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Synthesis and Properties of New Donors Linked Directly With Two or Three Tetrathiafulvalene Units

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SYNTHESIS AND PROPERTIES OF NEW DONORS LINKED DIRECTLY WITH TWO OR THREE TETRATHIAFULVALENE UNITS

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Abstract Synthesis and properties of new donors in which two or three TTF frameworks are linked with some dihedral angles to form extended π-conjugated systems are described. Complexation of these TTF derivatives with DDQ and iodine affords moderately conductive charge transfer complexes. Cyclic voltammetry indicates that the electron-ability of TTF-trimers is reduced by comparison of that of TTF-monomer but is slightly enhanced comparing with that of TTF-dimers.

Keywords: Tetrathiafulvalene, conductivity, charge transfer, redox potential

INTRODUCTION

Since the discovery of highly conductive cation radical salts of tetrathiafulvalene (TTF) derivatives, much effort has been put into the synthesis of donor molecules that endow their salts with metallic properties.[1] The importance of the following two strategies has been recognized for the modification on TTF skeleton: (i) the increase of dimensionality of conducting path in the cation radical salts, (ii) the decrease of on-site Coulombic repulsion in their dicationic states. In this context, molecular design of new donors satisfying both guidelines mentioned above is of considerable interest. Recently, the studies of donors containing linked TTF moieties have been reported extensively and the achievement of the guidelines have become a center of attraction.[2,3] Similarly to the reported donors, TTF-dimer **1** with directly linked two TTF units is one of the most promising donors and also is expected to form segregated stacks in its radical salts or charge-transfer complexes as TTF-monomers do. Thus, if the two TTF units in the molecule participate in the stacking array, the additional directions of TTF columns fixed with a certain dihedral angle will be possible. Contrary to that their complexed **1** or **2** will give no segregated stacks, an unique stacking mode will also be expected. Therefore, these donors are much interested in studying the relationship between the electrical conductivity and stacking array.

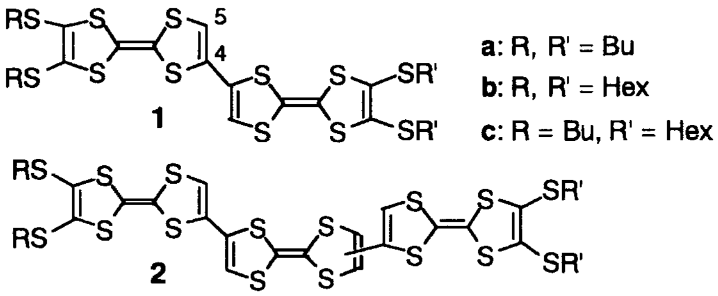
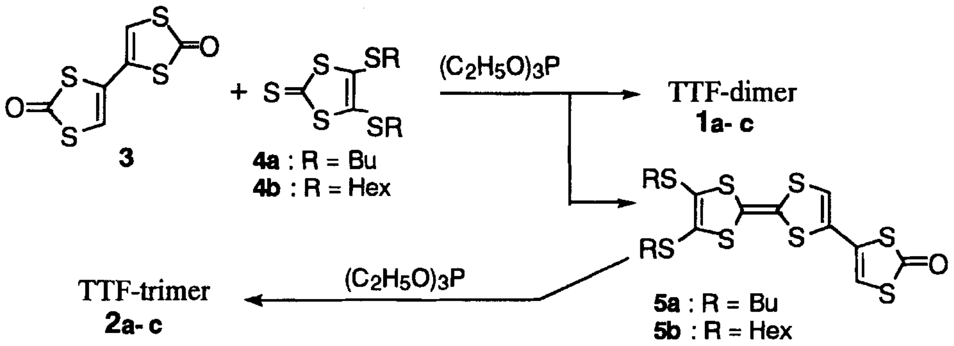


FIGURE 1 New TTF-dimers and -trimers.

Our research has been directed to the synthesis of more extended π-electron donors containing several number of TTF moieties. On-site Coulombic repulsion in its dicationic state is expected to decrease because of the extension of the donor π-electron system.[2] We now wish to report the synthesis of new donors containing two or three TTF units, their electrochemical behavior, and electrical conductivities of their charge transfer complexes with DDQ and iodine salts.

