SYNTHESES, SPECTROSCOPIC PROPERTIES, AND POLYMERIZATIONS OF 2,2'-BITELLUROPHENE, 2,2':5',2"-TERTELLUROPHENE, AND RELATED HYBRID TERCHALCOGENOPHENES§

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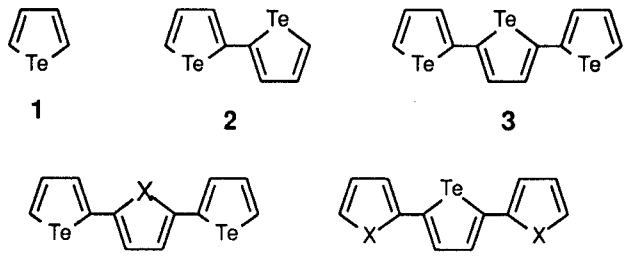
Abstract—2,2'-Bitellurophene, 2,2':5',2"-tertellurophene, and related hybrid terchalcogenophenes have been synthesized as a novel extended series of tellurophene homologues. The molecular and crystal structures of 2,2'-bitellurophene were elucidated by an X-Ray crystallographic analysis and compared with those of 2,2'-bithiophene and 2,2'-biselenophene. The molecular structure adopts an almost completely planar transoid conformation, as seen for the other bichalcogenophenes, but the crystal structure is quite different, comprising a unique herringbone-type of molecular packing with heteroatomic interactions of tellurium. The electronic absorption spectra of the tellurophenes are characterized by strong π–π^* transitions which appear in the longer wavelength region than those of thiophene and selenophene analogues and are systematically red-shifted with the increasing number of the conjugated tellurophene units. On the other hand, the emission spectra suffer marked extinction owing to a heavy atom effect of tellurium, and only the extended tertellurophene shows weak fluorescence in the visible region. The elevation of the HOMO levels of the tellurophenes is suggested by low oxidation potentials in the cyclic voltammograms. Consequently, ready electrolytic and chemical oxidative coupling reactions are liable to occur to give filmy or powdered polytellurophenes, whose conductivities are wide-ranging with the order of 10^{-3}–10^{-9} S cm^{-1}, depending on the original tellurophene species and the polymerization conditions.

§Dedicated to Professor Teruaki Mukaiyama on the occasion of his 73th birthday.

INTRODUCTION

Tellurium-containing compounds are of current interest,[1] because they are particularly promising as advanced functional materials owing to a strong nonbonded electronic interaction of tellurium.[2] One of such prototypical compounds is tellurophene (**1**),[1,3] the heaviest member of the series of chalcogenophenes, but the chemistry of tellurophene, as compared to those of the other five-membered heterocycles, has been little studied, and much less the conjugated homologues. The α-conjugated homologues of tellurophene are expected to be electrically as conductive as those of thiophene and selenophene. Although Japanese patents previously claimed the preparation of a highly conductive polytellurophene (64 S cm^{-1}) by electrolysis of tellurophene itself,[4] Sugimoto and coworkers reported that the conductivity of polytellurophene prepared chemically using $FeCl_3$ is much lower (10^{-6} S cm^{-1}) than those of polythiophene (10^{2} S cm^{-1}) and polyselenophene (10^{-2} S cm^{-1}).[5] This has prompted us to study the undeveloped conjugated homologues of tellurophene, which might provide more precise information on the potential of tellurophene for conductive materials. We here report the syntheses, spectroscopic properties, and polymerizations of 2,2'-bitellurophene (**2**) and 2,2':5',2"-tertellurophene (**3**) in detail.[6] In addition, related tellurophene-containing hybrid terchalcogenophenes (**4**–**7**) are also discussed.[7]



