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THE FIRST OLIGOSELENOPHENES: SYNTHESIS AND PROPERTIES

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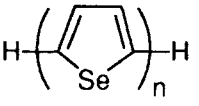
Abstract A series of oligoselenophenes with well-defined structures up to the hexamer has been synthesized using the Stille coupling reactions, and their physical properties have been studied by electronic absorption and emission spectroscopy as well as cyclic voltammetry. Their spectra systematically change with increasing conjugated chain lengths, and the correlations are reminiscent of those for oligothiophene series, suggesting that conjugation forms of both π-electronic systems are very similar. In addition, the oligoselenophenes, on iodine doping, have relatively high conductivities comparable to those of the oligothiophene counterparts, which increase up to approximately 10^{-2} Scm^{-1} with an increasing number of the selenophene units.

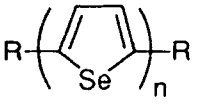
Keywords: Oligoselenophene, polyselenophene, conducting polymer, electronic absorption spectrum, emission spectrum, cyclic voltammogram

INTRODUCTION

Polythiophene is attracting current attention as one of electrically conducting polymers with the advantages of its environmental stability and structural versatility.[1] In this connection, various oligothiophenes have been recently developed as its model compounds as well as processing functional materials.[2] Selenophene (**1**) is the heavy homologue of the series of chalcogenophenes and essentially shows chemical and physical properties similar to those of thiophene,[3] but polyselenophene has been little studied[4] and none of oligoselenophenes have been known. This is presumably because, except for inaccessibility of selenophenes, polyselenophene is not so conductive as polythiophene.[4] It is speculated that the less conductivity of polyselenophene might be mainly ascribed to smaller polymerization degree, i.e., shorter conjugated chain length base on its poor solubility. This is supported by the fact that soluble poly(3-alkylselenophenes) have higher conductivities.[5] However, influence of the selenium atom on the electron distribution and therefore on the electron conduction of the polyselenophene system remains unclear. Since selenium generally shows a stronger heteroatomic interaction than sulfur, replacement of sulfur

by selenium often offers a method of choice for the search of highly conducting organic materials.[6] Thus, an important question is how selenophene can serve as an effective constituent unit in conducting polymers. Oligoselenophenes with well-defined structures might provide some useful information on the matter. This paper describes the synthesis and properties of a series of α-conjugated selenophenes **2-5** and derivatives **6-14** as the first oligoselenophenes. The substituent groups of **6-14** serve to improve the poor solubilities of oligoselenophenes.





1 : n=1
2: n=2
3: n=3
4: n=4
5: n=5

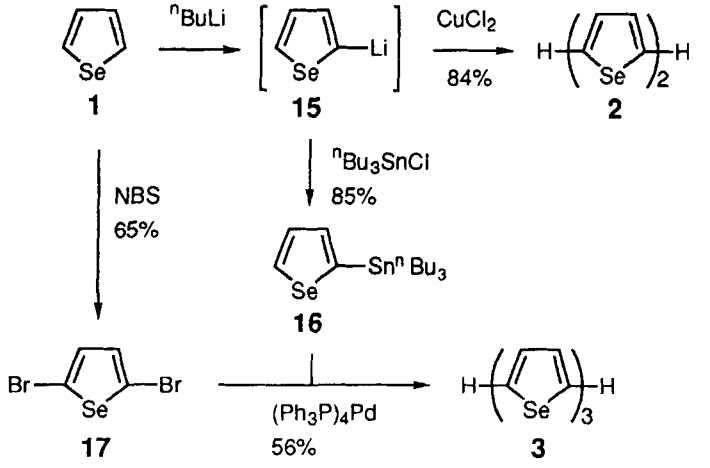
6: n=2, R=$(CH_2)_5CH_3$
7: n=3, R=$(CH_2)_5CH_3$
8: n=4, R=$(CH_2)_5CH_3$
9: n=5, R=$(CH_2)_5CH_3$
10 : n=2, R=$CH[O(CH_2)_{11}CH_3](CH_2)_{11}CH_3$
11 : n=3, R=$CH[O(CH_2)_{11}CH_3](CH_2)_{11}CH_3$
12 : n=4, R=$CH[O(CH_2)_{11}CH_3](CH_2)_{11}CH_3$
13 : n=5, R=$CH[O(CH_2)_{11}CH_3](CH_2)_{11}CH_3$
14 : n=6, R=$CH[O(CH_2)_{11}CH_3](CH_2)_{11}CH_3$