SYNTHESIS

TTF-dimers **1** and trimers **2** were synthesized as shown in Scheme 1. Coupling reactions of 4,4'-bi-1,3-dithiole-2,2'-dione **3**, which was prepared according to the literature with some modification[4], with 4,5-disubstituted-1,3-dithiole-2-thiones **4** were carried out in triethyl phosphite at 120°C for 4.5 h, and then the reaction products were purified by column chromatography on silica gel to give the desired TTF-dimers **1** in moderate yields as orange crystals (**1a**: 25%, **1b**: 21%). The unsymmetrical TTF-dimer **1c** was further purified by gel permeation chromatography with chloroform as an eluant (**1c**: 15%). TTF-trimers were also synthesized by cross-coupling reactions. Reactions of **4** with **3** in refluxing benzene in the presence of triethyl phosphite for 6-10h afforded half coupled TTF derivatives in good yields (**5a** : 37%, **5b** : 33%). Self-coupling of **5** proceeded with triethyl phsphite in refluxing toluene for 12 h under nitrogen atmosphere. The reaction mixture was chromatographed on silica gel with hexane-benzene (3:1) as an eluent to give **2** as orange fine crystals (**2a** : 13%, **2b** : 13%).



SCHEME Synthetic routes of **1** and **2**.

The unsymmetrical TTF-trimer **2c** was prepared by cross-coupling of **5a** and **5b** in a manner similar to that of symmetrical donor **2a**, and further purified by gel permeation chromatography with chloroform as an eluent, giving orange micro-crystals (4.6%). The syn or anti geometry referring to the two terminal TTF groups in TTF trimer **2** was not clear.

NMR AND ELECTRONIC SPECTRA

^{1}H NMR spectra of TTF-derivatives **1** and **2** were recorded in $CDCl_3$ solution at room temperature. Olefinic proton signals of TTF-dimers **1** and TTF-trimers **2** were observed as singlets at 6.22 and 6.21-6.23 ppm, respectively. The fact that there is no difference between the chemical shifts of olefinic protons of **1** and **2** suggests that dihedral angle of the two linked TTF units in TTF-dimers **1** is almost equal to that of TTF-trimers **2**. ^{13}C NMR chemical shifts of C-4 and C-5 carbon atoms of inner two 1,3-dithiole rings of TTF-dimers **1** as shown in Fig. 1 were observed at 118 ppm (quarternay carbon atoms) and ca. 111 ppm (tertiary carbon atoms), respectively. The same chemical shifts in ^{13}C NMR of TTF-trimer **2** were observed at 118 ppm (quarternay carbon atoms) and ca. 111 ppm (tertiary carbon atoms). These spectral data also support that dihedral angles of TTF units in TTF-dimers and -trimers are almost the same.

The electronic spectra of TTF derivatives **1** and **2** were measured in chloroform. The spectra of **1** were shown in Fig. 2 and the data were summarized in Table 1.

The absorption maxima of **1a-c** are observed at 316, 330, and 415 nm in all cases. Molar extinction coefficients of **1b** are the smallest among three TTF-dimers **1** in the range of measurement (300–600 nm). This hypochromic shift of **1b** indicates that the TTF units of different molecules are associated to each other in the solution by the hydrophobic interaction among long alkyl chains and intermolecular distances between two TTF frameworks in **1b** are the shortest of the three TTF-dimers **1**.