1 **2** **3**

4 X=S
5 X=Se

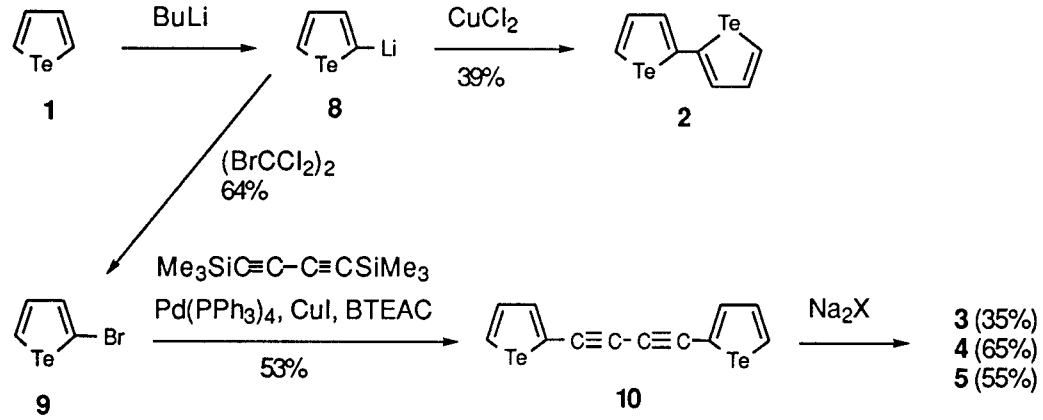
6 X=S
7 X=Se

RESULTS AND DISCUSSION

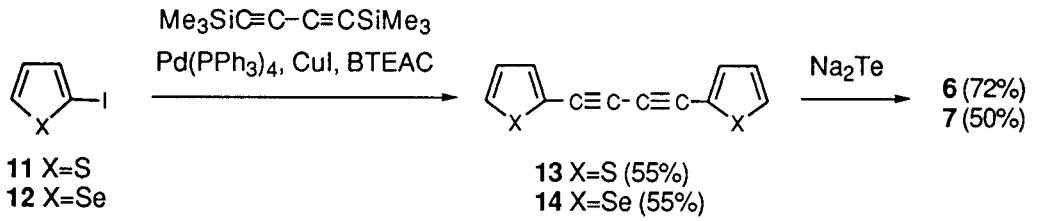
Syntheses

2,2'-Bitellurophene (**2**) was prepared in 39% yield by copper(II) chloride-promoted oxidative coupling reaction of 2-lithiotellurophene (**8**)[8] derived from lithiation of tellurophene (**1**) in dry ether (Scheme 1). An alternative treatment of **8** with 1,2-dibromotetrachloroethane gave 2-bromotellurophene (**9**)[9] in 64% yield, which was then coupled with 1,4-bis(trimethylsilyl)butadiyne in benzene under phase-transfer conditions employing catalytic tetrakis(triphenylphosphine)palladium, copper(I) iodide, benzyltriethylammonium chloride (BTEAC) as a phase-transfer agent, and large excess of 2.5 M aq sodium hydroxide to give 1,4-bis(2-tellurienyl)butadiyne (**10**) in 53% yield. Subsequent treatment of **10** with sodium telluride, which was prepared from tellurium powder with sodium formaldehyde sulfoxylate (Rongalite) and sodium hydroxide in ethanol–DMF, gave 2,2':5',2"-tertellurophene (**3**) in 35% yield. Similar treatments of **10** with sodium sulfide and with sodium selenide afforded the hybrid terchalcogenophenes (**4**) (65%) and (**5**) (55%), respectively.

The other hybrid terchalcogenophenes (**6**) and (**7**) were similarly prepared *via* bis(2-thienyl)-1,3-butadiyne (**13**) and bis(2-selenienyl)-1,3-butadiyne (**14**) from 2-iodothiophene (**11**) and 2-iodoselenophene (**12**), respectively (Scheme 2).



Scheme 1



Scheme 2

Molecular and crystal structures of 2,2'-bitellurophene

An X-Ray crystallographic analysis disclosed that the molecular structure of **2**, like that of 2,2-bithiophene,[10] is completely planar with a two-fold axis at the center and adopts a transoid conformation around the central single bond (Figure 1). The length of the central single bond is 1.46 Å, reflecting a reasonable conjugation between both tellurophene rings. The bond lengths and angles of the tellurophene rings are essentially similar to those of tellurophene (**1**) itself analyzed by microwave spectroscopy.[11] The crystal structure is characterized by packing of a herringbone type of molecular layers in the *ab* plane, in which the molecules are arrayed with alternative tilting and sliding (Figure 2). The herringbone angle is 74.0°. There are no short heteroatomic contacts due to tellurium between the face-to-face molecules in the layer, but a reasonable Te•••Te contact between the nearest molecules in the neighboring layers (4.31 Å). These interactive layers do not coincide by a sliding along the *c*-axis. This molecular arrangement is quite different to that of 2,2'-bithiophene which also comprises molecular arrays of a herringbone-type but no such interactive layers in the longitudinal direction of the molecules. For comparison, we studied the X-Ray crystallographic analysis of 2,2'-biselenophene, which turned out to also take a planar transoid conformation (Figure 3) and to have essentially the same crystal structure (Figure 4) as 2,2'-bithiophene. The herringbone angle is 60.6°, which is nearly the same as that (59.5°) of bithiophene,[10b] but much smaller than that of bitellurophene. In addition, analogously to bithiophene, there are no heteroatomic interactions between the neighboring molecules not only in the transverse direction but also in the longitudinal direction. The unique interactive structure of bitellurophene thus suggests that the tellurophene system may possess promising solid-state properties, such as charge transport through marked heteroatomic interactions. Recent structural studies of a series of α-oligothiophenes have revealed that

higher homologues, though the appearance of polymorphism, retain essentially a common herringbone type of molecular arrangement, as represented by 2,2'-bithiophene.[12] In this regard, it is expected that higher tellurophene homologues also have interactive crystal structures similar to that of 2,2'-bitellurophene.

