Novel Electron Acceptors Bearing a Heteroquinonoid System. 4.[1]
Syntheses, Properties, and Charge-Transfer Complexes of
2,7-Bis(dicyanomethylene)-2,7-dihydrobenzo[2,1-*b*:3,4-*b'*]dithiophene,
2,7-Bis(dicyanomethylene)-2,7-dihydrobenzo[1,2-*b*:4,3-*b'*]dithiophene,
and
2,6-Bis(dicyanomethylene)-2,6-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene

Shu Yoshida, Masanori Fujii, Yoshio Aso, Tetsuo Otsubo,* and Fumio Ogura*

*Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Kagamiyama, Higashi-Hiroshima 724, Japan*

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The three title compounds were prepared as novel hetero-TCNQ electron acceptors comprising the quinonoid skeletons of different benzodithiophene types between two dicyanomethylene groups. On the basis of cyclic voltammetry, they have electron affinities comparable to or stronger than that of TCNQ. In addition, the extensive building blocks serve to induce the effective reduction of on-site coulombic repulsion. They thus behaved as superior electron acceptors for forming electrically conductive charge-transfer complexes. In particular, 2,7-bis(dicyanomethylene)-2,7-dihydrobenzo-[2,1-*b*:3,4-*b'*]dithiophene was the most tractable in terms of stability and solubility, giving a variety of conductive complexes with typical electron donors of TTT, TTF, and TPBP types. Most of these complexes showed a characteristic broad electronic transition in the infrared region of 2.9–4.0 kcm^{-1}, supporting the idea that their crystal structures assume a stacking form of segregated donor and acceptor columns with mixed valence states.

The heterocyclic analogues of 7,7,8,8-tetracyanoquinodimethane (TCNQ) are generically called hetero-TCNQs and have the potential for novel electron acceptors forming organic metals. Thiophene-TCNQ (1) is a representative hetero-TCNQ which was first synthesized by Gronowitz and Uppström in 1974,[2] but attracted little attention as an electron acceptor because of its weak electron-accepting ability.[3,4] We previously studied its polyconjugated homologues 2 and 3[4] and fused homologues 4 and 5[5] in search of superior electron acceptors endowed with reduced on-site coulombic repulsion and increasing heteroatomic interactions, both of which are requisites for components of conductive molecular complexes.[6] It was found that they, like simple 1, still had weak electron affinities and had to be improved by introduction of additional electron-withdrawing groups. Such modification is, however, rather unfavorable because the additional substituent groups may sterically hinder the formation of molecular complexes. Ideally, it is desirable to design hetero-TCNQs with strong electron affinities by themselves. The weak electron affinities of hetero-TCNQs are mainly due to less aromaticity of new aromatic sextets arising from the heteroquinonoid rings upon the reduction process.[7] Thus, incorporation of heteroquinonoid rings inducing high aromaticity is essential for the improvement of hetero-TCNQs. On the basis of this consideration and pursuing
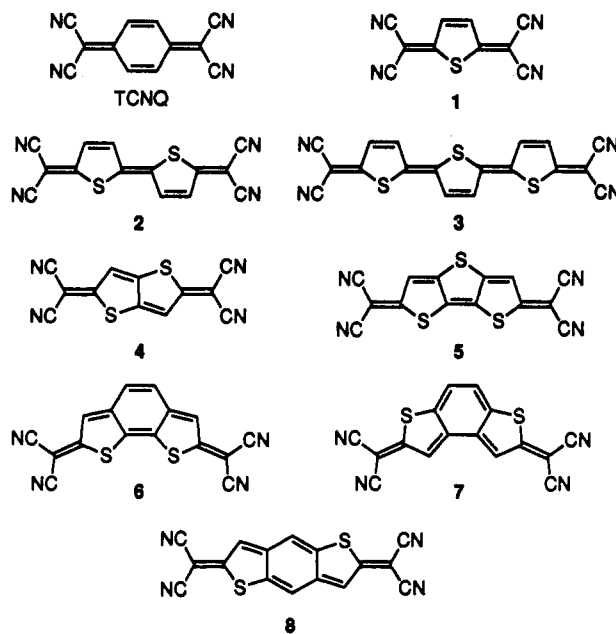
our studies on extended hetero-TCNQs, we have focused on the quinonoid systems of different benzodithiophene types as such potential rings and designed 2,7-bis-(dicyanomethylene)-2,7-dihydrobenzo[2,1-*b*:3,4-*b'*]dithiophene (6), 2,7-bis(dicyanomethylene)-2,7-dihydrobenzo-[1,2-*b*:4,3-*b'*]dithiophene (7), and 2,6-bis(dicyanomethylene)-2,6-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene (8). The central quinonoid skeletons might contribute to enhance their electron affinities as well as reduced on-site coulombic repulsion. Here, we report on the syntheses and properties of these novel hetero-TCNQs.[8]