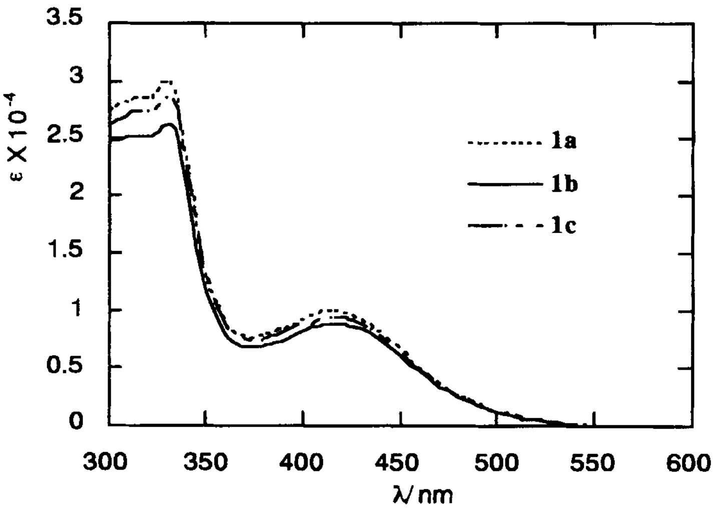


FIGURE 2 Electronic spectra of **1** in chloroform.

The side alkyl chains with TTF-dimer are considered to play a role to keep two TTF moieties closely in distances like a fastener (fastener effect)[5]. Since the fastener effect is observed only in the solid state, the reason of keeping in short distances between two TTF planes are not clear. The investigation to estimate the effects of these side chains on their absorption spectra by changing concentration of donors, temperature, and solvents are now in progress.

TABLE 1 The electronic spectral data of TTF-dimers and -trimers in chloroform.

Compound	λ_{max} (ε) in nm		
1a	316 (28600)	330 (29900)	415 (10100)
1b	316 (25200)	330 (26200)	415 (8850)
1c	316 (27400)	330 (28600)	415 (9600)
2a	318sh (57800)	328 (59500)	412 (23500)
2b	318sh (46400)	328 (47800)	412 (19300)
2c	316 (45700)	328 (47300)	412 (18500)

The absorption maxima of TTF-dimers **1** and TTF-trimers **2** are observed to be at the same wavelengths in all cases. This suggests that π-conjugation in trimers **2** is extended over only the two TTF moieties as if these were dimer systems. Although the mixture of syn and anti isomers is possible to be formed in the cases of trimers **2**, no evidence is obtained to show the existence of two isomers from NMR spectra and the separation of the mixture to each isomer is unsuccessful. Similar tendency about the hypochromic shift in TTF-trimers **2** as well as TTF-dimers **1** are also observed. In general, the absorption maxima of syn isomer appear at shorter wavelength than those of anti isomer. This observed result is considered from the existence of syn isomer with some extent in the mixture as one of the possibilities. Therefore the hydrophobic interactions among the long alkyl chanis are not predominant due to the skewed conformation in the cases of **1**.

ELECTROCHEMICAL PROPERTIES

The electrochemical properties of new TTF-dimers **1** and TTF-trimers **2** were studied by cyclic voltammetry. The redox potentials of **1** and **2** were measured by using tetrabutylammonium perchlorate as a supporting electrolyte in CH_2Cl_2 and the results were summarized along with those of TTF as a reference in Table 2.

TABLE 2 Redox potentials of TTF-dimers and -trimers in dichloromethane.

Compound	E_1	E_2	E_3	E_4	E_5	E_2-E_1
1a	0.28	0.45	0.74			0.17
1b	0.30	0.47	0.76			0.17
1c	0.28	0.44	0.72			0.16
2a	0.21	0.34	0.45	0.53	0.72	0.13
2b	0.20	0.34	0.45	0.54	0.74	0.14
2c	0.21	0.36	0.47	0.54	0.72	0.15
TTF	0.11	0.44				0.33

V vs. Ag/Ag^+, Pt electrode, 0.1M Bu_4NClO_4, scan rate 100mV/s.

Cyclic voltammograms of **1** and **2** showed three pairs and five pairs of reversible redox waves, respectively. **Both of E_1 and E_2 waves of 1 correspond to one-electron** redox processes, whereas the third E_3 wave shows two-electron process. Similar situations were observed for TTF trimers **2**. The reversible one-electron redox processes are observed for E_1 through E_4 and the last E_5 is two-electron redox process. The E_1 values of **2** are higher by 0.10-0.11V than that of TTF, but are lower by 0.07-0.10 V than those of TTF-dimers **1**. Judging from E_1 values, the donor abilities of **2** are somewhat reduced in all cases compared with that of TTF, but increased compared with those of TTF-dimers **1**. The ΔE ($=E_2-E_1$) values of **1** are smaller by 0.17-0.19 V than those of TTF, indicating that on-site Coulombic repulsion in their dicationic states is considerable reduced by extended and delocalized π-electron systems in **1**. The ΔE values of **2** are somewhat smaller by 0.03-0.04 V than those of **1**, suggesting that the two mono- cationic dithiole rings is kept in the distance. Consequently, on-site Coulombic repulsion in their dicationic states is also decreased compared with the cases of TTF-dimers **1** as expected.