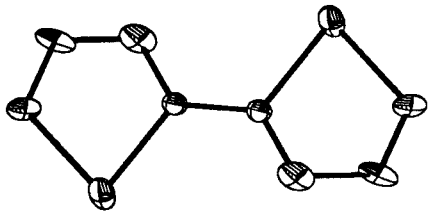


Figure 1. Molecular structure of 2,2'-bitellurophene (**2**)

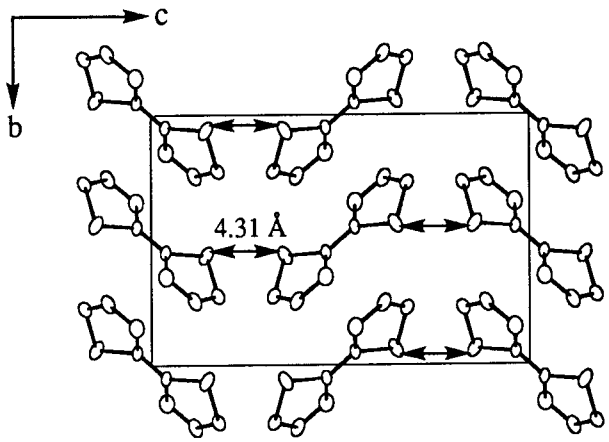


Figure 2. Crystal structure of 2,2'-bitellurophene (**2**) viewed along the *a*-axis

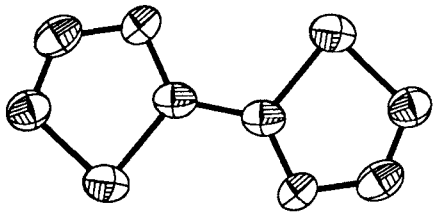


Figure 3. Molecular structure of 2,2'-biselenophene

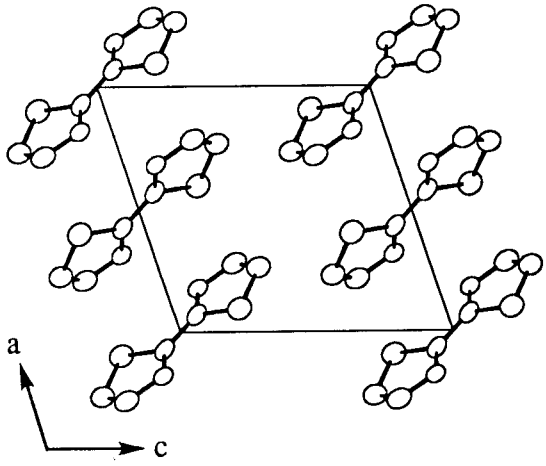


Figure 4. Crystal structure of 2,2'-biselenophene viewed along the *b*-axis

Electronic spectra

In the electronic spectrum, tellurophene (**1**) strongly absorbs UV light at 281 nm, which is a much longer wavelength than those of thiophene (230 nm) and selenophene (250 nm), indicating an effective reduction of HOMO–LUMO energy gap by introduction of tellurium.[13] The tellurophene homologues (**2**) and (**3**) demonstrate further large red-shifts of the absorption band to 362 and 423 nm, respectively, causing their

coloration, yellow for **2** and orange for **3** (Figure 5). As shown in Table 1, these absorption maxima are also located in the longest wavelengths in each series of the bi- and ter-chalcogenophenes. The hybrid terchalcogenophenes (**4**–**7**) show intermediate red-shifts as expected. On a more detailed comparison, the absorption maxima of **4** and **6** are very similar (391 and 388 nm, respectively), and of **5** and **7** are the same (402 nm), accordingly indicating that tellurium replacement in the inner heterocyclic ring is more effective for the red shift than in the outer ring.