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Scheme 1
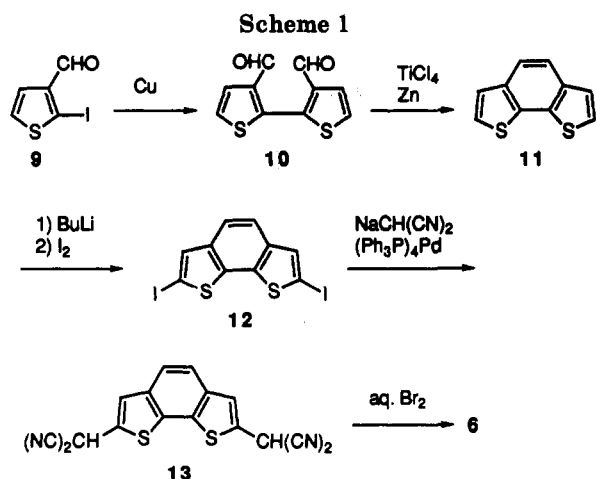
Results and Discussion

The syntheses of compounds 6, 7, and 8 were accomplished from benzo[2,1-*b*:3,4-*b'*]dithiophene (11),[9] benzo[1,2-*b*:4,3-*b'*]dithiophene (14),[10] and benzo[1,2-*b*:4,5-*b'*]dithiophene (17),[11] respectively, which were available according to the literature. In addition, as an alternative improved method, 11 was prepared via Ullmann coupling of 2-iodothiophene-3-carbaldehyde (9) followed by Mukaiyama reaction[12] of the resulting 2,2'-bithiophene-3,3'-dicarbaldehyde (10) with low-valent titanium (Scheme 1). These isomeric benzodithiophenes were thus treated with 2 equiv of *n*-butyllithium in tetrahydrofuran containing excess tetramethylethylenediamine at −70 °C and then with excess iodine at room temperature to give the corresponding diiodo derivatives 12, 15, and 18 in high yields. The subsequent substitution reactions with sodium dicyanomethanide[13] in the presence of catalytic tetrakis-(triphenylphosphine)palladium in refluxing tetrahydrofuran gave bis(dicyanomethyl)benzodithiophenes 13, 16, and 19 in good to high yields. Dehydrogenation with bromine, DDQ, or lead tetraacetate readily gave the desired hetero-TCNQs 6–8. The yields of this final step were essentially high but often drastically decreased during purification.

14 R=H
15 R=I
16 R=CH(CN)₂

17 R=H
18 R=I
19 R=CH(CN)₂
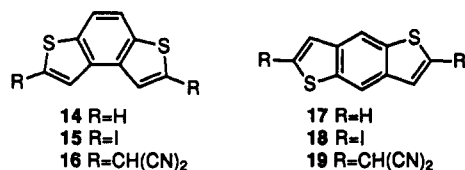
Compounds 6–8 are stable in the solid state but tend to slowly decompose in air-containing solution. In particular, 7 with an *o*-benzoquinoidal ring is especially air-sensitive. In addition, there are marked differences among their solubilities in common solvents. For example, the C_{2h} symmetrical isomer 8 has a poor solubility of only 9.9 × 10⁻⁶ M in tetrahydrofuran. On the other hand, the two C_{2v} symmetrical isomers 6 and 7 have better solubilities of 5.4 × 10⁻⁴ M and 3.7 × 10⁻⁵ M, respectively. It is thus