Several attempts to complex **2a** with tetracyanoquinodimethane (TCNQ) were unsuccessful, presumably due to the insufficient donor ability compared with that of TTF. However, complexes of **2a** with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) and with iodine were easily formed in benzene as black fine needles or powders. The measurement of their electrical conductivities were carried out by two-probe method on compressed pellets at room temperature, and the results were summarized in Table 3 The ratios of donor to acceptor were determined by elemental analyses.

We are currently engaged in preparation of single crystals of **1** and **2** suitable for an X-ray crystallographic analysis, and detailed investigations on their electrical properties will be reported elsewhere.

TABLE 3 Electrical conductivities of the complexes of TTF-dimers and -trimers.

Donor	Acceptor	Crystal form	D:A	σ_{rt} /S cm^{-1}
1a	DDQ	black fine needles	2:3	1.22×10^{-3}
1a	I_3	black powder	1:2	1.43×10^{-3}
1c	DDQ	black fine needles	2:3	2.25×10^{-5}
1c	I_3	black powder	2:3	1.01×10^{-4}
2a	DDQ	black powder	undecided	1.98×10^{-4}
2b	I_3	black powder	3:4	1.22×10^{-3}
2c	DDQ	black powder	undecided	8.04×10^{-5}
2c	I_3	black powder	2:3	2.81×10^{-3}

EXPERIMENTAL

General Procedures.

All the melting points were uncorrected. ^{1}H NMR spectra (270 MHz) and ^{13}C NMR spectra (68 MHz) were recorded on a JEOL QX-270 in $CDCl_3$ solutions using Me_4Si as an internal standard. Mass spectra were obtained at an ionization energy of 70eV on Hitachi MS–2000S. IR spectra were recorded on a JACSO FT/IR VALOR–III spectrometer. UV-VIS spectra were taken on a Hitachi 220A spectrophotometer. Cyclic voltammetry was carried out on a BAS CV-50W. Electrical conductivities were measured on compressed pellets with a two-probe method. Elemental analyses were performed at the Service Centre of the Elementary Analysis of Organic Compounds affiliated to the Faculty of Science in Kyushu University. Gel permeation chromatography was carried out at JAICO LC-908 (eluent: $CHCl_3$).

2,2'-Bis[4,5-bis(butylthio)-1,3-dithiol-2-ylidene]-4,4'-bi-1,3-dithiole **1a.**

A mixture of 4,4'-bi-1,3-dithiole-2,2'-dione **3**[3] (1.00 g, 4.27 mmol), 4,5-bis(butylthio)-1,3-dithiole-2-thione **4a** (4.28 g, 13.8 mmol), and triethyl phosphite (50 ml) was heated at 140°C for 4.5 hr with stirring under nitrogen atmosphere. To the cooled mixture, ice and 7-10% aq. HCl solution were added and it was allowed to stand for overnight. The mixture was extracted several times with benzene, and the combined organic layer was washed with a saturated solution of sodium chloride and was dried over anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, the residue was chromatographed on silica gel with hexane-benzene (8:1) to afford **1a** as orange fine crystals (820 mg, 25%), mp 118.1-120.0°C. Anal, Calcd for $C_{28}H_{38}S_{12}$: C, 44.28; H, 5.05%. Found: C, 44.24; H 5.08%. ^{1}H NMR (270 MHz, δ ppm) 0.93 (12H, t, J=6.8 Hz), 1.40-1.67 (m, 16H), 2.82 (8H, t, J= 6.7 Hz), 6.22 (s, 2H). ^{13}C NMR (68 MHz, δ ppm) 13.6, 21.7, 31.8, 36.0, 111.0, 118.0, 127.9, 128.0. UV-VIS ($CHCl_3$) λ_{max} (ε) : 316 (28600), 330 (29900), 415 (10100) nm; MS m/z 758 (M^+).