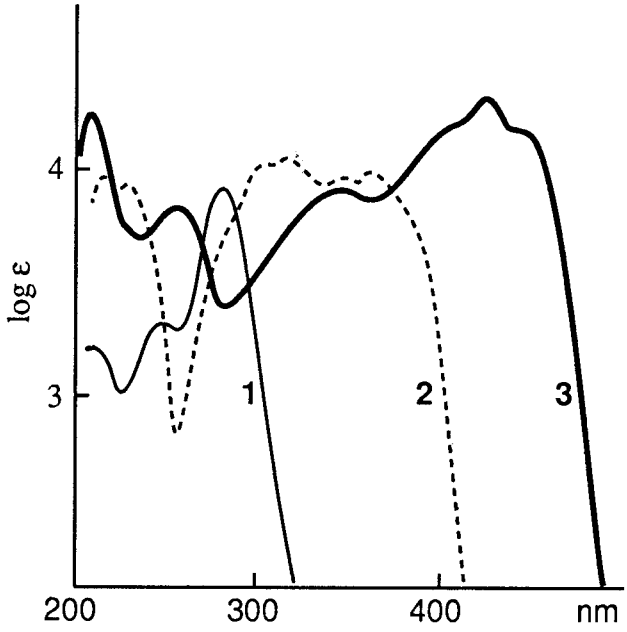


Figure 5. Electronic spectra of a series of tellurophenes (**1**–**3**) in THF

Table 1. The longest-wavelength absorption maxima of a series of chalcogenophenes[a]

Chalcogenophene	λ_{max}/nm (log ε)	Chalcogenophene	λ_{max}/nm (log ε)
thiophene	230 (3.91)	terthiophene	353 (4.37)
selenophene	250 (3.87)	terselenophene	386 (4.39)
tellurophene (**1**)	281 (3.98)	tertellurophene (**3**)	423 (4.36)
bithiophene	304 (3.98)	**4**	391 (4.39)
biselenophene	328 (3.10)	**5**	402 (4.40)
bitellurophene (**2**)	362 (3.98)	**6**	388 (4.30)
		7	402 (4.36)

[a]Measured in THF.

The fluorescent spectrum of thiophene is almost little detected, but those of bi- and ter-thiophenes are observable owing to a decrease of nonradiative decay.[14] It is also the case with the selenophene counterparts.[15] In contrast, not only tellurophene but also bitellurophene are non-fluorescent, and tertellurophene showed only weak fluorescence at 483 nm. The marked fluorescence extinction of the tellurophenes is presumably due to the heavy atom effect of tellurium.

Oxidation potentials

In a voltammetric study, tellurophene (**1**) shows an irreversible oxidation wave at 1.54 V, which is markedly lower than those (> 1.8 V) of thiophene and selenophene. This is consistent with lowering of the first ionization potential of tellurophene studied by photoelectron spectroscopy, and the apparent elevation of the HOMO level of tellurophene was suggested to be caused by the less electronegativity of tellurium than those of sulfur and selenium atoms.[16] As summarized in Table 2, the conjugated homologation of tellurophene further efficiently lowers the oxidation potential; 1.19 V of **2** and 0.94 V of **3** are also the lowest in the homologated chalcogenophene series.[17] The hybrid terchalcogenophenes (**4**–**7**) similarly have relatively low oxidation potentials at 0.97–1.04 V.

Table 2. Oxidation potentials of a series of chalcogenophenes[a]

Chalcogenophene	E_{ox}/V	Chalcogenophene	E_{ox}/V
thiophene	> 1.8	terthiophene	1.13
selenophene	> 1.8	terselenophene	1.04
tellurophene (**1**)	1.54	tertellurophene (**3**)	0.94
bithiophene	1.46	**4**	0.97
biselenophene	1.34	**5**	0.99
bitellurophene (**2**)	1.19	**6**	1.04
		7	1.03

[a]Measured in benzonitrile containing 0.1 M Bu_4NClO_4 using an Ag/AgCl standard electrode and Pt working electrode at scan rate 100 mV s^{-1}.

Polymerizations

The low oxidation potentials of the tellurophene homologues are expected to allow their ready oxidative coupling. With this expectation, we studied the polymerization of the tellurophenes by using both electrochemical and chemical oxidation techniques. The galvanostatic polymerization of tellurophene (**1**) in benzonitrile or nitrobenzene required a very high electric current density of 1 mA/cm^2, giving an insoluble black powder of poly(tellurophene) on the platinum electrode, whereas the homologues (**2**–**7**) more readily underwent electropolymerization under a low current density of 50 μA/cm^2, giving black films. As summarized in Table 3, the electrical conductivity of the poly(tellurophene) was very low, depending on the solvents used for polymerization, 10^{-7} S cm^{-1} (benzonitrile) and 10^{-11} S cm^{-1} (nitrobenzene). On the other hand, poly(bitellurophene) showed less solvent-dependent conductivities of the order of 10^{-6} S cm^{-1}. Although poly(tertellurophene) and the hybrid poly(terchalcogenophene)s of **4** and **5** were nearly insulating (10^{-9} S cm^{-1}), the other hybrid polymers derived from **6** and **7** had somewhat improved conductivities of 10^{-5} S cm^{-1}.

