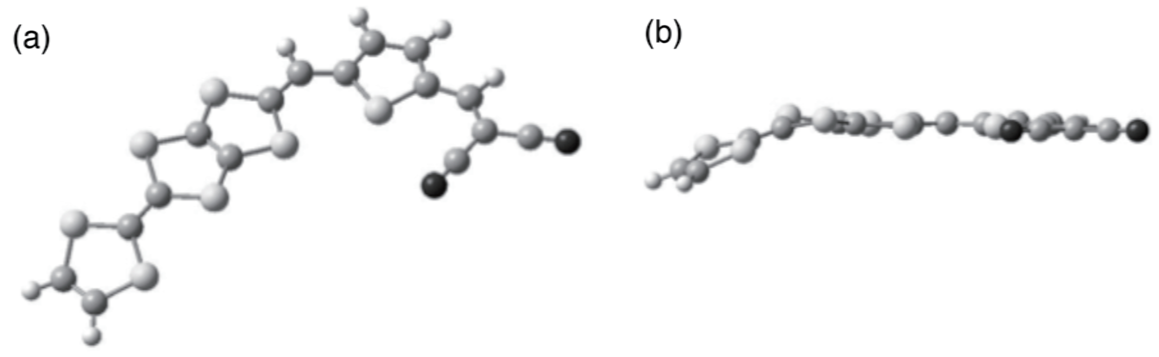


Figure 3. An optimized structure of **1A**; (a) top view and (b) side view

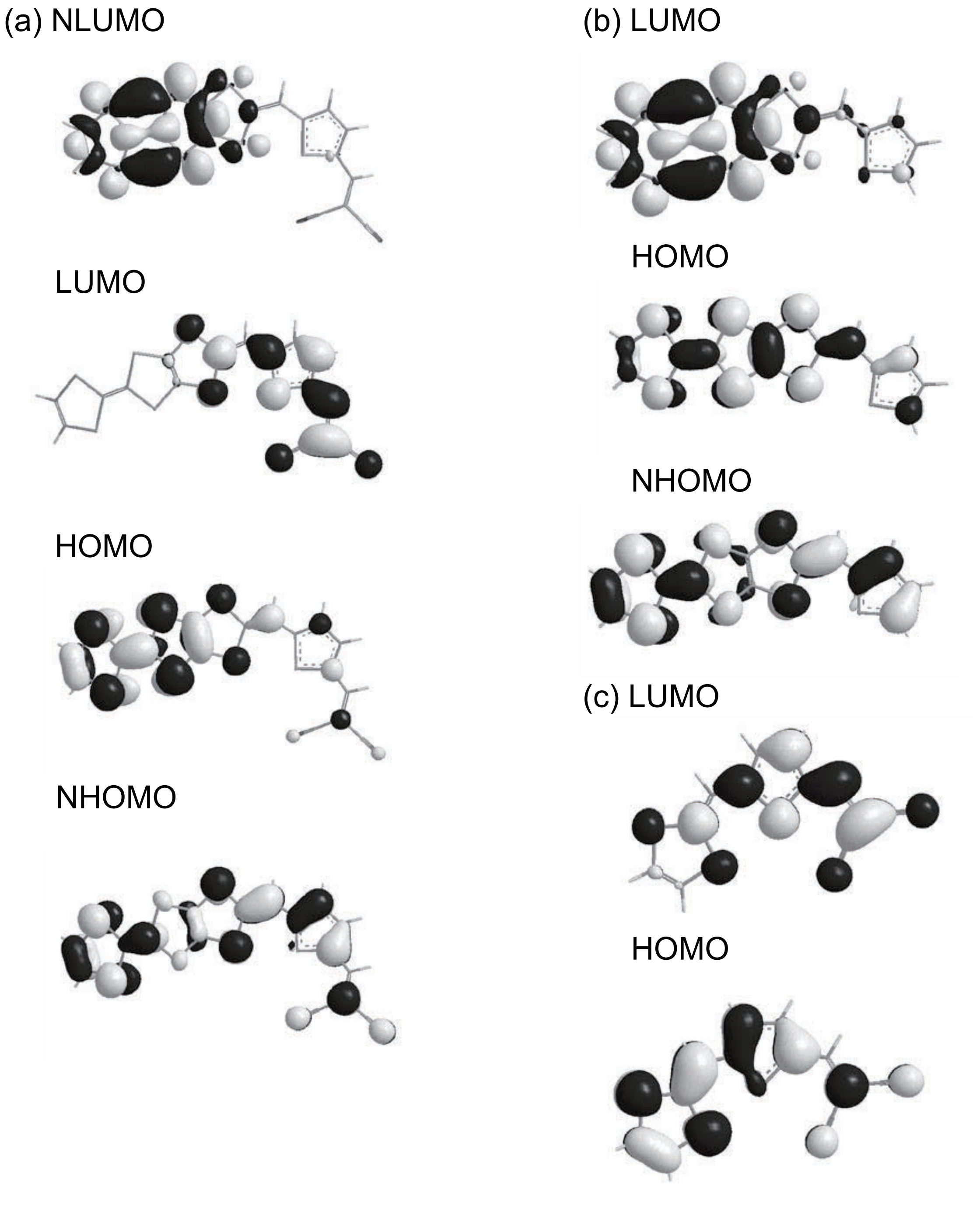


Figure 4. Molecular orbitals of (a) **1A**, (b) **5A**, and (c) **6A**

Table 1. Energy levels of the frontier orbitals of **1A** and its related compounds

	1A	**5A**	**6A**
NLUMO	-1.578		
LUMO	-2.856	-1.251	-2.747
HOMO	-5.141	-4.733	-5.467
NHOMO	-5.658	-5.277	

more close to the NHOMO-LUMO gap in **1A** (2.802 eV) than HOMO-LUMO gap in **1A** (2.285 eV). The absorption maximum at the longest wavelength region of **1a** was comparable to that of **6** as mentioned above. Considering the shape of the molecular orbitals and their energy difference obtained from the molecular orbital calculation, it is suggested that this absorption might be attributed to NHOMO-LUMO transition and that the HOMO-LUMO transition is forbidden.

Electrochemical properties of **1** were investigated by cyclic voltammetry. Figure 5 shows deconvoluted cyclic voltammograms of **1b** in benzonitrile and THF. All the derivatives exhibited three pairs of one-electron oxidation processes in both benzonitrile and THF. On the other hand, an irreversible reduction process was observed only in THF. The redox potentials of **1** are summarized in Table 2. All the