2,2'-Bis[4,5-bis(hexylthio)-1,3-dithiol-2-ylidene]-4,4'-bi-1,3-dithiole **1b.**

A mixture of **3** (1.03 g, 4.40 mmol), 4,5-bis(hexylthio)-1,3-dithiole-2-thione **4b** (4.98 g, 13.6 mmol), and triethyl phosphite (51 ml) was heated at 140°C for 4.5 hr with stirring under nitrogen atmosphere. The work up was carried out in a manner similar to that of **1a** to give **1b** as orange fine crystals (804 mg, 21%), mp 112.5-113.6°C. Anal, Calcd for $C_{36}H_{54}S_{12}$: C, 49.60; H, 6.26%. Found: C, 49.56; H, 6.29%. ^{1}H NMR (270 MHz, δ ppm) 0.89 (12H, t, J= 6.8 Hz), 1.26-1.68 (m, 32H), 2.81 (8H, t, J= 7.3 Hz), 6.22 (s, 2H). ^{13}C NMR (68 MHz, δ ppm) 14.0, 22.6, 28.2, 29.7, 31.3, 36.4, 111.0, 118.0, 126.9, 127.9, 128.0; UV-VIS ($CHCl_3$) λ_{max} (ε) : 316 (25200), 330 (26200), 415 (8850) nm; MS m/z 870 (M^+).

2-[(4,5-Bis(butylthio)-1,3-dithiol-2-ylidene]-2'-[4,5-Bis(hexylthio)-1,3-dithiol-2-ylidene]-4,4'-bi-1,3-dithiole **1c.**

A mixture of **3** (1.01 g, 4.30 mmol), **4a** (2.50 g, 6.80 mmol), **4b** (2.14 g, 6.90 mmol), and triethyl phosphite (50 ml) was heated at 140°C for 4.5 hr with stirring under nitrogen atmosphere. A similar workup was carried out to that of **1a** to afford a mixture of cross-coupling products and two self-coupling products of **4a** and **4b**. The former mixture was further separated by gel-permeation chromatography (GPC) with chloroform as an eluent to give **1c** as orange fine crystals (525 mg, 15%), mp 98.5-100.0°C. Anal, Calcd for $C_{32}H_{46}S_{12}$: C, 47.12; H 5.70%. Found: C, 47.14; H, 5.64%. ^{1}H NMR (270 MHz, δ ppm) 0.89 (6H, t, J= 8.9 Hz), 0.93 (6H, t, J= 7.3 Hz), 1.26-1.67 (m, 24H), 2.82 (8H, t, J=7.3 Hz), 6.22 (s, 2H). ^{13}C NMR (68 MHz, δ ppm) 13.6, 14.0, 21.7, 22.6, 28.2, 29.7, 31.3, 31.8, 36.0, 36.4, 110.7, 111.0, 118.0, 126.9, 127.9, 128.0; UV-VIS ($CHCl_3$) λ_{max} (ε) : 316 (27400), 330 (28600), 415 (9600) nm; MS m/z 814 (M^+).

2-[4,5-Bis(butylthio)-1,3-dithiol-2-ylidene]-4-(1,3-dithiole-2-on-4-yl)-1,3-dithiole **5a.**

A mixture of **3** (1.51 g, 6.41 mmol), **4a** (2.19 g, 7.05 mmol), and triethyl phosphite (40 ml) in benzene (225 ml) was refluxed for 6 hr with stirring under nitrogen atmosphere. After the reaction mixture was cooled to room temperature, ice and 10% aq. HCl solution were added and it was allowed to stand for overnight. The reaction mixture was extracted with benzene, and the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel with hexane-benzene (2:1) to afford **5a** as orange crystals (1.19 g, 37%), mp 71.1-71.9°C. Anal, Calcd for $C_{17}H_{20}OS_8$: C, 41.09; H 4.06%. Found: C, 41.10; H, 4.07%. IR (KBr) 1645 cm^{-1} (C=O); MS m/z 496 (M^+).