RESULTS AND DISCUSSION

Synthesis

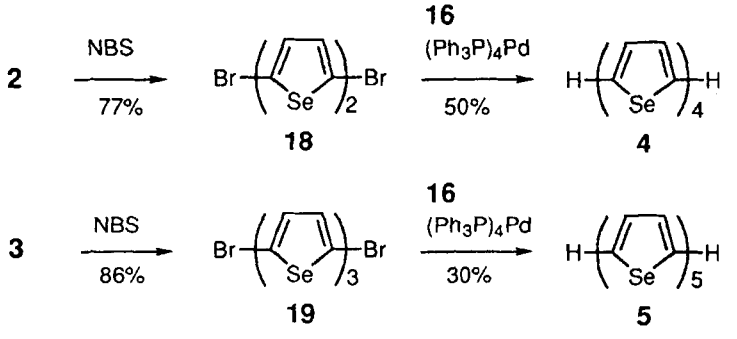
In order to investigate the chemistry of oligoselenophenes, efficient syntheses of α-linked selenophenes are clearly needed. Although 2,2'-biselenophene (**2**) was previously prepared by copper-catalyzed Ullmann coupling of 2-iodoselenophene[7] and Ni(0)-induced reductive coupling of 2-bromoselenophene,[8] we have found that the most efficient method is via oxidative coupling of 2-lithioselenophene (**15**): selenophene (**1**) was lithiated with butyllithium to 2-lithioselenophene (**15**), which was then treated in situ with copper (II) chloride to give 2,2'-biselenophene (**2**) in 84% yield (Scheme 1). This method was, however, ineffective for further extension of biselenophene (**2**) to quaterselenophene (**4**). In this case, the initial monolithiation of **2** competed with the subsequent dilithiation, resulting in the formation of a complex mixture containing **4** and higher homologues.

Alternatively, we have found that the Stille coupling reactions are successful in constructing all the present oligoselenophenes including **4**: bromination of **1** with *N*-



Scheme 1

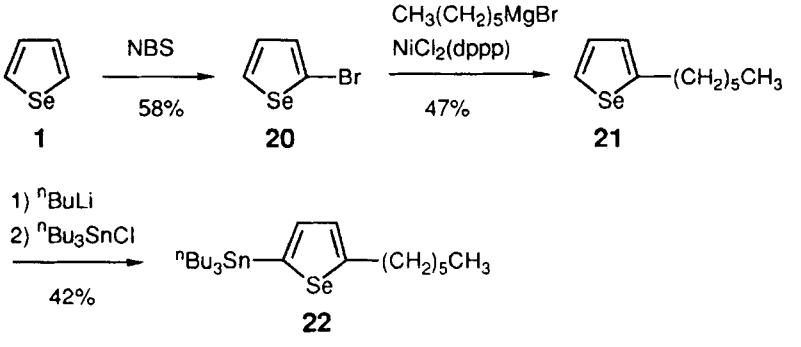
bromosuccinimide (NBS) gave 2,5-dibromoselenophene (**17**) in 65% yield, which was then reacted with 2-tributylstannylselenophene (**16**) in the presence of tetrakis(triphenylphosphine)palladium(0) to give 2,2':5',2"-terselenophene (**3**) in 56% yield.[9] A similar combination of NBS bromination and Stille coupling reaction was applied equally well to the preparation of quaterselenophene (**4**) from **2** and quinqueselenophene (**5**) from **3** (Scheme 2). But further attempted preparation of sexiselenophene from **4** was unsuccessful. This is considered to arise mainly from less reactivity due to poor solubilities of the precursory dibromo quaterselenophene as well as the formed sexiselenophene. In fact, solubilities of the oligoselenophenes drop drastically with an increasing chain length. For example, biselenophene (**2**) and terselenophene (**3**) have good solubilities above 10^{-1} M in common solvents, such as



