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Novel Electron Acceptors Bearing a Heteroquinonoid System. I. Synthesis and Conductive Complexes of 5,5′-Bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene and Related Compounds

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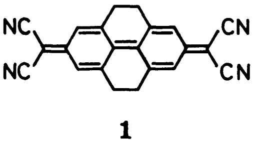
Novel electron acceptors bearing a heteroquinonoid system, 5,5′-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene, its 3,3′-dichloro, 3,3′-dibromo, and 3,3′,4,4′-tetrabromo derivatives, and 5,5″-bis(dicyanomethylene)-5,5″-dihydro-$\Delta^{2,2':5',2''}$-terthiophene were synthesized by the action of tetracyanoethylene oxide or by Pd(0)-catalyzed substitution reactions with sodium dicyanomethanide on the corresponding α,α'-dihalogeno-heteroaromatics. They showed very small on-site Coulomb repulsion as expected, and afforded several highly conductive molecular complexes with electron donors such as hexamethylenetetratellurafulvalene.

A very large amount of recent work in terms of structural organic chemistry and of material science has been directed toward the design and synthesis of new electron acceptor molecules which can be a potential component of organic electrical conductors. In particular, an excellent acceptor, 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), giving many conductive charge-transfer complexes, has been widely modified to improve its physical properties up to date.[1] In this current, extension of quinonoid conjugation of TCNQ has been examined to develop new acceptors with smaller on-site Coulomb repulsion in dianion state.[2] Though 13,13,14,14-tetracyanodiphenoquinodimethane (TCNDQ) had attracted considerable interest as one of such candidates, it turned out to be a nonpersistent molecule in neutral state owing to steric repulsion between the biphenylic ortho hydrogens.[3] This was followed by stable isolation of an ethano-bridged derivative of TCNDQ (**1**).[2a] On the other hand, 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (**2**) has been known as a heteroquinonoid isologue of TCNQ, which was casually synthesized by Gronowitz and Uppström.[4] Though the introduced sulfur atom is expected to act advantageously on the formation of its molecular complexes, **2** has stirred little attention because of its inferior electron-accepting ability and insulating molecular complex formation.[5] Much more extension of quinonoid conjugation in **2** might improve its ability as a component of conductive complex regarding effective diminution of on-site Coulomb repulsion and enlargement of band width. The most expected compounds are 5,5′-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene (**3a**) and 5,5″-bis(dicyanomethylene)-5,5″-dihydro-$\Delta^{2,2':5',2''}$-terthiophene (**4**). Supposedly, the trans geometry is more preferable for **3a**, because the biphenylic hydrogen repulsion must be advantageously avoided. On the other hand, **4** is a moreover extended homologue of **2**, in which some advanced character involving much smaller on-site Coulomb repulsion and large polarizability is expected.[6] Now we would like to report the syntheses and properties of **3a**, its derivatives with halogeno-substituents (**3b**—**d**), and **4**. As expected, these acceptors showed very small on-site Coulomb repulsion in their dianion state, and afforded semi- to highly conductive molecular complexes with various electron donors.


TCNQ


TCNDQ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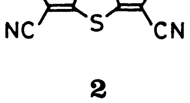
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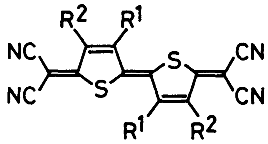
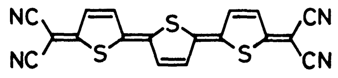

3a : $R^1 = R^2 = H$
3b : $R^1 = Cl,\ R^2 = H$
3c : $R^1 = Br,\ R^2 = H$
3d : $R^1 = R^2 = Br$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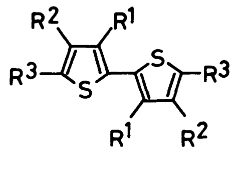
Results and Discussion

Synthesis. Gronowitz and Uppström reported that 2,5-dibromothiophene reacted with tetracyanoethylene oxide (TCNEO) in refluxing 1,2-dibromoethane to afford **2** and carbonyldicyanide.[4] At the same time, 2,3,5-tri- and 2,3,4,5-tetrabromothiophenes were formed as minor by-products because the reaction stoichiometrically generated bromine. We have found a similar reaction to be applicable toward bi- and terthiophene systems. 5,5′-Dibromo-2,2′-bithiophene (**5a**)[7] was treated with 0.75 equivalent of TCNEO in