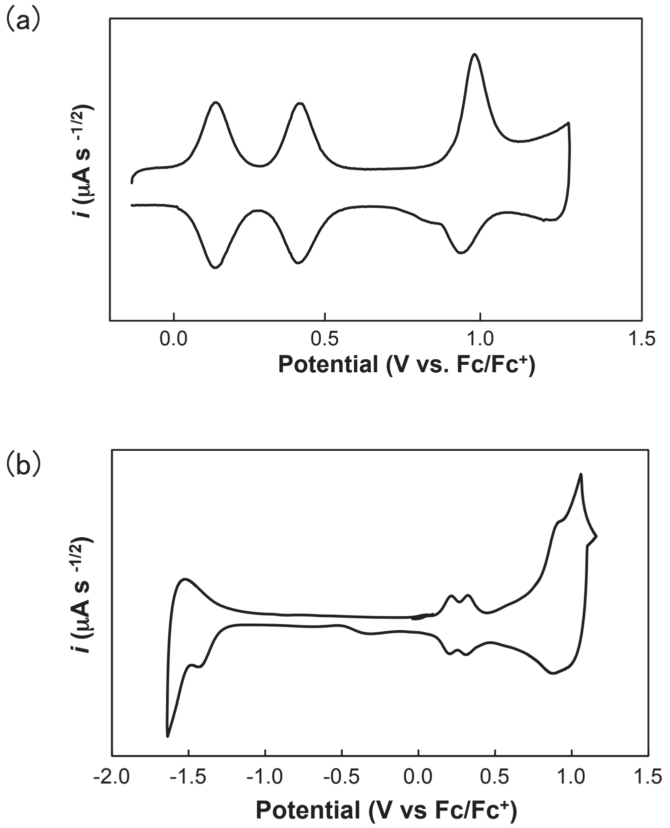


Figure 5. Deconvoluted cyclic voltammograms of **1b** (a) in PhCN and (b) in THF

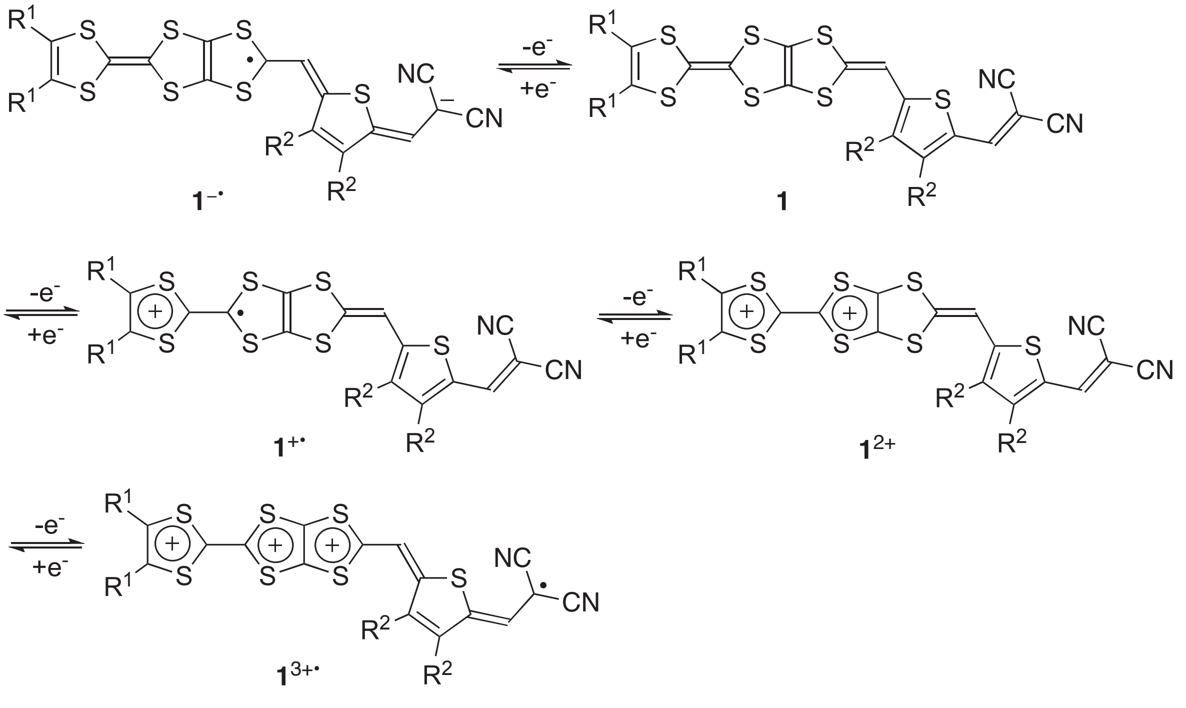
Table 2. Redox potentials of **1** containing 0.1 M $^{n}\mathrm{Bu_4N{\cdot}PF_6}$ (V vs Fc/Fc$^+$)

compound	solvent	E_1^{red}	E_1^{ox}	E_2^{ox}	E_3^{ox}
1a	THF	-1.36	0.11	0.22	0.81
1b	PhCN	-[a]	0.13	0.40	0.96
1b	THF	-1.38	0.12	0.23	0.81
1c	THF	-1.38	0.11	0.22	0.74
5	PhCN	-[a]	0.10	0.37	0.81
6	THF	-1.40	0.36		

[a] Not observed.

oxidation potentials of **1b** were higher than those of **5**, indicating that the oxidized species of **1b** were destabilized owing to electron withdrawing effect of the dicyanomethylidene moiety. The E_3^{ox} of **1a** shifted by 0.15 V to high potential region than **5**, while first and second ones shifted by only 0.03 V. The third oxidation process was more affected by the dicyanomethylidene moiety than the first and second ones, suggesting that the positive charges formed by the first and second oxidations mainly distributed in the TTF moiety (see Scheme 2). The 1,3-dithiol-2-ylidene unit fused with TTF, which is located more closely to the dicyanomethylidene moiety, mainly contributed to the third oxidation process (see also Scheme 2). On the other hand, the reduction potential of **1a** shifted by 0.04 V to positive voltage region compared with that of **6**. This result suggested the radical anion of **1a** might be destabilized owing to the presence of electron-donating TTF unit. The E_3^{ox} value of **1c** was lower by 0.07 V than that of **1a**. This result can be explained by contribution of a resonance structure in which a positive charge delocalized in a methoxy group as shown in Figure 6.