Scheme 2

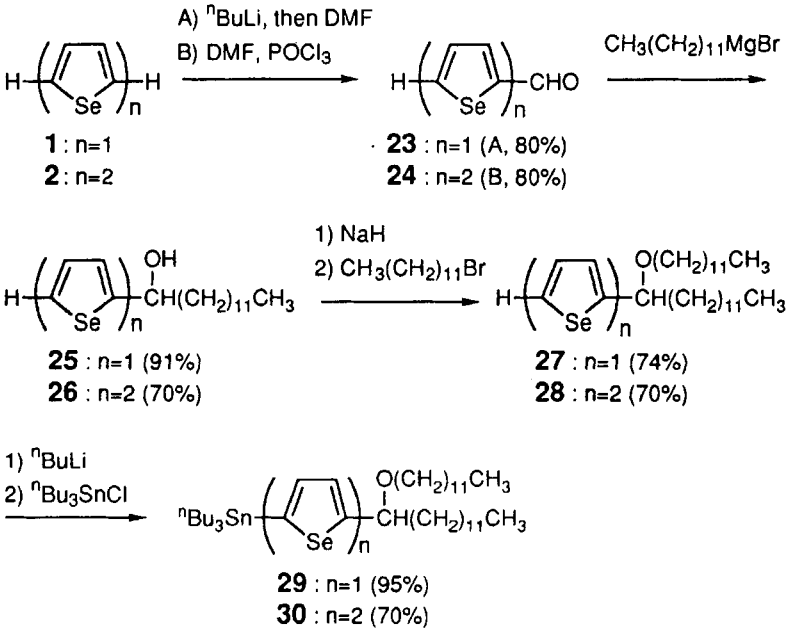
tetrahydrofuran, chloroform, and chlorobenzene. On the other hand, quaterselenophene (**4**) has only solubilities of the order of 10^{-4} M, and quiqueselenophene (**5**) below 10^{-5} M. Although the structures of these compounds were definitely characterized by spectroscopic analyses as summarized in Table 1, the limited solubilities of the high oligoselenophenes seriously prevented detailed investigations on their physical properties.

One might expect that, as seen for oligothiophene series,[2] introduction of long alkyl groups can improve the solubilities of oligoselenophenes. In this regard, first of all we designed the derivatives **6-9** bearing hexyl groups at the terminal α-positions. For this purpose, 2-hexyl-5-tributylstannylselenophene (**22**) was prepared according to Scheme 3 and similarly used for the Stille coupling reactions. These modified oligoselenophenes, when compared to the parent ones, have about one order of magnitude better solubilities in common solvents.

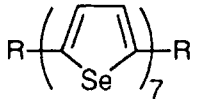


Scheme 3

In search of more soluble and tractable oligoselenophenes, we next studied other derivatives **10-14** bearing 1-dodecyloxytridecyl groups, which were obtained by use of either of the two Stille coupling reagents **29** and **30** available according to Scheme 4. For the quinqueselenophene **13**, two approaches are possible; both Stille coupling reactions between **17** and **30** and between **19** and **29** were equally successful. The dodecyloxytridecyl group relative to the hexyl group effects marked solubility enhancement, e.g., **13** has approximately three orders of magnitude larger solubilities than **9**. Thanks to this substituent effect, the sexiselenophene **14** was obtained in reasonable yield (21%) by a coupling reaction between **18** and **30**. Furthermore, the higher member, septiselenophene (**31**) was also prepared by a combination of **19** and **30**, but its complete purification was very difficult because of its trace yield.[10]



Scheme 4



31 : R=CH[O(CH$_2$)$_{11}$CH$_3$](CH$_2$)$_{11}$CH$_3$

TABLE 1. Yields and selective physical and spectroscopic data of oligoselenophenes **2-14**

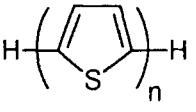
2	Yield 84% from **1**; colorless plates from ethanol; mp 47-47.5 °C; ^{1}H NMR δ 7.21 (dd, J=3.9, 5.6 Hz, 2H), 7.25 (d, J=3.9 Hz, 2H), 7.86 (d, J=5.6 Hz, 2H); IR 1431, 1206, 1043, 1030, 820, 750, 681 cm^{-1}.
3	Yield 56% from **16** and **17**; yellow leaflets from hexane-chloroform; mp 176-177.5 °C; MS *m/z* 390 (M$^+$); ^{1}H NMR δ 7.15 (s, 2H), 7.22 (dd, J=5.6, 3.9 Hz, 2H), 7.25 (dd, J=3.9, 1.5 Hz, 2H), 7.88 (dd, J=5.6, 1.5 Hz, 2H); IR 1473, 1208, 1040, 797, 793, 750, 688, 669 cm^{-1}.
4	Yield 50% from **16** and **18**; orange leaflets from chlorobenzene; mp>300 °C; MS *m/z* 520 (M$^+$); IR 1503, 1456, 1437, 1204, 1061, 1039, 824, 795, 754, 687, 675 cm^{-1}.

TABLE 1 (continued).