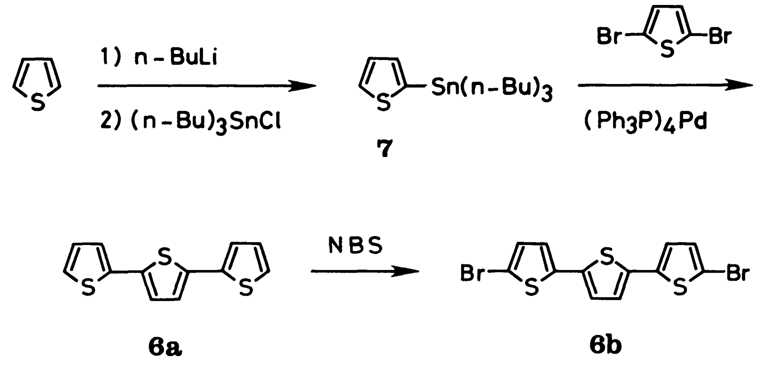
5a : $R^1 = R^2 = H$, $R^3 = Br$
5b : $R^1 = R^3 = Cl$, $R^2 = H$
5c : $R^1 = Br$, $R^2 = R^3 = H$
5d : $R^1 = R^3 = Br$, $R^2 = H$
5e : $R^1 = R^2 = R^3 = Br$

refluxing 1,2-dibromoethane for 8 h to afford **3a** in 42% yield on TCNEO. 3,3′,5,5′-Tetrachloro-2,2′-bithiophene (**5b**) was prepared from one-step treatment of thiophene with sulfuryl chloride and iron powder according to the procedure of Sone et al.[8] In a similar reaction of **5b** and TCNEO, the resulting 3,3′-dichloro-5,5′-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene (**3b**) was contaminated by further chlorinated one which was caused by chlorine stoichiometrically generated in the reaction, and was difficult to sufficiently purify. This reaction needed to be carried out in the presence of excessive copper(I) chloride as a reducing agent in refluxing 1,3-dibromopropane to obtain pure **3b** in a reasonable yield of 30%. 3,3′,5,5′-Tetrabromo-2,2′-bithiophene (**5d**) was prepared by bromination of 3,3′-dibromo-2,2′-bithiophene (**5c**)[9] (81% yield) or **5a** (90% yield) with NBS in refluxing chloroform–acetic acid (1 : 1 v/v). When **5d** was treated with an excess of TCNEO in refluxing 1,3-dibromopropane, 3,3′-dibromo-5,5′-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene (**3c**) was obtained in 27% yield. Treatment of **5a** with an excess of bromine in refluxing carbon disulfide afforded 3,3′,4,4′,5,5′-hexabromo-2,2′-bithiophene (**5e**) in 95% yield. A similar treatment of **5e** with TCNEO gave 3,3′,4,4′-tetrabromo-5,5′-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene (**3d**) in only 1.5% yield, whereas addition of an excess of copper(I) bromide fairly improved the yield up to 12%.

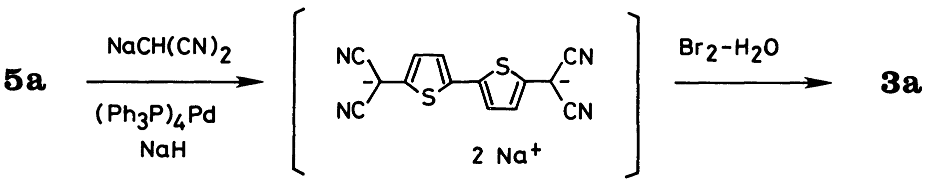
In the presence of palladium(0) catalyst, a cross coupling reaction[10] between 2,5-dibromothiophene and tributyl(2-thienyl)tin (**7**), which was prepared in 89% yield from 2-thienyllithium and chlorotributyltin, afforded 2,2′:5′,2″-terthiophene (**6a**) in 59% yield as shown in Scheme 1. This procedure is a practical alternative to the reported methods to obtain **6a**.[11,12] The NBS treatment of **6a** in chloroform–acetic acid (1 : 1 v/v) afforded 5,5″-dibromo-2,2′:5′,2″-terthiophene (**6b**) in 94% yield. The subsequent reaction of **6b** with 0.75 equiv of TCNEO in 1,2-dibromoethane at reflux gave 5,5″-bis(dicyanomethylene)-5,5″-dihydro-$\Delta^{2,2':5',2''}$-terthiophene (**4**) in 11% yield on TCNEO.

Sodium dicyanomethanide prepared in situ from malononitrile and sodium hydride was allowed to react with **5a** and **6b** in refluxing 1,2-dimethoxyethane containing a catalytic amount of tetrakis(triphenylphosphine)palladium(0),[13] followed by oxidation with bromine water, to successfully synthesize **3a** and **4** in 68% and 73% yield, respectively. Scheme 2 illustrates the conversion of **5a** into **3a**.