2-[4,5-Bis(hexylthio)-1,3-dithiol-2-ylidene]-4-(1,3-dithiole-2-on-4-yl)-1,3-dithiole **5b.**

A mixture of **3** (250 mg, 1.07 mmol), **4b** (391 mg, 1.07 mmol), and triethyl phosphite (6.9 ml) in benzene (30 ml) was refluxed for 16 hr with stirring under nitrogen atmosphere. A similar workup procedure as described for **5a** gave **5b** as orange crystals (193 mg, 33%), mp 87.5-88.4°C. Anal. Calcd for $C_{21}H_{28}OS_8$: C, 45.60; H 5.11%. Found: C, 45.54; H, 5.09%. IR (KBr) 1646 cm^{-1} (C=O); MS m/z 552 (M^+).

4,4'(5')-Bis[[2-[4,5-bis(butylthio)-1,3-dithiol-2-ylidene]-1,3-dithiol-4-yl]-2,2'-bi-1,3-dithiol-ylidene **2a.**

A mixture of **5a** (200 mg, 4.03 mmol) and triethyl phosphite (10 ml) in toluene (20 ml) was refluxed for 12 hr with stirring under nitrogen atmosphere. The crude product was obtained by a similar manner as described for **1a.** It was purified by column chromatography on silica gel with hexane–benzene (3:1) to afford **2a** as orange fine crystals (26 mg, 13%), mp 142.1-142.9°C. Anal. Calcd for $C_{34}H_{40}S_{16}$: C, 42.45; H 4.20%. Found: C, 42.49; H, 4.25%. ^{1}H NMR (270 MHz, δ ppm) 0.93 (12H, t, J= 7.3 Hz), 1.40-1.65 (16H, m), 2.82 (8H, t, J= 7.1 Hz), 6.23 (4H, s). ^{13}C NMR (68 MHz, δ ppm) 14.0, 21.7, 31.8, 36.1, 111.0, 111.2, 118.0, 118.2, 126.8, 127.0, 127.9, 128.0; UV-VIS ($CHCl_3$) λ_{max} (ε) : 318sh (57800), 328 (59500), 412 (23500) nm; MS m/z 960 (M^+).

4,4'(5')-Bis[[2-[4,5-bis(hexylthio)-1,3-dithiol-2-ylidene]-1,3-dithiol-4-yl]-2,2'-bi-1,3-dithiol-ylidene 2b.

A mixture of **5b** (200 mg, 3.63 mmol) and triethyl phosphite (10 ml) in toluene (20 ml) was refluxed for 14.5 hr with stirring under nitrogen atmosphere. A similar workup procedure as described for **2a** afforded **2b** as orange fine crystals (25 mg, 13%), mp 153.5-154.3°C. Anal. Calcd for $C_{42}H_{56}S_{16}$: C, 46.96; H 5.27%. Found: C, 46.65; H, 5.20%. ^{1}H NMR (270 MHz, δ ppm) 0.89 (12H, t, J= 6.6 Hz), 1.28-1.68 (32H, m), 2.82 (8H, t, J=7.3 Hz), 6.22 (4H, s). ^{13}C NMR (68 MHz, δ ppm) 14.0, 22.6, 28.2, 29.7, 31.3, 36.4, 111.0, 111.2, 118.0, 118.2, 126.8, 126.9, 127.9, 128.0; UV-VIS ($CHCl_3$) λ_{max} (ε) : 318sh (46400), 328 (47800), 412 (19300) nm; MS m/z 1072 (M^+).

4-[2-[4,5-Bis(butylthio)-1,3-dithiol-2-ylidene]-1,3-dithiol-4-yl]-4'(5')-[2-[4,5-bis(hexylthio)-1,3-dithiol-2-ylidene]-1,3-dithiol-4-yl]-2,2'-bi-1,3-dithiol-ylidene 2c.