5	Yield 30% from **16** and **19**; red powder from chlorobenzene; mp>300 °C; MS *m/z* 648 (M^+); IR 1502, 1456, 1435, 1202, 1063, 1040, 789, 752, 669 cm^{-1}.
6	Yield 42% from **21**; pale yellow needles from ethanol; mp 25-26 °C; MS *m/z* 430 (M^+); ^1H NMR δ 0.88 (t, J=7.1 Hz, 6H), 1.28 (m, 12H), 1.67 (qui, J=7.6 Hz, 4H), 2.88 (t, J=6.2 Hz, 4H), 6.78 (d, J=4.0 Hz, 2H), 6.95 (d, J=4.0 Hz, 2H); IR 2950-2850, 1464, 1421, 1208, 1043, 828, 793, 725 cm^{-1}.
7	Yield 40% from **17** and **22**; pale yellow needles from ethanol; mp 157-159 °C; MS *m/z* 558 (M^+); ^1H NMR δ 0.89 (t, J=6.8 Hz, 6H), 1.28 (m, 12H), 1.67 (qui, J=7.6 Hz, 4H), 2.88 (t, J=7.4 Hz, 4H), 6.81 (d, J=3.6 Hz, 2H), 7.01 (d, J=3.6 Hz, 2H), 7.06 (s, 2H); IR 2955-2851, 1456, 1210, 1059, 795, 781 cm^{-1}.
8	Yield 47% from **18** and **22**; yellow fine crystals from chlorobenzene; mp 274-276 °C; MS *m/z* 688 (M^+); ^1H NMR δ 0.89 (t, J=3.8 Hz, 6H), 1.24-1.45 (m, 12H), 1.66 (qui, J=7.5 Hz, 4H), 2.84 (t, J=7.4 Hz, 4H), 6.82 (d, J=3.8 Hz, 2H), 7.03 (d, J=3.8 Hz, 2H), 7.04 (d, J=3.8 Hz, 2H), 7.08 (d, J=3.8 Hz, 2H); IR 2957-2850, 1456, 1204, 1065, 793 cm^{-1}.
9	Yield 30% from **19** and **22**; red fine crystals from chlorobenzene; mp>300 °C; MS *m/z* 816 (M^+); IR 2955-2850, 1455, 1202, 1067, 791 cm^{-1}.
10	Yield 85% from **27**; colorless needles from ethanol; mp 42-43 °C; ^1H NMR δ 0.87 (t, J=6.7 Hz, 12H), 1.25-1.43 (m, 76H), 1.55 (m, 4H), 1.67 (m, 2H), 1.83 (m, 2H), 3.30 (dt, J=8.9, 6.6 Hz, 2H), 3.50 (dt, J=8.9, 6.7 Hz, 2H), 4.32 (t, J=6.6 Hz, 2H), 6.92 (d, J=3.9 Hz, 2H), 7.04 (d, J=3.9 Hz, 2H); IR 2920-2851, 1468, 1098, 797, 723 cm^{-1}.
11	Yield 85% from **17** and **29**; pale yellow plates from ethanol-hexane; mp 36-37 °C; ^1H NMR δ 0.87 (t, J=6.7 Hz, 12H), 1.25-1.43 (m, 76H), 1.55 (m, 4H), 1.67 (m, 2H), 1.83 (m, 2H), 3.30 (dt, J=8.9, 6.6 Hz, 2H), 3.50 (dt, J=8.9, 6.7 Hz, 2H), 4.32 (t, J=6.6 Hz, 2H), 6.94 (d, J=3.9 Hz, 2H), 7.05 (d, J=3.9 Hz, 2H), 7.07 (s, 2H); IR 2920-2851, 1468, 1458, 1100, 789, 722, 669 cm^{-1}.
12	Yield 64% from **18** and **29**; orange plates from dichloromethane; mp 81-82.5 °C; ^1H NMR δ 0.87 (t, J=6.9 Hz, 12H), 1.25-1.43 (m, 76H), 1.55 (m, 4H), 1.67 (m, 2H), 1.83 (m, 2H), 3.31 (dt, J=9.1, 6.8 Hz, 2H), 3.51 (dt, J=9.1, 6.8 Hz, 2H), 4.33 (t, J=6.6 Hz, 2H), 6.95 (d, J=4.0 Hz, 2H), 7.06 (d, J=4.0 Hz, 2H), 7.09 (s, 4H); IR 2918-2849, 1466-1458, 1099, 787, 721 cm^{-1}.
13	Yield 46% form **17** and **30**; 32% from **19** and **29**; dark red fine crystals from chloroform; mp 114.5-116 °C; ^1H NMR δ 0.87 (t, J=6.9 Hz, 12H), 1.25-1.43 (m, 76H), 1.55 (m, 4H), 1.67 (m, 2H), 1.83 (m, 2H), 3.31 (dt, J=9.1, 6.8 Hz, 2H), 3.51 (dt, J=9.1, 6,8 Hz, 2H), 4.33 (t, J=6.6 Hz, 2H), 6.95 (d, J=4.0 Hz, 2H), 7.18 (d, J=4.0 Hz, 2H), 7.10 (m, 6H); IR 2920-2851, 1458, 1102, 787, 722, 669 cm^{-1}.
14	Yield 21% from **18** and **30**; dark red fine crystals from chloroform; mp 135.5-137.5 °C; ^1H NMR δ 0.87 (t, J=6.9 Hz, 12H), 1.25-1.43 (m, 76H), 1.55 (m, 4H), 1.67 (m, 2H), 1.83 (m, 2H), 3.31 (dt, J=9.1, 6.8 Hz, 2H), 3.51 (dt, J=9.1, 6.8 Hz, 2H), 4.33 (t, J=6.6 Hz, 2H), 6.96 (d, J=3.8 Hz, 2H), 7.07 (d, J=3.8 Hz, 2H), 7.09-7.11 (m, 8H); IR 2920-2851, 1466, 1456, 1099, 789, 720, 669 cm^{-1}.