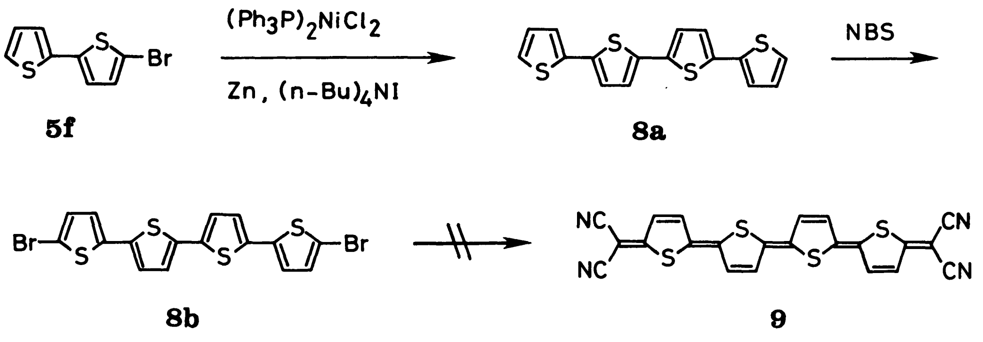
Nickel(0)-catalyzed coupling reaction[14] of 5-bromo-2,2′-bithiophene (**5f**)[15] gave 2,2′:5′,2″:5″,2‴-quaterthiophene (**8a**) in 87% yield, and its subsequent reaction with NBS afforded 5,5‴-dibromo derivative (**8b**) in 87% yield as shown in Scheme 3. Both TCNEO and malononitrile treatments, however, failed in synthesizing 5,5‴-bis(dicyanomethylene)-5,5‴-dihydro-



Scheme 1.



Scheme 2.



Scheme 3.

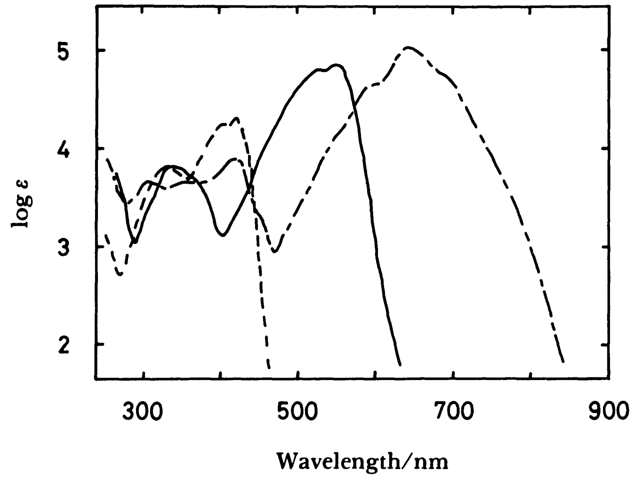


Fig. 1. Electronic spectra of **2** (-------), **3a** (——), and **4** (—·—·) in dichloromethane.

Table 1. Conductivities of Acceptors

Acceptor	Conductivity[a]/S cm^{-1}
2	$<10^{-11}$
3a	1.2×10^{-6}
3b	4.9×10^{-7}
3c	2.7×10^{-6}
3d	6.9×10^{-5}
4	1.7×10^{-6}
TCNQ	8.1×10^{-10}

a) Measured on compressed pellets with a two-probe method at RT.

Table 2. Half-Wave Reduction Potentials[a]

Acceptor	$E^1_{1/2}$	$E^2_{1/2}$	ΔE/V
2	0.07	−0.54	0.61
3a	−0.03	−0.26	0.23
3b	0.18	−0.06	0.24
3c	0.20	0.03	0.17
3d	0.28	0.13	0.15
4	−0.03	−0.03	0
TCNQ	0.25	−0.47	0.72

a) Cyclic voltammetry was carried out at RT in dichloromethane containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate using Ag/AgCl as a reference electrode and platinum as a working electrode at a scan rate of 100 mV s^{-1}.

$\Delta^{2,2':5',2'':5'',2'''}$-quaterthiophene (**9**).

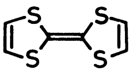
Structure. The electronic spectra of **2**, **3a**, and **4** are shown in Fig. 1. These spectra strikingly resemble each other in shape, and their absorption maxima in the visible region are bathochromically shifted largely with extending their conjugation systems (**2**: $\lambda_{max}(\varepsilon)$ 330(6400), 400(18000), 421(20300); **3a**: 343(7000), 525 (65700), 550(73100); **4**: 304(4710), 358(4530), 415(7640), 643(106000) nm), suggesting nearly planar quinonoid structures in these molecules. Although TCNDQ is too unstable to isolate as mentioned before,[3] **3a**—**d** and **4** are extremely stable compounds whose decomposition points are not observed below 300 °C. These facts are attributable to trans geometry of these molecules, being capable of avoiding steric repulsion between hydrogen or halogen atoms at 3,3′-position.