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Table 1. Electronic Absorption Data,[a] Electrical Conductivities,[b] and Half-Wave Redox Potentials[c] of Hetero-TCNQs

acceptor	λ_{max} (log ϵ)/nm	σ/S cm⁻¹	$E_{1/2}(1)/$ V	$E_{1/2}(2)/$ V	$\Delta E/$ V
5	546.5 (4.77)	5.6 × 10⁻⁷	+0.03	−0.20	0.23
			+0.01	−0.29	0.30
6	294 (3.79), 498 (4.60), 582 (4.49)	1.3 × 10⁻⁶	+0.26	−0.01	0.27
			+0.15	−0.15	0.30
7	340 (4.29), 459 (4.07), 486 (4.10), 720 (4.08)	2.1 × 10⁻⁶	+0.32	+0.09	0.23
			+0.25	−0.03	0.28
8	541 (4.81)	1.4 × 10⁻⁷	+0.20	−0.05	0.25
		d			
TCNQ	395 (4.72)	8.1 × 10⁻¹⁰	+0.26	−0.32	0.58
			+0.20	−0.43	0.63

[a] Measured in tetrahydrofuran. [b] Measured on a compressed pellet at room temperature by a two-probe method. [c] Measured at scan rate 100 mV s⁻¹ in dimethylformamide (upper berth) or in benzonitrile (lower berth) containing 0.1 M tetrabutylammonium perchlorate by use of an Ag/AgCl standard electrode and platinum working electrodes. [d] Compound 8 is insoluble in benzonitrile.

noteworthy that, of these hetero-TCNQs, 6 is the most tractable material in terms of both stability and solubility.

Compounds 6–8 are deeply colored materials, and the deep coloring is due to strong π–π* transitions in the visible region, as shown in Figure 1. Table 1 summarizes the absorption maxima, which appear at much longer wavelengths than λ_{max} 395 nm of TCNQ. Furthermore, the spectral shapes of 6–8 are quite different from one another, reflecting their isomeric π-conjugated systems. Although the electronic structure of 6 is considered to be formally close to that of 5 comprising three fused heterocyclic rings, the spectrum of 8 with a characteristic strong transition at λ_{max} 541 nm rather resembles that of 5 (λ_{max} 546.5 nm). On the other hand, the spectra of 6 and 7 have two divided visible absorptions. In particular, the longer wavelength band of 7 shows a marked bathochromic shift, extending to the near-infrared region. Table 1 also shows the electrical conductivities of 6–8 measured on compressed pellets of the single components, which are of the order of 10⁻⁶–10⁻⁷ S cm⁻¹, almost equal to that of 5 and higher by 3 orders of magnitude than that of TCNQ. This is probably indicative of increasing intermolecular contacts due to introduction of the extensive heteroquinonoid systems.