Physical Properties

The physical properties of the present oligoselenophenes **1-14** together with oligothiophenes **32-37** are summarized in Table 2. The electronic spectra of all the selenophenes are characterized by a strong π–π^* transition in the long-wavelength region. The absorptions are markedly bathochromically and hyperchromically shifted with an increase of the chain length, and the magnitude of the shifts convergently decrease in order. In addition, the hexyl and the dodecyloxytridecyl groups also cause some shifts. The absorption maxima of **1-5** appear at longer wavelengths by nearly 30 nm than those of the corresponding thiophene counterparts, but the systematical spectral change in the series is reminescent of that seen for α-oligothiophene series.[11] This suggests that conjugation forms of both π-electronic systems are very similar. Emission spectra also demonstrate similar spectral changes in both series. While selenophene (**1**) like thiophene (**32**)[12] is not fluorescent, the homologues **2-14** show an emission band, which becomes stronger as the number of the selenophene units increases. The bathochromic shifts are in harmony with those of the absorptions, and the Stoke shifts lie around 50-70 nm.



32 : n=1
33: n=2
34 : n=3
35 : n=4
36 : n=5
37 : n=6

Table 2 also shows the oxidation peak potentials of the selenophene series, which were measured by cyclic voltammetry. The non-substituted selenophenes **2-4** exhibit an irreversible oxidation wave, which is systematically shifted lower in order. The oxidation potentials are somewhat lower than those of the respective thiophene counterparts, reflecting a less electronegative effect of selenium than sulfur. Repetitive cyclic voltammetry led to regular enhancement of the intensity accompanied with appearance of a new wave at ca. 0.8 V, forming a blue deposit on the surface of the electrode. This material was considered to correspond to polyselenophene in the oxidation state, which immediately turned brown on exposure to air. On the other hand, the cyclic voltammetry of the substituted oligoselenophenes **6-14** exhibits one or

TABLE 2. The longest-wavelength absorption bands, emission bands, oxidation peak potentials, and iodine-doped electrical conductivities of oligoselenophenes together with oligothiophenes.

Compd	Absorption[a]	Emission[a]	E_{pa}[b]/V	σ[c]/Scm^{-1}
	λ_{max}(log ε)/nm	λ_{max}/nm		
1 (n=1)	250 (3.87)	----[d]	>1.8	-------[f]
2 (n=2)	328 (4.08)	382	1.34[e]	1.5×10^{-5}
3 (n=3)	386 (4.39)	445	1.04[e]	1.5×10^{-3}
4 (n=4)	435 (4.52)	482	0.97[e]	3.2×10^{-3}
5 (n=5)	450 (-----)[f]	518	------[f]	9.0×10^{-3}
6 (n=2)	340 (4.22)	400	1.24, 1.52	8.6×10^{-6}
7 (n=3)	397 (4.42)	451	0.96, 1.18, 1.29	9.8×10^{-5}
8 (n=4)	435 (4.54)	496	0.89, 1.09, 1.15	3.9×10^{-4}
9 (n=5)	463 (4.63)	530	0.86, 0.98	1.6×10^{-3}
10 (n=2)	341 (4.22)	394	1.28	9.0×10^{-6}
11 (n=3)	398 (4.42)	458	0.96, 1.19	1.1×10^{-5}
12 (n=4)	435 (4.53)	496	0.87	8.8×10^{-5}
13 (n=5)	463 (4.63)	528	0.85, 1.04	1.0×10^{-4}
14 (n=6)	483 (4.71)	555	0.81, 0.92	1.5×10^{-4}
32 (n=1)	220 (3.90)	----[d]	>1.8	-------[f]
33 (n=2)	304 (3.76)	368	1.46[e]	-------[f]
34 (n=3)	353 (3.95)	412	1.13[e]	3.2×10^{-3}
35 (n=4)	394 (4.07)	451	1.06[e]	4.0×10^{-3}
36 (n=5)	419 (4.10)	480	0.98[e]	8.7×10^{-3}
37 (n=6)	437 (4.16)	504	0.96[e]	3.3×10^{-2}