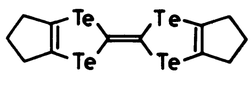
Table 1 shows electrical conductivities of these acceptors (**3a**—**d** and **4**) on a compressed pellet together with those of **2** and TCNQ. It is very interesting that **3a**—**d** and **4** are all highly conductive for a pellet sample of a neutral organic compound in contrast to much lower conductivities of **2** and TCNQ, and reminicent of the most conductive, neutral organic compound, tetrakis(methyltelluro)tetrathiafulvalene.[16] This is realized as an increase of the intermolecular interactions due to extension of their heteroquinonoid conjugation.

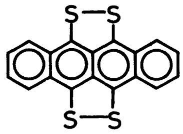
Redox Property. The redox behavior of acceptors **3a**—**d** and **4** was determined by cyclic voltammetry in dichloromethane. Table 2 summarizes their half-wave reduction potentials together with those of **2** and TCNQ. All **3a**—**d** show two pairs of reversible redox waves. The first half-wave potential ($E^1_{1/2}$) of **3a** is lower than that of **2**, indicating a smaller electron affinity of **3a**. However, since its second one ($E^2_{1/2}$) is higher, the difference (ΔE) between $E^1_{1/2}$ and $E^2_{1/2}$ becomes smaller. This unambiguously demonstrates much more diminution of on-site Coulomb repulsion in the dianion state of **3a**. Acceptor **4** shows almost the same $E^1_{1/2}$ value as **3a** does. It is remarkable that its second wave coalesces into its first one as if its on-site Coulomb repulsion were minimized.

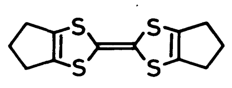
The electron-withdrawing halogen substituents of **3b** and **3c** can actually increase the weak electron-accepting ability of parent **3a**, resulting in the $E^1_{1/2}$ values comparable to that of TCNQ. The additional 5,5′-dibromo substituents of **3d**, however, do not so much raise its $E^1_{1/2}$ as its 3,3′-dibromo substituents. Compounds **3b—d** also show very small ΔE values. Both large electron affinity and quite small on-site Coulomb repulsion thus allow **3b—d** to behave as superior electron acceptors.

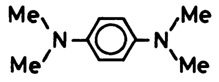
Molecular Complex. These acceptors did form molecular complexes with electron donors such as tetrathiafulvalene (TTF), tetrathiotetracene (TTT), hexamethylenetetrathiafulvalene (HMTTF), tetramethylphenylenediamine (TMPDA), tetraphenylbipyranylidene (TPBP), hexamethylenetetratellurafulvalene (HMTTeF), 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-ditellurole (ADTe), and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF). Table 3 summarizes physical properties of the isolated complexes.

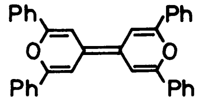

TTF

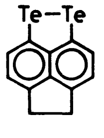

HMTTeF

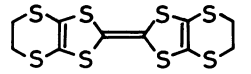

TTT


HMTTF


TMPDA


TPBP


ADTe


BEDT-TTF

Acceptor **2** gave no crystalline complexes with typical donors such as TTT, TMPDA, HMTTF, ADTe, and BEDT-TTF because of its weak accepting ability. It, however, formed nearly insulating 1:1 complexes with TTF and HMTTeF. The TTF and HMTTeF complexes carry no charge transfer, as indicated by no shift in wavenumber of the nitrile stretching vibration absorption (ν_{CN}) in the IR spectra on complexation.[17] On the other hand, **2** formed a highly conductive 1:1 complex with a stronger donor TPBP. A considerable lower wavenumber shift of ν_{CN} (2184 cm^{-1}) of the complex than that (2222 cm^{-1}) of neutral **2** clearly indicates the existence of certain charge transfer, which might be related to its high conductivity.

Acceptor **3a** gave 1:1 complexes with TTF and TTT. These complexes are little ionic on the basis of ν_{CN} nearly comparable to that (2220 cm^{-1}) of **3a** but semiconductive. Acceptor **4** complexed TTF, TTT, TPBP, and HMTTeF. The stoichiometry of these complexes except TTT complex is rich in acceptor. Their ν_{CN} values, referring to that (2213 cm^{-1}) of **4**, indicate no charge transfer in the TTF and HMTTeF complexes and some charge transfer in the TTT and TPBP complexes. Their conductivities are, however, close to metallic, regardless of degree of the charge transfers. Comparison of three TTF complexes of **2**, **3a**, and **4**, though they are all nonionic, demonstrates a marked increase in conductivity in order of the extensive acceptor. These results strongly support that the diminished on-site Coulomb repulsion of the extensive conjugated acceptor makes a significant contribution to the formation of conductive molecular complexes.

Acceptors **3b—d**, further endowed by stronger electron-accepting abilities, could form complexes with all the given donors. However, complexation of **3b** with ADTe and of **3d** with BEDT-TTF failed. Most of complexes obtained were very highly conductive. In particular, marvelously high conductivity of 170 S cm^{-1} was observed for **3b**·HMTTeF in a compressed pellet state.