Spectroelectrochemistry of **1a** was investigated in order to elucidate the electronic structures of the oxidized species. Figure 7 shows the UV-vis-NIR spectra of **1a**, **5**, and their oxidized species in



Scheme 2. Redox process of **1**

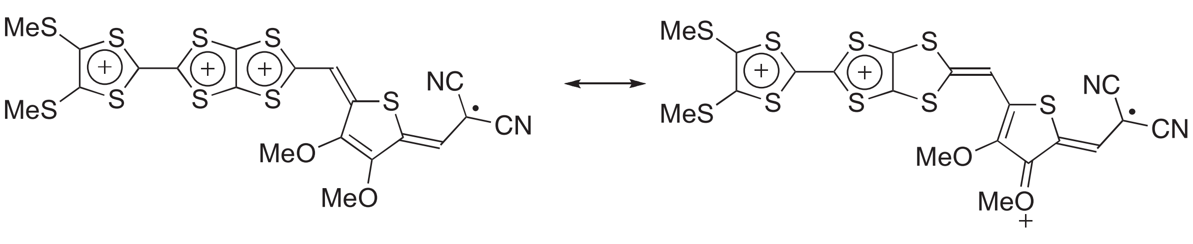


Figure 6. Plausible resonance structures of **1c**$^{3+\bullet}$

benzonitrile. All the oxidized species exhibited new absorption bands in the longer wavelength region at 935-1220 nm. These bands of oxidized species for **1a** blue-shifted to the shorter wavelength region, as the oxidation state became higher. Similar spectra were obtained for the oxidized species of **5** except for **5**$^{2+}$ in which a new shoulder band appeared at 1770 nm. The absorption bands at the longest wavelength region of **1a** and **5** in mono- and dicationic states were probably due to be ICT from the 1,3-dithiol-2-ylidene unit fused with TTF to the oxidized TTF moiety. The ICT bands of **1a**$^{+\bullet}$ and **1a**$^{2+}$ significantly blue-shifted compared with those of **5**, because the donating ability of the 1,3-dithiole-2-ylidene unit of **1a** is weakened owing to the presence of electron-withdrawing the dicyanomethilidene moiety compared with **5**.

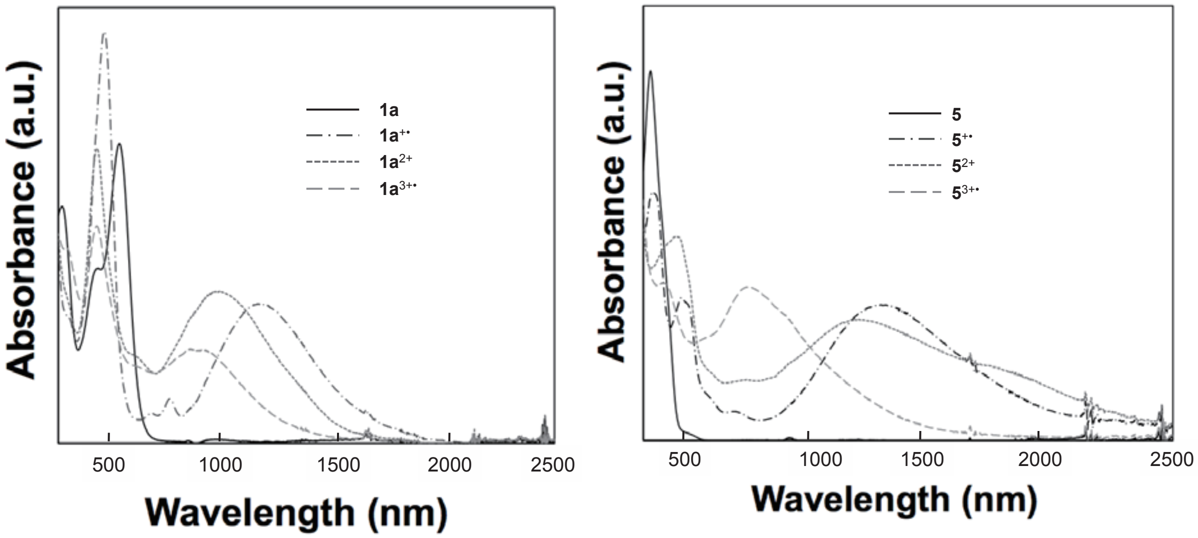


Figure 7. UV-vis-NIR Spectra of **1a**, **1a**$^{+\bullet}$, **1a**$^{2+}$, and **1a**$^{3+\bullet}$ (left), and **5**, **5**$^{+\bullet}$, **5**$^{2+}$, and **5**$^{3+\bullet}$ (right) generated by applying at a constant voltage in benzonitrile solution

The electrical conductivity of **1a** was measured on a compressed pellet using two-probe technique. It exhibited relatively high conductivity of 8.5 x 10^{-6} S cm^{-1} at room temperature in spite of a single-component material. On the other hand, the compound **5**, which has no dicyanomethylidene moiety, showed low conductivity of σ_{rt} = 1.6 x 10^{-9} S cm^{-1} on a compressed pellet. The conductivity of **6** was too low to be measured probably owing to little effective intermolecular overlap derived from small π-conjugation of the donor moiety.