As already mentioned, the reduction potentials of hetero-TCNQs are lower than that of TCNQ. As summarized in Table 1, the first reduction potentials of the present hetero-TCNQs 6–8 are, however, greatly enhanced as compared with those of the previous hetero-TCNQ 1–5 and comparable to that of TCNQ. In particular, 7 with an *o*-benzoquinoidal ring has a higher reduction potential than do 6 and 8 with a *p*-benzoquinoidal ring. In addition, the second reduction potentials are more greatly enhanced owing to insertion of the extensive heteroquinonoid building blocks between the two electron-withdrawing dicyanomethylene groups. As a result, the differences between the first and second potentials of 6–8 become much smaller than that of TCNQ. These results indicate that hetero-TCNQs 6–8 have the advantages of not only strong electron affinities but also effective reduction of on-site coulombic repulsion.
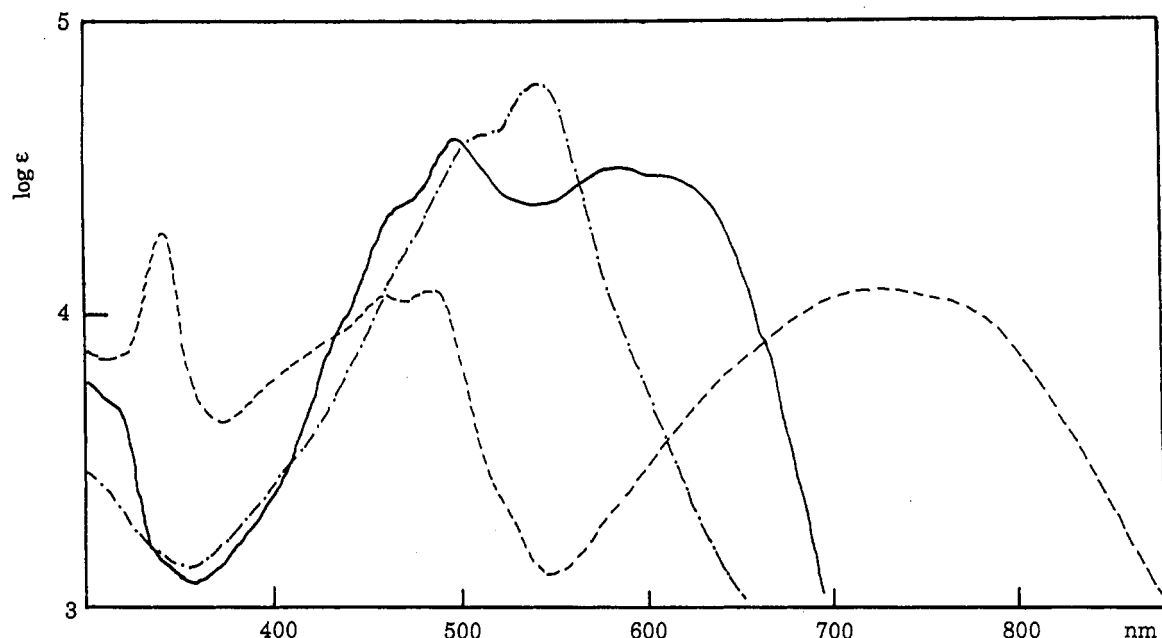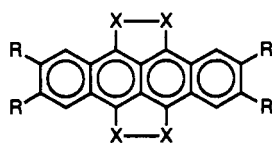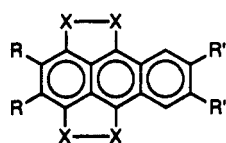
Figure 1. Electronic absorption spectra of hetero-TCNQs 6 (—), 7 (- - -), and 8 (– · –) in tetrahydrofuran.
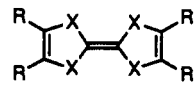
As shown in Table 2, the most tractable electron acceptor 6 formed a variety of charge-transfer complexes with typical electron donors, such as 5,6,11,12-tetrathiotetracene (TTT),[14] 2,3,8,9-tetramethyl-5,6,11,12-tetrathiotet-
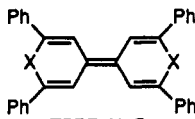

TTT	X=S, R=H	
TMTTT	X=S, R=Me	
TST	X=Se, R=H	

2,3-DMTTA	X=S, R=Me, R'=H
TMTTA	X=S, R=R'=Me
TSA	X=Se, R=R'=H
2,3-DMTSA	X=Se, R=Me, R'=H
6,7-DMTSA	X=Se, R=H, R'=Me
TMTSA	X=Se, R=R'=Me
DMTTeA	X=Te, R=Me, R'=H

TTF	X=S, R=H
TMTSF	X=Se, R=Me
HMTTeF	X=Te, R,R=(CH2)3

TPBP	X=O
TPTP	X=S

racene (TMTTT),[15] tetraselenotetracene (TST),[16] 2,3-dimethyl-1,4,9,10-tetrathioanthracene (2,3-DMTTA),[17] 2,3,6,7-tetramethyl-1,4,9,10-tetrathioanthracene (TMTTA),[17] 1,4,9,10-tetraselenoanthracene (TSA),[18] 2,3-dimethyl-1,4,9,10-tetraselenoanthracene (2,3-DMTSA),[17] 6,7-dimethyl-1,4,9,10-tetraselenoanthracene (6,7-DMTSA),[17] 2,3,6,7-tetramethyl-1,4,9,10-tetraselenoanthracene (TMTSA),[17] tetrathiafulvalene (TTF), tetramethyltetraselenafulvalene (TMTSF),[19] hexamethylenetetratellurafulvalene