The chemical oxidative polymerization of tellurophene (**1**) with $FeCl_3$ in chloroform gave a black powdery poly(tellurophene), whose conductivity was 10^{-11} S cm^{-1} for an as-grown sample, but, upon iodine doping, increased to 10^{-8} S cm^{-1} roughly comparative to that of the above poly(tellurophene) sample obtained by electropolymerization. Similar chemical polymerizations of **2** and **3** also gave black powders;

the doped conductivity of the poly(bitellurophene) was the same as the electropolymerized filmy sample, whereas the poly(tertellurophene) was more conductive (10^{-5} S cm^{-1}). The hybrid poly(terchalcogenophene)s also showed similar or better conductivities; in particular, the polymers prepared from **6** and **7** had considerably improved conductivities of the order of 10^{-3} S cm^{-1}.

Table 3. Electrical conductivities (S cm^{-1}) of polytellurophenes[a]

Monomer	Electropolymerization	Chemical polymerization	
		as-grown	I_2 doped[b]
1	1.3×10^{-7} (1.6×10^{-11})[c]	4.7×10^{-11}	2.2×10^{-8}
2	7.6×10^{-6} (1.5×10^{-6})[c]	6.0×10^{-12}	1.1×10^{-6}
3	7.0×10^{-9}	3.7×10^{-12}	3.3×10^{-5}
4	1.0×10^{-9}	6.0×10^{-9}	6.6×10^{-8}
5	2.0×10^{-9}	1.3×10^{-7}	2.7×10^{-5}
6	1.1×10^{-5}	3.7×10^{-7}	4.6×10^{-3}
7	2.9×10^{-5}	4.4×10^{-5}	1.6×10^{-3}

[a]Measured on compressed pellets by a two-probe method. [b]Exposed to iodine vapor for 24 h. [c]Values in parentheses indicate the conductivities of the polymers prepared in nitrobenzene, otherwise the polymerizations were carried out in benzonitrile.

We have previously found that both comparable members of oligothiophene and oligoselenophene series have essentially the same electrical conductivities, and accordingly the different conductivities of polythiophene and polyselenophene result principally from polymerization degrees.[15] It is similarly speculated that the low conductivities of the present polytellurophenes are due to their limited polymerization degrees. A control oxidative coupling experiment of bichalcogenophenes with $FeCl_3$ disclosed the rather high reactivity of bitellurophene: the relative reaction rates of bitellurophene, biselenophene, and bithiophene were estimated to be roughly 5:3:2. The poorer solubility of the tellurophene system must hamper extensive polymerization. In addition, the higher reactivity of the tellurophene system may induce an undesirable β-coupling reaction in the chain-propagating process. The limited propagation was spectroscopically supported by observation of a shorter electronic absorption maximum (401 nm) of the poly(bitellurophene) film than that (451 nm) of poly(bithiophene). The relatively high conductivities of the polymers derived from **6** and **7** might be attributed to an improvement of polymerization degree owing to the enhanced solubility of the hybrid systems.

CONCLUSION

Bitellurophene (**2**) and tertellurophene (**3**) as well as related hybrid terchalcogenophenes (**4**–**7**) have been prepared as a novel extended series of tellurophene homologues. The crystal structure of **2** revealed a unique herringbone-type of molecular packing with heteroatomic interactions of tellurium. The electronic spectra of the tellurophene homologues demonstrated smaller HOMO–LUMO energy gaps than the

corresponding thiophene and selenophene ones, and elevation of the HOMO levels was supported by a voltammetric study. Electropolymerization of **2** and **3** gave polymeric films, while $FeCl_3$-induced polymerization produced polymeric powders. Both type of polymers showed less conductivities than 10^{-5} S cm^{-1}, suggesting limited degrees of polymerization. On the other hand, the polymers derived from the hybrid terchalcogenophenes (**6**) and (**7**) had much improved conductivities of the order of 10^{-3} S cm^{-1}, suggesting increasing polymerization degrees. These results imply that the tellurophene system has a potential as a component of conductive materials, although its further molecular modification for enhanced solubilization is inevitable for the utilization .