Conclusion

The accepting ability of 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (**2**) was successfully improved by

Table 3. Molecular Complexes of **2**, **3a—d**, and **4**

Complex[a]	Appearance	Found (Calcd)[b]/%			ν_{CN}[c]/cm^{-1}	dp[d]/°C	Conductivity[e] /S cm^{-1}
		C	H	N			
2·TTF[f]	Golden yellow needles	46.12; (46.36;	1.41; 1.46;	13.22 13.52)	2221	168	6.8×10^{-9}[g]
2·TPBP	Dark brown powder	78.29; (78.32;	3.83; 3.88;	7.57 8.30)	2184	193	4.9×10^{-1}

Table 3. (Continued)

Complex[a]	Appearance	Found (Calcd)[b]/%			ν_{CN}[c]/cm^{-1}	dp[d]/°C	Conductivity[e] /S cm^{-1}
		C	H	N			
2·HMTTeF	Dark brown	30.14;	1.77;	5.54	2221	200	5.5×10^{-9}[g]
	powder	(30.14;	1.61;	6.39)			
3a·TTF[f]	Brown powder	48.15;	1.62;	11.37	2217	195	2.2×10^{-4}
		(48.37;	1.62;	11.28)			
3a·TTT	Deep blue fine	58.79;	1.65;	8.93	2219	>300	3.0×10^{-4}
	needles	(59.60;	1.88;	8.69)			
3b·TTF[f]	Deep brown	42.45;	1.07;	9.88	2197	228	19
	powder	(42.48;	1.07;	9.91)			
3b·TTT	Green needles	53.72;	1.41;	7.55	2190	>300	4.6
		(53.85;	1.41;	7.85)			
$(\mathbf{3b})_2$·TMPDA	Black fine cryst	51.93;	2.16;	14.92	2192	>300	7.3×10^{-1}
		(51.47;	2.27;	15.80)			
3b·TPBP	Deep green	69.67;	3.04;	6.50	2193	>300	8.3×10^{-5}[g]
	fine cryst	(69.82;	3.17;	6.78)			
3b·HMTTF	Black fine	48.58;	1.92;	8.68	2199	>300	6.3
	needles	(48.37;	2.19;	8.68)			
3b·HMTTeF	Dark brown	30.12;	1.30;	5.23	2180	236	170
	powder	(30.38;	1.37;	5.45)			
$(\mathbf{3b})_2$·BEDT	Deep green	41.80;	1.10;	10.14	2218	274	2.3×10^{-7}[g]
-TTF	needles	(41.23;	1.09;	10.12)			
3c·TTF[f]	Green fine	36.70;	0.92;	8.56	2203	235	15
	needles	(36.70;	0.92;	8.56)			
3c·TTT	Green fine	47.86;	1.26;	6.78	2203	>300	13
	needles	(47.87;	1.26;	6.98)			
3c·TMPDA[f]	Dark green	46.22;	2.83;	13.15	2198	220	2.9×10^{-2}
	fine needles	(46.92;	2.95;	13.65)			
3c·TPBP	Green powder	62.66;	2.73;	5.39	2196	>300	4.5×10^{-1}
		(63.03;	2.87;	6.13)			
3c·HMTTF	Dark blue	42.46;	1.91;	7.50	2194	220	22
	prisms	(42.51;	1.92;	7.63)			
3c·$(\mathrm{HMTTeF})_2$	Dark green	25.75;	1.62;	3.12	2169	270	57
	powder	(25.59;	1.47;	3.14)			
3c·ADTe	Dark green	36.41;	1.10;	6.24	2193	250	6.3×10^{-1}
	powder	(36.42;	1.18;	6.53)			
3c·BEDT	Dark green	34.65;	1.50;	6.61)	2218	265	2.2×10^{-7}[g]
-TTF	powder	(34.53;	1.21;	6.71)			
3d·TTF	Deep green fine	29.87;	0.47;	6.90	2200	202	31
	needles	(29.57;	0.50;	6.90)			
3d·TTT	Deep green fine	40.17;	0.77;	5.75	2193	>300	18
	needles	(40.02;	0.84;	5.83)			
$(\mathbf{3d})_3$·$(\mathrm{TMPDA})_2$	Green powder	34.35;	1.22;	9.32	2192	161	7.1×10^{-1}
		(34.60;	1.50;	10.41)			
3d·TPBP	Deep green	54.17;	2.18;	4.84	2195	294	11
	powder	(53.76;	2.26;	5.22)			
3d·HMTTF	Dark brown	35.16;	1.29	6.11	2200	>300	39
	powder	(34.99;	1.36;	6.28)			
3d·HMTTeF	Black powder	24.24;	0.97;	3.30	2182[i]	225	29
		(24.54;	0.95;	4.40)			
3d·ADTe	Black powder	30.73;	0.83;	4.78	2195	278	6.6×10^{-1}
		(30.76;	0.79;	5.52)			
$(\mathbf{4})_5$·TTF[h]	Black powder	55.53;	1.65;	13.49	2215	>300	3.3×10^{-3}
		(56.26;	1.84;	11.74)			
4·TTT	Black powder	58.58;	1.88;	7.20	2204	>300	7.2×10^{-1}
		(59.48;	1.94;	7.71)			
$(\mathbf{4})_5$·$(\mathrm{TPBP})_2$	Black powder	67.10;	2.97;	8.32	2209	286	3.7×10^{-1}
		(67.84;	2.81;	10.01)			
$(\mathbf{4})_2$·HMTTeF	Dark brown	39.97;	2.32;	6.72	2215	214	1.1
	powder	(40.73;	1.71;	7.92)			