Table 3. Absorption maxima of **1a**, **5**, **6**, and their oxidized species in benzonitrile

Oxidation state	**1a**	**5**	**6**
D	535	336	356, 557
D$^{+\bullet}$	508, 1220	354 486, 1318	352, 747
D^{2+}	478, 1023	456, 1208, 1770	
D$^{3+\bullet}$	478, 935	398, 750	

SUMMARY

In summary, we have succeeded in the synthesis of new donor-acceptor diads **1a**-**c**. Infrared and electronic spectra suggested that the molecules **1a**-**c** were situated in an ICT state from 1,3-dithiol-2-ylidene fused TTF moiety to dicyanomethylidene moiety, and the degree of CT was estimated to be about 0.3 from wavenumber of cyano stretching absorption band. The molecular orbital calculations based on DFT theory suggested the contribution of NHOMO-LUMO transition to the absorption band at the longest wavelength region in the electronic spectra of **1**. Cyclic voltammetry and spectroelecrochemistry indicated that positive charges in the mono- and dicationic states mainly distributed in the TTF moiety, and that ICT occurred from the 1,3-dithiol-2-ylidene unit fused with TTF moiety to oxidized TTF moiety. The compound **1a** exhibited relatively high electrical conductivity of 8.5 x 10^{-6} S cm^{-1} on a compressed pellet at room temperature in spite of a single-component material, while **5** and **6** showed lower conductivity than **1a**. The results obtained in this work bring much expectation that donor-acceptor diads possessing DT-TTF donor unit are a promising candidate to develop highly conducting purely organic single-component conductors.

EXPERIMENTAL

General Methods

^{1}H NMR spectra were recorded on JEOL NM-SCM270 spectrometer, operating at 270 MHz. Spectra are reported (in δ) with referenced to Me_4Si. $CDCl_3$ was used as solvent. MS spectra were determined on a SHIMADZU QP5050A Spectrometer, Applied Biosystem MALDI TOFMS Voyager-DE^{TM} PRO, and JEOL JMS-LX2000. Electronic spectra were recorded on Perkin Elmer Japan LAMBDA 750. Melting points were determined with a Yanaco MP-J3. The gaussian03 program package was used to all the optimized calculations. Cyclic voltammetry was performed by using a ALS/chi 617B Electrochemical analyzer. The cell for the cyclic voltammetry consisted of a Pt disk working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ reference electrode. The measurements were carried out in benzonitrile or THF solution containing 0.1 M $Bu_4N^+PF_6^-$ as a supporting electrolyte. All redox potentials were measured against Ag/Ag^+ and converted to vs. Fc/Fc^+. Spectroelectrochemistry was performed on a sample placed within a quartz cell with a path length of 1 mm. Pt gauze (100 mesh) was used as an optically transparent electrode. The reference and auxiliary electrodes were Ag and Pt wire respectively. UV-Vis-NIR spectra were acquired by using the same instrument as that described above. A fixed-potential electrolysis was performed by using the same electrochemical analyzer as that employed for the cyclic voltammetry measurement.

Typical Procedure for the Preparation of 4

4a: To a solution of **2a** (0.15 g, 0.30 mmol) and 2,5-thiophenedicarboxaldehyde (**3A**) (63 mg, 0.45 mmol) in THF (3 mL), a 0.5 M THF solution of LDA was slowly added at -78 °C under argon atmosphere. After the mixture was warmed up at 0 °C, MeOH was added. The resultant precipitate was filtered off, and washed with MeOH. The precipitate was purified by column chromatography on silica gel using CH_2Cl_2 elution to afford **4a** (98 mg, 0.20 mmol) in 66% yield; purple solid; mp 172-173 °C; IR (KBr) 2915, 1630, 1561, 1427, 1397, 1277, 1054, 765 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.68 (d, 1H), 6.93 (d, 1H), 6.88 (s, 1H), 6.85 (s, 1H), 2.45 (s, 3H), 2.43 (s, 3H); MS (MALDI) m/z = 494 [M^+]; Anal. Calcd for $C_{15}H_{10}OS_9$: C, 36.41; H, 2.04. Found: C, 36.44; H, 2.04.