ACKNOWLEDGMENTS

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EXPERIMENTAL

General. Melting points are uncorrected. All chemicals and solvents are of reagent grade. All the reactions were carried out in a nitrogen atmosphere. Tellurophene (**1**) was prepared according to the method reported by Lohner *et al.*[18] ^{1}H NMR spectra were measured in deuteriochloroform with a Hitachi R-1200 (60 MHz) or a Bruker AMX-400wb (400 MHz) instrument, ^{13}C NMR with a Bruker AMX-400wb (100 MHz), IR spectra on KBr disk with a Shimadzu FTIR-8100A, UV/VIS spectra in THF with a Shimadzu UV-3100, MS spectra with a Shimadzu GCMS-QP-2000, and CV with a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator.

2,2'-Bitellurophene (2)

Into a solution of tellurophene (**1**) (1.53 g, 8.5 mmol) in dry ether (20 mL) was added butyllithium (5.22 mL, 8.51 mmol, 1.63 M in hexane) at rt, and the mixture was stirred for 30 min to generate the 2-lithiotellurophene (**8**).[8] After cooling down to –78 °C, copper(II) chloride (1.55 g, 11.5 mmol) was added, and the mixture was stirred at –78 °C for 3 h and then warmed up to rt. Some pieces of ice were added, and then the insoluble material was filtered off and washed with hexane (200 mL). The filtrate and washing were combined, washed with brine, and dried ($MgSO_4$). The solvent was evaporated, and the residue was purified by column chromatography on silica gel (hexane) followed by recrystallization from chloroform to give **2** (0.60 g, 39%) as pale yellow plates: mp 180–180.5 °C; ^{1}H NMR (400 MHz) δ 7.45 (dd, J = 4.0, 0.8 Hz, 2H), 7.66 (dd, J = 6.9, 4.0 Hz, 2H), 8.68 (dd, J = 6.9, 0.8 Hz, 2H); ^{13}C NMR δ 124.6, 136.3, 137.6, 146.8; MS *m/z* 362 (M^+); UV-vis λ_{max}/nm (log ε) 385 sh (3.77), 362 (3.98), 317 (4.04), 304 (4.03), 230 (3.95), 216 (4.00); IR ν_{max}/cm^{-1} 1440, 1210, 1020, 830, 700; Anal. Calcd for $C_8H_6Te_2$: C, 26.89; H, 1.69. Found: C, 26.83; H, 1.69.

2-Bromotellurophene (9)

Into an ethereal solution of 2-lithiotellurophene (**8**) generated from tellurophene (**1**) (1.0 g, 5.5 mmol) as above described was added 1,2-dibromo-1,1,2,2-tetrachloroethane (2.06 g, 6.3 mmol) at –78 °C, and the mixture was stirred at –78 °C for 3 h and then warmed up to rt. Some pieces of ice were added, and then

the mixture was filtered. The filtrate was washed with brine and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography on silica gel (hexane) to give **9** (0.92 g, 64%) as a pale yellow liquid:[9] ^1H NMR (60 MHz) δ 7.40 (dd, J = 4.3, 7.2 Hz, 1H), 7.70 (dd, J = 1.5, 4.3 Hz, 1H), 8.81 (dd, J = 1.5, 7.2 Hz, 1H); Anal. Calcd for C_4H_3BrTe: C, 18.58; H, 1.17. Found: C, 18.47; H, 1.13.

1,4-Bis(2-tellurienyl)-1,3-butadiyne (10)

2-Bromotellurophene (**9**) (1.93 g, 7.4 mmol) was mixed with bis(trimethylsilyl)-1,3-butadiyne (700 mg, 3.6 mmol) in deaerated benzene (20 mL). To the mixture were successively added $Pd(PPh_3)_4$ (300 mg, 0.24 mmol), CuI (80 mg, 0.42 mmol), benzyltriethylammonium chloride (TEBAC) (60 mg, 0.26 mmol), and deaerated 2.5 M NaOH aq (20 mL). The mixture was stirred at 40 °C for 2 days, and the resulting precipitate was filtered off and washed with dichloromethane. The filtrate and washing were combined and treated with saturated NH_4Cl aq. solution (30 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The organic layers were combined, washed with brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2) and then gel-permeation liquid chromatography (JAIGEL 1H/2H column) to give **10** (804 mg, 53%) as pale yellow crystals from chloroform–hexane: mp 108–108.5 °C; ^1H NMR (60 MHz) δ 7.71 (dd, J = 6.8, 3.8 Hz, 2H), 7.94 (dd, J = 3.8, 1.3 Hz, 2H), 9.09 (dd, J = 6.8, 1.3 Hz, 2H); MS *m/z* 410 (M^+); Anal. Calcd for $C_{12}H_6Te_2$: C, 35.55; H, 1.49. Found; C, 35.44; H, 1.46.