[a]Measured in THF. [b]vs. Ag/AgCl, benzonitrile solvent, 0.1 *M* tetrabutylammonium perchlorate supporting electrolyte, Pt electrode, scan rate 100 mVs^{-1}. [c]Measured on compressed pellets by a two-probe method. [d]Not observed. [e]Irreversible. [f]Not measured.

more reversible oxidation waves. The oxidation waves, as compared with those of the parent ones, are considerably simplified by blocking of the active sites for polymerization and lowered by the substituent effects, and accordingly the second and third oxidation waves are observed for some of the compounds. The first oxidation waves also demonstrate low-potential shifts with an increase of the chain length.

The oligoselenophenes are insulating in the neutral state ($<10^{-9}$ Scm^{-1}), but, on iodine doping, show relatively high conductivities of 10^{-3}-10^{-5} Scm^{-1}. These values tend to increase gradually with an increasing selenophene unit. It is worth noting that the conductivity (9×10^{-3} Scm^{-1}) of quinqueselenophene (**5**) very approaches that (1.1×10^{-2} Scm^{-1}) of polyselenophene derived by electropolymerization of biselenophene (**2**). Interestingly, the doped conductivities of **3**-**5** are nearly equal to those of the relative I_2-doped α-oligothiophenes, also supporting similarity of both π-electronic

systems. The substituted derivatives, on the other hand, have lower conductivities by one order of magnitude than the parent ones, indicating some sterical influence of the substituent groups.

CONCLUSION

The present α-oligoselenophenes demonstrate systematic changes of their spectroscopic properties depending on the chain lengths, and the correlations are very similar to those seen for α-oligothiophene series. In addition, they, on iodine-doping, have high conductivities comparable to those of the relative oligothiophenes. These results suggest that the conjugation form of α-linked selenophenes is very similar to that of thiophene series, and selenophene can serve as an effective constituent unit in conducting polymers.

DEDICATION

This paper is dedicated to Professor Fumio Ogura and Professor Yusei Maruyama in honor of their retirements from successful academic careers in Hiroshima University and in Institute for Molecular Science, respectively.

ACKNOWLEDGMENT

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EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR spectra were measured in deuteriochloroform with a JEOL JNM-LA400 (400 MHz) instrument, IR spectra on KBr disk with a Shimadzu FTIR-8100A, UV/VIS spectra in THF with a Shimadzu UV-3100, Emission spectra in THF with a Shimadzu RF-5000, and MS spectra at 70 eV with a Shimadzu GCMS-QP2000. Selenophene (**1**) was prepared on a preparative scale by a thermal reaction of acetylene with selenium at 400-450 °C,[13] and 2-formylselenophene (**23**) by lithiation of selenophene (**1**) followed by treatment with DMF according to the literature.[14] All new compounds gave satisfactory C, H combustion analyses within an error of 0.3 %.

2,2'-Biselenophene (**2**) (General method for the preparation of biselenophenes)
Into a stirred solution of selenophene (**1**) (15 g, 0.12 mol) in dry ether (200 mL) at 0 °C under a nitrogen atomosphere was added a 1.64 *N* hexane solution of butyllithium (73.6 mL, 0.12 mol) over a period of 10 min, and the mixture was stirred for 1 h at RT

to form 2-lithioselenophene (**15**) . After copper (II) chloride (21.2 g, 0.16 mol) was portionwise added to the mixture cooled to -70 °C, the mixture was stirred overnight at RT, diluted with ether (100 mL), and filtered. The solid was thoroughly washed with ether, and the filtrate and washings were combined and successively washed with water, 1 *N* hydrochloric acid, 5% sodium hydrogen carbonate aqueous solution, and finally water. After dryness ($MgSO_4$), the solvent was evaporated and the residue was purified by column chromatography on silica gel with hexane followed by recrystallization from ethanol to give **2** as colorless plates (12.5 g, 84%): mp 47-47.5 °C (lit.,[7] 49 °C).