a) Obtained from chlorobenzene unless otherwise described. b) Calculated as stoichiometry indicated for the complex. c) Measured with a KBr disk method unless otherwise mentioned. d) Decomposition point. e) Measured on compressed pellets at RT with a four-probe method unless otherwise described. f) Obtained from acetonitrile. g) Measured on compressed pellets with a two-probe method at RT. h) Obtained from benzonitrile. i) Measured with a Nujol mull method.

introduction of both extensive heteroquinonoid conjugation and electron-withdrawing substituents. For compounds **3a** and **4** the extensive conjugation was very effective for diminution of on-site Coulomb repulsion, which is a requisite for designing conductive molecular complexes. In addition, it was proved that compounds **3b—d** possessing both small on-site Coulomb repulsion and large electron affinity are reliable electron acceptors for forming a variety of very high conductive molecular complexes.

Experimental

General. Melting points are uncorrected. All solvents are of reagent grade. Elemental analyses were measured by Mr. Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. Electron donors used to prepare the molecular complexes, TTF,[18] TTT,[19] HMTTF,[20] TPBP,[21] BEDT-TTF,[22] and ADTe[23] were obtained according to the published procedures except commercially available TMPDA and HMTTeF. NMR spectra were recorded on a JEOL PMX-60 spectrometer (60 MHz) using tetramethylsilane as an internal standard. IR spectra were taken on a Hitachi 260-30 or Perkin-Elmer 1600 FTIR spectrophotometer with a nujol mull or a KBr disk method. MS spectra were measured on a Shimadzu GC-MS QP-1000A Mass spectrometer at 70 eV using a direct insertion technique. Electronic absorption spectra were recorded on a Shimadzu UV-160 spectrophotometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator.

5,5′-Bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene (3a). A) Using TCNEO. A mixture of **5a** (324 mg, 1.00 mmol) and TCNEO (216 mg, 1.50 mmol) in dry 1,2-dibromoethane (15 cm^3) was heated under reflux for 8 h, and the solution was diluted with carbon tetrachloride (60 cm^3) at 0 °C. The resulting precipitate was collected by filtration and purified by column chromatography on silica-gel with dichloromethane, followed by recrystallization from acetonitrile, giving **3a** as deep violet fine needles (92 mg, 42% yield on TCNEO): mp>300 °C; IR (KBr) 2220 (CN), 1525, 1500 (C=C) cm^{-1}; MS *m/z* 292 (M$^+$, 100%); Anal. ($C_{14}H_4N_4S_2$) C, H, N.

B) Using Sodium Dicyanomethanide. Malononitrile (156 mg, 2.40 mmol) was added to an ice-cooled suspension of sodium hydride (192 mg, 60% oily, 4.80 mmol) in 1,2-dimethoxyethane (8 cm^3) under nitrogen atmosphere, and the mixture was stirred at RT for 20 min. To this solution were added **5a** (324 mg, 1.00 mmol) and tetrakis(triphenylphosphine)palladium(0) (156 mg, 0.100 mmol), and the mixture was heated under reflux for 4 h. The reaction mixture was treated with saturated bromine water (30 cm^3) at 0 °C and diluted with cold water (50 cm^3). The resulting precipitate was collected by filtration on Hyflo Super-Cel, Soxhlet-extracted with dichloromethane, concentrated in vacuo, and recrystallized from chlorobenzene to give **3a** (199 mg, 68%).

3,3′-Dichloro-5,5′-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene (3b). A mixture of **5b** (2.43 g, 8.00 mmol), TCNEO (11.5 g, 80.0 mmol), and copper(I) chloride (5.54 g, 56.0 mmol) in dry 1,3-dibromopropane (130 cm^3) was heated under reflux for 6 h. The solution was twice column-chromatographed on silica gel with dichloromethane, followed by recrystallization from acetonitrile to give **3b** as deep violet fine crystals (880 mg, 30%): mp>300 °C; IR (KBr) 2217 (CN), 1503 (C=C) cm^{-1}; MS *m/z* 360 (M$^+$, 100%); Anal. ($C_{14}Cl_2H_2N_4S_2$) C, H, N.