(HMTTeF), tetraphenylbipyranilidene (TPBP),[20] tetraphenylbithiopyranilidene (TPTP).[21] In addition, some complexes were obtained from 7 with TTT and TST and from 8 with TTT, HMTTeF, and 2,3-dimethyl-1,4,9,10-tetratelluroanthracene (DMTTeA).[17] All of the complexes thus formed have high electrical conductivities ranging from 6.9 × 10⁻³ to 25 S cm⁻¹, supporting the potential of hetero-TCNQs 6–8 as superior electron acceptors. The nitrile vibrational frequencies of these complexes were observed in the markedly lower wavenumber region (2178–2205 cm⁻¹) of their infrared spectra as compared to neutral 6 (2218 cm⁻¹), 7 (2218 cm⁻¹), and 8 (2222 cm⁻¹). The shifts are not necessarily correlated with the magnitude of the conductivities, but clearly indicate considerable charge transfer which yields charge carriers.[22] It is well known that highly conductive charge transfer complexes generally assume crystal structures consisting of segregated stacking columns of donor and acceptor components with mixed valence states, in contrast to the crystal structures of mixed-stacking columns for insulating or poorly conductive complexes.[23–26] The former stacking form can be readily characterized by the appearance of a low-energy charge-transfer transition in the solid-state electronic spectrum.[27] Most of the complexes of 6 and all of the complexes of 8 showed such a characteristic broad absorption in the infrared region of 2.9–4.0 kcm⁻¹.

Experimental Section

General Methods. Melting points are uncorrected. All chemicals and solvents are of reagent grade. NMR spectra were

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Table 2.   Properties of Charge-Transfer Complexes of Hetero-TCNQs 6-8

complex	appearance[a]	dp/°C	A:D[b]	found (calcd)/% C	H	N	ν_{CN}[c] cm⁻¹	$h\nu$[c]/kcm⁻¹	σ[d]/S cm⁻¹
6·TTT	purple powder[e]	>300	1:1	60.56	1.81	8.12	2180	3.2, 7.8, 11.4	3.3
				(61.05)	1.81	8.38)			
6·TMTTT	black powder	>300	1:1	62.55	2.62	8.06	2190	7.7, 9.3	9.5 × 10⁻²
				(62.96)	2.78	7.73)			
6·TST	deep green powder	>300	1:1	47.65	1.42	6.30	2190	3.2, 7.8, 11.3	5.8
				(47.68)	1.41	6.54)			
6·2,3-DMTTA	purple powder	>300	1:1	59.34	2.19	8.66	2192	7.7	4.0 × 10⁻¹
				(59.42)	2.18	8.66)			
6·TMTTA	purple fine needles	>300	1:1	60.32	2.45	8.02	2200	3.5, 7.9	6.9 × 10⁻³
				(60.51)	2.69	8.30)			
6·TSA	deep purple powder	>300	1:1	44.59	1.37	6.72	2190	7.7, 11.3	1.1
				(44.68)	1.25	6.95)			
6·2,3-DMTSA	deep green powder	>300	4:3	48.07	1.82	7.68	2192	3.4, 7.7	1.2
				(47.71)	1.64	7.95)			
6·6,7-DMTSA	black powder	>300	4:5	44.61	1.84	6.44	2193	7.6	6.3 × 10⁻¹
				(44.86)	1.73	5.81)			
6·TMTSA	purple fine needles	295	1:1	48.13	2.08	6.50	2204	3.5, 7.8	2.9 × 10⁻²
				(47.35)	2.10	6.50)			
6·TTF	black fine needles[e]	>300	1:1	50.67	1.74	9.81	2195	3.2, 7.0	1.1
				(50.75)	1.55	10.76)			
6·TMTSF	black powder	>300	2:1	46.53	2.03	9.77	2200	3.1, 6.4	5.4 × 10⁻¹
				(46.68)	1.87	10.37)			
6·HMTTeF	black fine needles[e]	220	2:1	39.70	1.58	8.01	2185	3.2, 6.4, 7.8	2.3
				(40.67)	1.55	8.62)			
6·TPBP	purple fine needles	>300	2:1	72.50	3.36	9.75	2205	3.1, 6.9	1.3
				(72.25)	2.94	10.21)			
6·TPTP	black powder	275	2:1	69.56	3.22	9.67	2205	2.9, 6.7	1.3
				(70.19)	2.86	9.92)			
7·TTT	purple needles[f]	>300	1:1[g]	58.46	2.00	7.11	2186	5.5, 7.7	1.7 × 10⁻¹
				(58.51)	1.79	7.38)			
7·TST	black powder[f]	>300	1:1	47.30	1.40	6.44	2178	5.2, 6.7	8.5 × 10⁻²
				(47.68)	1.41	6.54)			
8·TTT	deep green powder[e]	>300	1:1	60.41	2.02	7.61	2192	4.0, 8.1, 9.3	4.5
				(61.05)	1.81	8.38)			
8·DMTTeA	black powder[e]	>300	2:1	43.51	2.11	7.56	2194	4.0, 7.9, 10.6	7.0 × 10⁻²
				(42.85)	1.35	8.33)			
8·HMTTeF	deep green powder[e]	>300	1:1	34.33	1.65	5.50	2193	3.4, 8.3	25
				(34.21)	1.64	5.70)			