2-Tributylstannylselenophene (**16**) (General method of tributylstannylation)[9,15]
Into a stirred solution of 2-lithioselenophene (**15**), prepared from selenophene (**1**) (5.0 g, 38.2 mmol) and butyllithium (23.3 mL, 38.2 mmol) in dry ether (50 mL) and cooled to -70 °C, was added tributyltin chloride (8.9 mL, 38.2 mmol) in a nitrogen atmosphere, and the mixture was stirred overnight at RT and then treated with hexane (50 mL), which was washed with brine, and dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography on silica gel with hexane to give **16** as a pale yellow oil (10 g, 85%): ^{1}H NMR δ 0.86 (t, J=7.3 Hz, 9H), 1.05 (m, 6H), 1.35 (m, 6H), 1.56 (m, 6H), 7.50 (m, 2H), 8.35 (d, J=4.0 Hz, 1H).

2,5-Dibromoselenophene (**17**) (General method of NBS bromination)
Into a stirred solution of selenophene (**1**) (10 g, 77 mmol) in chloroform-acetic acid (1:1 v/v 100 mL) was portionwise added NBS (27.4 g, 154 mmol), and the mixture was stirred at RT for 1 h and then at 50 °C for 30 min. The mixture was poured into water (100 mL) and extracted with dichloromethane. The extract was successively washed with water, 5% sodium hydrogen carbonate aqueous solution, and brine. After dryness ($MgSO_4$), the solvent was evaporated and the residue was purified by column chromatography on silica gel with hexane to give **17** as a pale yellow oil (14.5 g, 65%): ^{1}H NMR δ 7.00 (s, 2H).

5,5'-Dibromo-2,2'-biselenophene (**18**)
Yield 77% from NBS dibromination of biselenophene (**2**); colorless leaflets from chloroform; 174.5-175.5 °C; MS *m/z* 418 (M^+); ^{1}H NMR δ 6.87 (d, J=4.2 Hz, 2H), 7.14 (d, J=4.2 Hz, 2H).

5,5''-Dibromo-2,2':5',2''-terselenophene (**19**)
Yield 86% from NBS dibromination of terselenophene (**3**); golden orange leaflets from chlorobenzene; mp 255.5-256 °C; MS *m/z* 548 (M^+); ^{1}H NMR δ 6.93 (d, J=4.1 Hz, 2H), 7.04 (s, 2H), 7.16 (d, J=4.1 Hz, 2H).

2-Bromoselenophene (**20**)

Yield 58% from NBS monobromination of selenophene (**1**); pale yellow oil; bp 55-57 °C/10 mmHg (lit.,[16] bp 59 °C/13 mmHg); MS *m/z* 210 (M^+); ^1H NMR δ 7.05 (dd, J=6.2, 4.0 Hz, 1H), 7.25 (dd, J=4.0, 1.0 Hz, 1H), 7.91 (dd, J=6.2, 1.0 Hz, 1H).

2,2':5',2"-Terselenophene (**3**) (General method of Stille coupling reaction)

A mixture of 2,5-dibromoselenophene (**17**) (2.0 g, 6.9 mmol), 2-tributylstannylselenophene (**16**) (6.8 g, 15.1 mmol), and tetrakis(triphenylphosphine)palladium (0.8 g, 0.76 mmol) in dry toluene (50 mL) was heated at reflux for 5 h under nitrogen atmosphere. After the solvent was evaporated, the residue was purified by column chromatography on silica gel with hexane followed by recrystallization from hexane-chloroform to give **3** as yellow leaflets (1.48 g, 56%).

2-Hexylselenophene (**21**)

Into a dry THF suspension (50 mL) containing magnesium turnings (1.49 g, 61 mmol) under nitrogen was dropwise added 1-bromohexane (10.0 g, 61 mmol) in such a rate as to induce mild reflux, and the mixture was refluxed for 30 min to form the Grignard reagent, which was added into a solution of 2-bromoselenophene (**20**) (11.55 g, 55 mmol), Ni(dppp)Cl_2 (360 mg), and dry THF (100 mL) at 0°C. The mixture was refluxed for 5 h, and 25% aq ammonium chloride (30 mL) was added with ice-cooling, and the mixture was stirred for 30 min at RT. The THF solvent was evaporated, and the residue was treated with ether (100 mL), which was successively washed with water, 1 *N* hydrochloric acid, and 5% aq sodium hydrogen carbonate, and dried ($MgSO_4$). After evaporation of the solvent, distillation of the residue gave a pale yellow oil of **21** (5.6 g, 47%): bp 100-105 °C/ 15 mmHg; MS *m/z* 216 (M^+); ^1H NMR δ 0.88 (t, J=6.2 Hz, 3H), 1.28 (m, 6H), 1.67 (m, 2H), 2.88 (t, J=6.2 Hz, 2H), 6.93 (dd, J=3.7, 1.1 Hz, 1H), 7.12 (dd, J=5.6, 3.7 Hz, 1H), 7.78 (dd, J=5.6, 1.1 Hz, 1H).