3,3′,5,5′-Tetrabromo-2,2′-bithiophene (5d). A) From 3,3′-Dibromo-2,2′-bithiophene (5c). A mixture of **5c** (1.30 g, 4.00 mmol) and NBS (1.50 g, 8.43 mmol) in chloroform-acetic acid (8 cm^3, 1:1 v/v) was heated under reflux for 5 h. The resulting solution was poured into water and extracted with chloroform. The organic layer was washed with 5% sodium hydrogencarbonate aqueous solution and water, and dried on anhydrous magnesium sulfate. After concentration in vacuo, the residual solid was recrystallized from chloroform–hexane to give **5d** as colorless prisms (1.57 g, 81%): mp 138.5—140.5 °C (lit,[24] 139—140 °C); ^{1}H NMR ($CDCl_3$) δ= 6.97 (s).

B) From 5a. NBS (392 mg, 2.20 mmol) was added to a solution of **5a** (324 mg, 1.00 mmol) in chloroform–acetic acid (9 cm^3, 1:1 v/v), and the mixture was heated under gentle reflux for 3 d. The solution was poured into water, and extracted with chloroform. The organic layer was worked up in the same way as described in Method A to give **5d** (436 mg, 90%).

3,3′-Dibromo-5,5′-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene (3c). A mixture of **5d** (120 mg, 0.25 mmol) and TCNEO (288 mg, 2.00 mmol) in dry 1,3-dibromopropane (3 cm^3) was heated under reflux for 2 h. The mixture was twice column-chromatographed on silica gel with dichloromethane, followed by recrystallization from acetonitrile to give **3c** as deep violet fine needles (31 mg, 27%): mp>300 °C; IR (KBr) 2224 (CN), 1510, 1495 (C=C) cm^{-1}; MS *m/z* 450 (M$^+$, 100%); Anal. ($C_{14}Br_2H_2N_4S_2$) C, H, N.

3,3′,4,4′,5,5′-Hexabromo-2,2′-bithiophene (5e). A mixture of **5a** (648 mg, 2.00 mmol), carbon disulfide (25 cm^3), and bromine (3.3 cm^3, 64 mmol) was heated under gentle reflux for 26 h. To this mixture was carefully added a saturated sodium hydrogensulfite aqueous solution (50 cm^3), and the mixture was vigorously stirred for several min. The resulting precipitate was collected by filtration, washed with water and methanol, and dried in vacuo. The organic layer of the filtrate was washed with 5% sodium hydrogencarbonate aqueous solution and water, and dried on anhydrous magnesium sulfate. After concentration in vacuo, the residual solid was combined with the above collected precipitate and recrystallized from chlorobenzene to give **5e** as colorless needles (1.21 g, 95%): mp 262—264 °C (lit,[25] 257—258 °C).

3,3′,4,4′-Tetrabromo-5,5′-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene (3d). A mixture of **5e** (128 mg, 0.200 mmol), TCNEO (576 mg, 4.00 mmol), and copper(I) bromide (201 mg, 1.40 mmol) in dry 1,3-dibromopropane (5 cm^3) was heated under reflux for 6 h. The solution was column-chromatographed on silica gel with chloroform, followed by recrystallization from chloroform to give **3d** as deep violet fine needles (15 mg, 12%): mp>300 °C; IR (KBr) 2217 (CN), 1500 (C=C) cm^{-1}; MS *m/z* 608 (M$^+$, 100%); Anal. ($C_{14}Br_4N_4S_2$) C, H, N.

Tributyl(2-thienyl)tin (7). Butyllithium (94 cm^3, 0.15 mol, 1.6 mol dm^{-3} hexane solution) was added to a solution of thiophene (12.6 g, 0.150 mol) in THF (120 cm^3) at 0 °C under nitrogen atmosphere, and the mixture was stirred at 50 °C for 30 min. To this solution was added chlorotributyltin (51.3 g, 0.150 mol, 95% purity) at 0 °C. The resulting suspension was stirred overnight at RT, concentrated, and filtered. The filtrate was distilled in vacuo to give **7** as colorless liquid (50.1 g, 89%): bp 118—125 °C/0.22 mmHg (lit,26) 150 °C/1 mmHg; 1 mmHg≈133.322 Pa); ^{1}H NMR (CCl_4) δ=0.5—2.3 (m, 27H), 6.9—7.3 (m, 2H), 7.3—7.6 (m, 1H).