1,4-Bis(2-thienyl)-1,3-butadiyne (13)

55% yield from 2-iodothiophene (**11**) by the sample procedure as described in the preparation of **10**: colorless needles from hexane; mp 92.5–93 °C (lit.,[7a] 92.5–93 °C); ^1H NMR (60 MHz) δ 7.20 (m, 2H), 8.75 (m, 4H); MS *m/z* 214 (M^+); Anal. Calcd for $C_{12}H_6S_2$: C, 67.26; H, 2.82. Found; C, 67.17; H, 2.69.

1,4-Bis(2-selenienyl)-1,3-butadiyne (14)

55% yield from 2-iodoselenophene (**12**)[19] by the sample procedure as described in the preparation of **10**: yellow needles from hexane; mp 78–79 °C; ^1H NMR (60 MHz) δ 7.37 (dd, J = 5.8, 3.8 Hz, 2H), 7.70 (dd, J = 1.1, 3.8 Hz, 2H), 8.24 (dd, J = 5.8, 1.1 Hz, 2H); MS *m/z* 310 (M^+); Anal. Calcd for $C_{12}H_6Se_2$: C, 46.78; H, 1.96. Found; C, 46.73; H, 1.90.

2,2':5',2"-Tertellurophene (3)

A mixture of tellurium powder (310 mg, 2.5 mmol), sodium formaldehyde sulfoxylate (492 mg, 3.2 mmol), sodium hydroxide (1.3 g, 32.5 mmol), and deaerated EtOH (15 mL) was heated under reflux for an hour to generate sodium telluride. 1,4-Bis(2-tellurienyl)-1,3-butadiyne (**10**) (200 mg, 0.49 mmol) dissolved in a mixed solvent of EtOH (10 mL) and DMF (2 mL) was slowly added to the stirred sodium telluride solution. The mixture was heated under reflux for 8 h and, after cooled to rt, exposed to air with stirring. The resulting inorganic deposits were filtered off, and then the filtrate was concentrated. The residual solid was taken up with CH_2Cl_2 (30 mL), washed with brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2) and then recrystallization from chloroform to give **3** (93 mg, 35%) as orange fine crystals: mp 275–276 °C; ^1H NMR (400 MHz) δ 7.34 (s, 2H), 7.45 (dd, J = 0.8, 4.1 Hz, 2H), 7.66 (dd, J = 6.7, 4.1 Hz, 2H), 8.70

(dd, J = 6.7, 0.8 Hz, 2H); MS m/z 536 (M^+); UV-vis λ_{max}/nm (log ε) 452 sh (4.18), 423 (4.36), 343 (3.98), 254 (3.89), 209 (4.31); IR ν_{max}/cm^{-1} 1460, 1210, 830, 800, 740, 680; Anal. Calcd for $C_{12}H_8Te_3$: C, 26.94; H, 1.51. Found: C, 26.81; H, 1.51.

2,5-Bis(2-tellurienyl)thiophene (4)

65% yield by similar heterocyclization reaction of **10** and sodium sulfide nonahydrate; yellow crystals from chloroform; mp 165.5–166.5 °C; ^1H NMR (400 MHz) δ 6.90 (s, 2H), 7.66 (dd, J = 1.3, 4.0 Hz, 2H), 7.71 (dd, J = 6.7, 4.0 Hz, 2H), 8.76 (dd, J = 6.7, 1.3 Hz, 2H); ^{13}C NMR δ 125.1, 125.9, 133.5, 138.2, 139.1, 143.0; MS m/z 440 (M^+); UV-vis (THF) λ_{max} /nm (log ε) 406 sh (4.26), 391 (4.39), 328 (4.00), 244 (3.86); IR ν_{max}/cm^{-1} 1440, 1210, 830, 790, 750, 730, 700; Anal. Calcd for $C_{12}H_8STe_2$: C, 32.79; H, 1.83. Found: C, 32.79; H, 1.80.

2,5-Bis(2-tellurienyl)selenophene (5)

55% yield by similar heterocyclization reaction of **10** and sodium selenide prepared from selenium powder and sodium formaldehyde sulfoxylate; yellow fine crystals from chloroform: mp 224–226 °C (decomp); ^1H NMR (400 MHz) δ 7.01 (s, 2H), 7.57 (dd, J =1.3, 4.0 Hz, 2H), 7.69 (dd, J = 6.7, 4.0 Hz, 2H), 8.75 (dd, J = 6.7, 1.3 Hz, 2H); MS m/z 488 (M^+); UV-vis (THF) λ_{max} /nm (log ε) 430 sh (4.19), 402 (4.40), 280 (3.85), 245 (3.85); IR ν_{max}/cm^{-1} 1456, 1441, 1207, 828, 789, 739, 697; Anal. Calcd for $C_{12}H_8SeTe_2$: C, 29.64; H, 1.66. Found: C, 29.50; H, 1.69.