A mixture of **5a** (418 mg, 8.42 mmol), **5b** (464 mg, 8.40 mmol), and triethyl phosphite (40 ml) in toluene (90 ml) was refluxed for 10 hr with stirring under nitrogen atmosphere. A similar workup procedure as described for **2a** and further purification by gel-permeation chromatography afforded **2c** as orange fine crystals (39 mg, 4.6%), mp 130.2-131.0°C. Anal. Calcd for $C_{38}H_{48}S_{16}$: C, 44.83; H 4.76%. Found: C, 44.92; H, 4.76%. ^{1}H NMR (270 MHz, δ ppm) 0.88 (6H, t, J= 6.8 Hz), 0.92 (6H, t, J=6.8 Hz), 1.26-1.67 (24H, m), 2.81 (4H, t, J=7.3 Hz), 2.82 (4H, t, J= 7.3 Hz), 6.21 (4H, s). ^{13}C NMR (68 MHz, δ ppm) 13.6, 14.0, 21.6, 22.5, 28.2, 29.7, 31.3, 31.7, 36.0, 36.3, 110.7, 110.8, 110.9, 111.0, 111.2, 118.0, 118.1, 126.8, 127.0, 127.8, 127.9;UV-VIS ($CHCl_3$) λ_{max} (ε) : 316 (45700), 328 (47300), 412 (18500) nm;

MS m/z 1016 (M^+).

Charge-Transfer Complexes

All complexes described in this report were prepared by mixing the two hot saturated solutions of donor and acceptor in benzene or chlorobenzene under an argon atmosphere. The complexes precipitated out on cooling were collected by filtration and dried under reduced pressure.

DEDICATION

This paper is dedicated to Professors Yusei Maruyama and Fumio Ogura for their outstanding contribution to the research fields of organic superconductors as well as organic metals from the standpoint of physical properties and structural organic chemistry.

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REFERENCES

1. J. Ferraris, D. O. Cowan, V. Walatka Jr., and J. H. Perlstein, J. Am. Chem. Soc., 95, 948 (1973); J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, A. J. Schultz, and M. -H. Whangbo, Prog. Inorg. Chem., 35, 51 (1987); R. Kato, A. Kobayashi, Y. Sasaki, and H. Kobayashi, Chem. Lett., 993 (1984); T. Nakamura, S. Iwasawa, H. Nakano, K. Inoue, T. Nogami, and H. Mikawa, Bull. Chem. Soc. Jpn., 60, 365 (1987); T. Suzuki, H. Yamochi, G. Srdanov, K. Hinkelmann, and F. Wudl, J. Am. Chem. Soc., 111, 3108 (1989); R. Kato, H. Kobayashi, and A. Kobayashi, Synth. Met., 42, 2093 (1991).
2. E. Nishikawa, H. Tatemitsu, Y. Sakata, and S. Misumi, Chem. Lett., 2131 (1986); H. Tatemitsu, E. Nishikawa, Y. Sakata, and S. Misumi, Synth. Met., 19, 565 (1987).
3. T. Otubo, Y. Aso, and K. Takimiya, Adv. Mater., 8, 203 (1996); M. Iyoda, Y. Kuwatani, N. Ueno, and M. Oda, J. Chem. Soc., Chem. Commun., 158 (1992); T. Tachikawa, A. Izuoka, R. Kumai, T. Sugawara, and Y. Sugawara, Solid State Commun., 82, 19 (1992); M. Mizutani, K. Tanaka, K. Ikeda, and K. Kawabata, Synth. Met., 46, 201 (1992); K. Bechaard, K. Lerstrup, M. Jϕrgensen, I. Johannsen, J. Christensen, and J. Larsen, Mol. Crst. Liq. Cryst., 181, 161 (1990).
4. J. R. Andersen, V. V. Patel, and E. M. Engler, Tetrahedron Lett., 239 (1978).
5. H. Inokuchi, G. Saito, P. Wu, K. Seki, T. B. Tang, T. Mori, K. Imaeda, T. Enoki, Y. Higuchi, K. Inaka, and N. Yasuoka, Chem. Lett., 1263 (1986).