2,2′:5′,2″-Terthiophene (6a). A solution of **7** (48.5 g, 130 mmol), 2,5-dibromothiophene (14.5 g, 60.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (3.47 g, 3.00 mmol) in toluene (200 cm^3) was heated at reflux for 18 h under nitrogen atmosphere. The reaction mixture was concentrated in vacuo and chromatographed on silica gel with hexane, followed by recrystallization from hexane to give **6a** as pale yellow plates (8.77 g, 59%): mp 89—91 °C (lit,27) 94—95 °C); ^{1}H NMR ($CDCl_3$) δ=6.9—7.2 (m); Anal. ($C_{12}H_8S_3$) C, H.

5,5″-Dibromo-2,2′:5′,2″-terthiophene (6b). NBS (11.9 g, 66.7 mmol) was portionwise added to a solution of **6a** (8.28 g, 33.3 mmol) in chloroform–acetic acid (1 : 1 v/v) at RT. The resulting suspension was suirred for an additional hour and then at 50—60 °C for 30 min. Precipitated solid was collected by filtration. The filtrate was successively washed with water, 5% sodium hydrogencarbonate aqueous solution, and again water, and dried on anhydrous magnesium sulfate. After concentration in vacuo, the residual solid was combined with the above precipitate and recrystallized from hexane–chloroform to give **6b** as yellow needles (12.7 g, 94%): mp 158—158.5 °C (lit,28) 160—161 °C); ^{1}H NMR (CS_2) δ=6.86 (s, 2H), 6.84 (d, J=3.7 Hz, 2H), 6.78 (d, J=3.7 Hz, 2H).

5,5″-Bis(dicyanomethylene)-5,5″-dihydro-$\Delta^{2,2':5',2''}$-terthiophene (4). A) Using TCNEO. A mixture of **6b** (406 mg, 1.00 mmol) and TCNEO (216 mg, 1.50 mmol) in dry 1,2-dibromoethane (16 cm^3) was heated under reflux for 2 h. The solution was twice column-chromatographed on silica gel with dichloromethane to give **4** (32 mg, 11% yield on TCNEO): deep green powder from chlorobenzene, mp> 300 °C; IR (KBr) 2213 (CN), 1480 (C=C) cm^{-1}; Found: m/z 374.0294. Calcd for $C_{18}H_6N_4S_3$: M, 373.9755.

B) Using Sodium Dicyanomethanide. Under a nitrogen stream, malononitrile (312 mg, 4.80 mmol) was added to an ice-cooled suspension of sodium hydride (384 mg, 9.60 mmol, 60% oily) in 1,2-dimethoxyethane (24 cm^3), and the mixture was stirred at RT for 20 min. To this suspension were added **6b** (812 mg, 2.00 mmol) and tetrakis(triphenylphosphine)palladium(0) (312 mg, 0.200 mmol). The mixture was heated under reflux for 4 h, and treated with saturated bromine water (40 cm^3). After dilution with cold water (20 cm^3), the resulting precipitate was collected by filtration on Hyflo Super-Cel, and Soxhlet-extracted with dichloromethane, followed by recrystallization from chlorobenzene to give **4** (546 mg, 73%).

2,2′:5′,2″:5″,2‴-Quaterthiophene (8a). A mixture of zinc powder (785 mg, 12.0 mmol), bis(triphenylphosphine)nickel(II) chloride (393 mg, 0.600 mmol), and tetrabutylammonium iodide (2.22 g, 6.00 mmol) in THF (15 cm^3) was stirred at RT under nitrogen atmosphere for 30 min. To the resulting reddish brown solution was added a solution of **5f** in THF (5 cm^3), and the solution was stirred at 50 °C for 2 h. After addition of water, precipitated solid was collected by filtration, and column-chromatographed on silica gel with carbon disulfide, followed by recrystallization from chloroform to give **8a** as yellow leaflets (867 mg, 87%): mp 216.5—218 °C (lit,12) 211—212 °C).

5,5‴-Dibromo-2,2′:5′,2″:5″,2‴-quaterthiophene (8b). NBS (911 mg, 5.12 mmol) was added to a solution of **8a** in carbon disulfide–chloroform–acetic acid (270 cm^3, 2 : 5 : 2 v/v), and the mixture was heated under gentle reflux for an hour. After cooling to 0 °C, the resulting precipitate was collected by filtration, washed with methanol, and dried. The filtrate was successively washed with water, 5% sodium hydroxide aqueous solution, and water, and dried over anhydrous magnesium sulfate. After concentration in vacuo, the residual solid was combined with the above precipitate, and recrystallized from chlorobenzene to give **8b** as orange leaflets (1.09 g, 87%): mp 260—263 °C (lit,24) 248 °C).

Preparation of Molecular Complexes. All molecular complexes described in this report were prepared by mixing the two hot saturated solutions of donor and acceptor in chlorobenzene, acetonitrile, or benzonitrile. The resulting complexes precipitated out immediately or on cooling appropriately, which were collected by filtration and dried in vacuo.

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