4b: The same manner as for **4a** was adopted for the synthesis of **4b** and a purple solid of **4b** was obtained in 78%; mp 117-119 °C; IR (KBr) 2916, 2788, 2372, 2345, 1653, 1560, 1543, 1497, 1429, 1221, 1051 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.56 (d, 1H), 6.88 (d, 1H), 6.85 (s, 1H), 2.72-2.79 (m, 4H), 1.2-1.6 (m, 20H), 0.82 (t, 6H); MS (MALDI) m/z = 634 [M^+]; Anal. Calcd for $C_{25}H_{30}OS_9$: C, 47.28; H, 4.76. Found: C, 47.11; H, 4.60.

4c: The same manner as for **4a** was adopted for the synthesis of **4c** and a purple solid of **4c** was obtained in 89%; mp 124-125 °C; IR (KBr) 2917, 2345, 1637, 1470, 1428, 1398, 1279, 1056 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 9.98 (s, 1H), 6.88 (s, 1H), 4.13 (s, 3H), 3.84 (s, 3H), 2.44 (s, 3H), 2.43 (s, 3H); MS (MALDI) m/z = 554 [M^+]; Anal. Calcd for $C_{17}H_{14}O_3S_9$: C, 36.80; H, 2.54. Found: C, 37.01; H, 2.51.

Typical Procedure for the Preparation of 1

1a: Acetic acid (0.3 mL) was added to a solution of **4a** (62 mg, 0.13 mmol), malononitrile (42 mg, 0.64 mmol), and ammonium acetate (224 mg, 2.90 mmol) in toluene (16 mL) under argon atmosphere. The reaction mixture was stirred for 2 h under reflux. After the reaction mixture was cooled down to room temperature, the precipitate was collected by filtration and washed with MeOH. The precipitate was column chromatographed on silica gel eluted with CH_2Cl_2 to afford **1a** (62 mg, 0.11 mmol) in 95% yield; a black solid; mp 228-230 °C; IR (KBr) 2211, 1570, 1536, 1501, 1422, 1349, 1282, 1062 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.63 (d, 1H), 6.93 (d, 1H), 6.86 (s, 1H), 2.45 (s, 6H); MS (MALDI) m/z = 542.14 [M^+]; Anal. Calcd for $C_{18}H_{10}N_2S_9$: C, 39.82; H, 1.86; N, 5.16. Found: C, 39.80; H, 2.07; N, 4.88.

1b: The same manner as for **1a** was adopted for the synthesis of **1b** and a black solid was obtained in 86%; mp 158-159 °C; IR (KBr) 2957, 2921, 2850, 2210, 1570, 1534, 1261, 1068 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.56 (d, 1H), 6.88 (d, 1H), 6.85 (s, 1H), 2.72-2.79 (m, 4H), 1.2-1.6 (m, 20H), 0.82 (t, 6H); MS (MALDI) *m/z* = 682.55 [M$^+$], HRMS (LDI): calcd for $C_{28}H_{30}N_2S_9$: 681.9895. Found: 981.9907.

1c: The same manner as for **1a** was adopted for the synthesis of **1c** and a black solid was obtained in 87%; mp 157-158 °C; IR (KBr) 2915, 2210, 1536, 1469, 1399, 1292, 1166, 1057 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.64 (s, 1H), 6.95 (s, 1H), 6.93 (s, 1H), 2.45 (s, 6H); MS (MALDI) *m/z* = 602 [M$^+$], HRMS (LDI): calcd for $C_{20}H_{14}N_2O_2S_9$: 601.8542. Found: 601.8525.

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12. The compound **5** was newly synthesized by the reaction of **2a** with 2-thiophenecraboaldehyde in the presence of LDA in THF at -78 °C. a purple solid; mp 177-178 °C; IR (KBr) 2917, 2375, 1571, 1545, 1421, 1312, 683, 671 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.56 (s, 1H), 6.88 (s, 1H), 6.85 (s, 1H), 2.76 (t, 4H), 1.2-1.6 (m, 20H), 0.82 (t, 6H); MS MS (MALDI) m/z = 466 [M$^+$]; Anal. Calcd for $C_{14}H_{10}S_9$: C, 36.02; H, 2.16. Found: C, 36.27; H, 2.22.
13. The molecular orbital calculation was carried out using the Gaussian 03 program. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Gaussian, Inc., Pittsburgh, PA, 2003.