[a] Prepared in chlorobenzene unless otherwise stated. [b] Estimated on the basis of elemental analyses. [c] Measured on a KBr disk. [d] Measured on a compressed pellet at room temperature by a four-probe method. [e] Prepared in o-dichlorobenzene. [f] Prepared in 1,2,4-trichlorobenzene. [g] Contained 0.5 M 1,2,4-trichlorobenzene originated from the solvent used in complexation.

recorded on a JEOL EX-270 (270 MHz) using deuteriochloroform as solvent. IR spectra were taken on a Hitachi 260-30 spectrometer with a KBr disk. MS spectra were measured at 70 eV on a Shimadzu QP-1000A spectrometer using a direct insertion technique. Electronic spectra were recorded on a Shimadzu UV-3100 spectrometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat equipped with a Hokuto Denko HB-104 function generator. Conductivity measurements were done with a Fuso Multi-Channel 4-Terminal Conductometer HECS 994.

2,2'-Bithiophene-3,3'-dicarbaldehyde (10). A mixture of 2-iodothiophene-3-carbaldehyde (9)[28] (2.38 g, 10 mmol) and copper (63.5 g, 1.00 mol) in DMF (30 mL) was stirred at 130 °C for 17 h and then filtered through a Celite filter. The filtrate was treated with water (100 mL) and extracted with benzene. The extract was dried (MgSO₄) and evaporated. Recrystallization from benzene gave brown plates, 878 mg (79% yield): mp 156–158 °C; IR 1667 cm⁻¹; ¹H NMR δ 7.54 (d, J = 6.0 Hz, 2H), 7.69 (d, J = 6.0 Hz, 2H), 9.93 (s, 2H); MS m/z 222 (M⁺). Anal. Calcd for C₁₀H₆S₂O₂: C, 54.04; H, 2.72. Found: C, 54.07; H, 2.68.

Benzo[2,1-b:3,4-b']dithiophene (11). Into a stirred solution of TiCl₄ (1.37 g, 7.2 mmol) in dry THF (50 mL) at -10 °C was added zinc powder (942 mg, 14.4 mmol) in a nitrogen atmosphere, and then a solution of 10 (266 mg, 1.2 mmol) in dry THF (25 mL) was slowly added under reflux over a period of 3.5 h. After addition, reflux was continued for a further 1.5 h, and then ice-water (100 mL) and aqueous 5% sodium hydrogen carbonate (50 mL) were successively added. The mixture was extracted with ether, and the extract was dried (MgSO₄). After evaporation of

the solvent, the residue was purified by column chromatography on silica gel with hexane followed by recrystallization from ethanol to give colorless plates, 157 mg (69% yield): mp 44–45 °C (lit.[9] mp 44 °C); ¹H NMR δ 7.39 (d, J = 5.1 Hz, 2H), 7.43 (d, J = 5.1 Hz, 2H), 7.77 (s, 2H); MS m/z 190 (M⁺). Anal. Calcd for C₁₀H₆S₂: C, 63.12; H, 3.18. Found: C, 63.08; H, 3.16.