2,5-Bis(2-thienyl)tellurophene (6)

72% yield from **13** and sodium telluride by the sample procedure as described in the preparation of **3**; yellow powder from chloroform; mp 189–189.5 °C; ^1H NMR (400 MHz) δ 7.19 (dd, J = 5.1, 1.4 Hz, 2H), 6.97 (dd, J = 5.1, 3.4 Hz, 2H), 7.01 (dd, J = 1.4, 3.4 Hz, 2H), 7.34 (s, 2H); MS m/z 346 (M^+); UV-vis (THF) λ_{max}/nm (log ε) 406 sh (4.14), 388 (4.30), 265 (3.64), 2.50 (3.64); IR ν_{max}/cm^{-1} 1458, 1423, 799, 785, 696, 682; Anal. Calcd for $C_{12}H_8S_2Te$: C, 41.91; H, 2.34. Found: C, 41.81; H, 2.44.

2,5-Bis(2-selenienyl)tellurophene (7)

50% yield from **14** and sodium telluride by the sample procedure as described in the preparation of **3**; yellow powder from chloroform; mp 221–222 °C; ^1H NMR (400 MHz) δ 7.12 (dd, J = 1.2, 3.8 Hz, 2H), 7.19 (dd, J = 5.6, 3.8 Hz, 2H), 7.46 (s, 2 H), 7.85 (dd, J = 5.6, 1.2 Hz, 2H); MS m/z 440 (M^+); UV-vis (THF) λ_{max}/nm (log ε) 430 sh (4.15), 402 (4.36), 285 (3.76), 255 (3.56); IR ν_{max}/cm^{-1} 1458, 1423, 839, 798, 785, 696, 682; Anal. Calcd for $C_{12}H_8Se_2Te$: C, 32.93; H, 1.84. Found: C, 32.83; H, 1.92.

General procedure of electrochemical polymerization

The chalcogenophene (0.1 mmol), tetrabutylammonium perchlorate (342 mg, 1.0 mmol), deaerated benzonitrile (5 mL) were placed in the cell equipped with Pt plate (1 cm^2) as anode and Pt wire as cathode. Polymerization was carried out on galvanostatic conditions (50 $\mu A/cm^2$ except 2 mA/cm^2 for tellurophene, 2–5 h, rt, and a nitrogen atmosphere). The black film deposited on the Pt electrode was collected, washed with ethanol, and dried in vacuo.

General procedure of chemical polymerization

Into the solution of the chalcogenophene (0.1 mmol) dissolved in chloroform (10 mL) was added $FeCl_3$ (18 mg, 0.11 mmol), and the mixture was stirred for 2–3 h at rt. The resulting brown powder was collected, washed with chloroform, and dried *in vacuo*.

Crystal structure determination

The X-Ray diffraction data were collected with a Rigaku AFC-6S automated four-circle diffractometer using Cu-Kα radiation (λ = 1.5418 Å) monochromated with a graphite plate. The intensity data were measured using ω-2θ scan technique. Because the intensities of the standard reflections decreased by 80% in the course of data collection for biselenophene, a linear correction was applied to the data. The structures were solved by heavy-atom methods and refined by full-matrix least-squares techniques with anisotropic temperature factors for the non-hydrogen atoms.

Crystal data of 2,2'-bitellurophene: pale yellow plates from chloroform, crystal dimensions 0.10 × 0.10 × 0.08 mm, $C_8H_6Te_2$, M = 357.34, orthorhombic, space group $Pcab$, a = 14.851(1), b = 9.8159(8), c = 6.0044(5) Å, V = 875.3(1) Å^3, Z = 4, D_{calcd} = 2.716 g cm^{-1}, N = 538, R = 0.050.

Crystal data of 2,2'-biselenophene: colorless plates from hexane, crystal dimensions 0.35 × 0.11 × 0.10 mm, $C_8H_6Se_2$, M = 260.06, monoclinic, space group $P2_1/a$, a = 8.263(2), b = 6.038(2), c = 8.785(1) Å, β = 108.75(1)°, V = 415.0(1) Å^3, Z = 2, D_{calcd} = 2.08 g cm^{-1}, N = 349, R = 0.068.

The atomic coordinates have been deposited in the Cambridge Crystallographic Data Centre and can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1Ez, UK.

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