2,7-Diiodobenzo[2,1-b:3,4-b']dithiophene (12). Into a mixed solution of dry THF (150 mL) and TMEDA (22.5 mL) cooled to -70 °C in a nitrogen atmosphere were added a 1.4 M hexane solution of n-butyllithium (32.7 mL, 45.7 mmol) and, 10 min later, a solution of 11 (3.85 g, 20 mmol) in dry THF (50 mL). After being stirred for 30 min at that temperature, a solution of iodine (14.6 g, 57 mmol) in dry THF (50 mL) was added. The mixture was stirred for 14 h without cooling, poured into water (300 mL), and then extracted with ether. The extract was washed with aqueous saturated sodium sulfite and then with aqueous 5% sodium hydrogen carbonate. After dryness (MgSO₄), evaporation followed by recrystallization from benzene gave colorless needles, 5.01 g (57% yield): mp 186–188 °C; ¹H NMR δ 7.59 (s, 2H), 7.59 (s, 2H); ¹³C NMR (67.8 MHz) δ 77.2, 119.3, 134.5, 137.0, 138.3; MS m/z 442 (M⁺). Anal. Calcd for C₁₀H₄S₂I₂: C, 27.17; H, 0.91. Found: C, 27.16; H, 0.91.

2,7-Bis(dicyanomethyl)benzo[2,1-b:3,4-b']dithiophene (13). Into a stirred solution of malononitrile (594 mg, 9.0 mmol) in dry THF (30 mL) in a nitrogen atmosphere was added sodium hydride (720 mg, 18 mmol as 60% oil) followed by, after 10 min, the diiodo compound 12 (1.33 g, 3.0 mmol) and tetrakis(triphenylphosphine)palladium (346 mg, 0.3 mmol). The mixture was refluxed for 1.5 h, and a small amount of 10% hydrochloric acid was added to neutralization. After the THF solvent was evaporated, 10% hydrochloric acid (5 mL) and water (20 mL)

(28) Gronowitz, S.; Dahlgren, T. *Chem. Scr.* 1977, *12*, 57–67.

were added. The resulting solid was collected by filtration and thoroughly washed with ethanol and then with hexane. Recrystallization from acetonitrile–benzene gave white fine crystals, 610 mg (64% yield): dp 280 °C; IR 2132, 2159, 2193, 2228, 2268 cm^{-1}; MS m/z 318 (M$^+$). Anal. Calcd for C$_{16}$H$_6$N$_4$S$_2$: C, 60.36; H, 1.90; N, 17.60. Found: C, 60.31; H, 1.87; N, 17.55.

2,7-Bis(dicyanomethylene)-2,7-dihydrobenzo[2,1-b:3,4-b']-dithiophene (6). Into a stirred suspension of 13 (1.0 g, 3.14 mmol) in dry acetonitrile (30 mL) cooled to 0 °C in a nitrogen atmosphere was added bromine water (20 mL). After addition of water (150 mL), the resulting solid was collected by filtration, dried, and chromatographed on silica gel with dichloromethane. Recrystallization from chlorobenzene gave bluish violet fine crystals, 470 mg (47% yield): dp 226 °C; IR 2218 cm^{-1}; MS m/z 316 (M$^+$); ^{1}H NMR δ 7.39 (s, 2H), 7.54 (s, 2H). Anal. Calcd for C$_{16}$H$_4$N$_4$S$_2$: C, 60.74; H, 1.27; N, 17.71. Found: C, 60.70; H, 1.27; N, 17.48.

2,7-Diiodobenzo[1,2-b:4,3-b']dithiophene (15). Compound 15 was prepared in 83% yield from benzo[1,2-b:4,3-b']dithiophene (14)[10] in a manner similar to that described for isomer 12: colorless needles from benzene–hexane; mp 175–176 °C (lit.[29] mp 176–177 °C); ^{1}H NMR δ 7.63 (s, 2H), 7.80 (s, 2H); ^{13}C NMR (67.8 MHz) δ 78.3, 117.5, 131.7, 134.3, 141.6; MS m/z 442 (M$^+$). Anal. Calcd for C$_{10}$H$_4$S$_2$I$_2$: C, 27.17; H, 0.91. Found: C, 27.16; H, 0.92.

2,7-Bis(dicyanomethyl)benzo[1,2-b:4,3-b']dithiophene (16). Compound 16 was prepared in 60% yield from diiodo derivative 15 in a similar manner as described for isomer 13: brown needles from acetonitrile; dp 210 °C; IR 2124, 2156, 2234, 2296 cm^{-1}; ^{1}H NMR δ 5.99 (s, 2H), 7.98 (s, 2H), 8.10 (s, 2H); MS m/z 318 (M$^+$). Anal. Calcd for C$_{16}$H$_6$N$_4$S$_2$: C, 60.36; H, 1.90; N, 17.60. Found: C, 60.32; H, 1.90; N, 17.60.

2,7-Bis(dicyanomethylene)-2,7-dihydrobenzo[1,2-b:4,3-b']-dithiophene (7). Into a stirred suspension of 16 (1.0 g, 3.14 mmol) in dry acetonitrile cooled to 0 °C was added DDQ (840 mg, 3.7 mmol) under a nitrogen atmosphere, and the mixture was refluxed for 1 h. The resulting solid was collected by filtration and thoroughly washed with dichloromethane using a Soxhlet

apparatus to give green fine crystals: 810 mg (81% yield); dp >300 °C; IR 2218 cm^{-1}; MS m/z 316 (M$^+$). Anal. Calcd for C$_{16}$H$_4$N$_4$S$_2$: C, 60.74; H, 1.27; N, 17.71. Found: C, 60.76; H, 1.48; N, 17.47.

2,6-Diiodobenzo[1,2-b:4,5-b']dithiophene (18). Compound 18 was prepared in 83% yield from benzo[1,2-b:4,5-b']dithiophene (17)[11] in a manner similar to that described for isomer 12: colorless leaflets from chlorobenzene; mp >300 °C ; ^{1}H NMR δ 7.65 (s, 2H), 8.24 (s, 2H); MS m/z 442 (M$^+$). Anal. Calcd for C$_{10}$H$_4$S$_2$I$_2$: C, 27.17; H, 0.91. Found: C, 27.22; H, 0.82.

2,6-Bis(dicyanomethyl)benzo[1,2-b:4,5-b']dithiophene (19). Compound 19 was prepared in 92% yield from diiodo derivative 18 in a manner similar to that described for isomer 13: a white powder; dp 250 °C; IR 2226 cm^{-1}; MS m/z 317.9994 (M$^+$); exact mass calcd for C$_{16}$H$_6$N$_4$S$_2$, 318.0032. Anal. Calcd for C$_{16}$H$_6$N$_4$S$_2$: C, 60.36; H, 1.90; N, 17.60. Found: C, 60.48; H, 1.91; N, 16.86.

2,6-Bis(dicyanomethylene)-2,6-dihydrobenzo[1,2-b:4,5-b']-dithiophene (8). Into a suspension of 19 (500 mg, 1.57 mmol) in dry dichloromethane (20 mL) cooled to –10 °C in a nitrogen atmosphere was added lead tetraacetate (1.77 g, 4 mmol), and the mixture was stirred for 30 min. After water (100 mL) was added, the resulting solid was collected by filtration with a Celite filter, extracted with dichloromethane (500 mL) using a Soxhlet apparatus for a few days, and then concentrated to one-fifth volume under nitrogen. Deep violet fine crystals formed on standing and cooling were collected by filtration, 50 mg (10% yield): mp >300 °C; IR 2222 cm^{-1}; MS m/z 316 (M$^+$). Anal. Calcd for C$_{16}$H$_4$N$_4$S$_2$: C, 60.74; H, 1.27; N, 17.71. Found: C, 60.69; H, 1.22; N, 17.61.

Charge-Transfer Complexes. All of the charge-transfer complexes described in this report were prepared by mixing two hot saturated solutions of donor and acceptor in chlorobenzene in a nitrogen atmosphere. The complexes precipitated out upon cooling and were collected by filtration and dried.

(29) Gronowitz, S.; Dahlgren, T. *Chem. Scr.* **1977**, *12*, 97–101.