2-Hexyl-5-tributylstannylselenophene (**22**)

Yield 42% from tributylstannylation of **21**; pale yellow oil; MS *m/z* 504 (M^+); ^1H NMR δ 0.89 (m, 12H), 1.16 (m, 2H), 1.42-1.70 (m, 24H), 2.91 (t, J=7.6 Hz, 2H), 7.25 (d, J=3.4 Hz, 1H), 7.31 (d, J=3.4 Hz, 1H).

5-Formyl-2,2'-biselenophene (**24**)

Into a stirred solution of DMF (1.4 mL, 18 mmol) in dry dichloromethane (5 mL) in a nitrogen atmosphere was added phosphorus oxychloride (0.37 mL, 3.9 mmol) with ice-cooling, and the solution was kept at 40 °C for 2 h. The resulting Vilsmeier reagent was dropwise added into a stirred solution of biselenophene (**2**) (3.0 g, 12 mmol) in dry dichloromethane (20 mL) with ice-cooling, and the mixture was stirred for 6 h at

RT. After the solvent was evaporated, the residue was treated with aq 1 *N* NaOH (50 mL) at 80 °C for 1 h and taken up with dichloromethane (100 mL), which was then washed with water and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography on silica gel with dichloromethane and then recrystallization from hexane-dichloromethane to give pale yellow crystals of **24** (2.8 g, 80%): mp 72.5-74 °C; IR 1655.1 cm^{-1} (C=O); MS *m/z* 290 (M^+); ^1H NMR δ 7.29 (dd, J=5.6, 3.9 Hz, 1H), 7.35 (d, J=4.0 Hz, 1H), 7.47 (dd, J=3.9, 1.0 Hz, 1H), 7.89 (d, J=4.0 Hz, 1H), 8.05 (dd, J=5.6, 1.0 Hz, 1H), 9.75 (s, 1H).

2-(1-Hydroxytridecyl)selenophene (**25**)

Into a dry ether solution (80 mL) containing magnesium turnings (2.75 g, 0.113 mol) was added 1-bromododecane (27 mL, 0.113 mol) in a nitrogen atmosphere, and the mixture was refluxed for 3 h. A solution of 2-formylselenophene (**23**) (15 g, 94 mmol) in dry ether (20 mL) was slowly added, and reflux was continued for additional 2 h. The reaction mixture was cooled to 0 °C and stirred with 25% aq ammonium chloride (30 mL) for 30 min. The organic layer was separated, washed with water and then 5% aq sodium hydrogen carbonate, and dried ($MgSO_4$). After evaporation, the residual solid was purified by column chromatography on silica gel with dichloromethane to give a pale yellow oil of **25** (28.2 g, 91%): IR 3355 cm^{-1} (OH); MS *m/z* 330 (M^+); ^1H NMR δ 0.87 (t, J=7.0 Hz, 3H), 1.30 (m, 20H), 1.75 (m, 2H), 2.31 (s, 1H), 4.86 (t, J=6.8 Hz, 1H), 7.09 (dd, J=3.6, 0.8 Hz, 1H), 7.16 (dd, J=5.6, 3.6 Hz, 1H), 7.90 (dd, J=5.6, 0.8 Hz, 1H).

5-(1-Hydroxytridecyl)-2,2'-biselenophene (**26**)

Yield 70% from **24** analogously to **25**; pale yellow crystals from hexane; mp 66-67.5 °C; IR 3422 cm^{-1} (OH); MS *m/z* 442 (M^+-18); ^1H NMR δ 0.87 (t, J=8.0 Hz, 3H), 1.25 (m, 20 H), 1.87 (m, 2H), 2.05 (s, 1H), 4.85 (t, J=8.0 Hz, 1H), 7.00 (d, J=3.6 Hz, 1H), 7.10 (d, J=3.6 Hz, 1H), 7.22 (m, 2H), 7.85 (dd, J=5.1, 1.5 Hz, 1H).

2-(1-Dodecyloxytridecyl)selenophene (**27**)

Into a solution of **25** (1.0 g, 3.0 mmol) in dry DMF was added sodium hydride (600 mg, 7.5 mmol, 62% in oil) in a nitrogen atmosphere, and the mixture was stirred for 20 min at RT. 1-Bromododecane (0.9 ml, 3.6 mmol) was added, and the mixture was stirred for 5 h, treated with water (20 mL), and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and filtered through a short column of silica gel with hexane. After evaporation, the residue was purified by gel-permeation liquid chromatography with chloroform to give a pale yellow oil of **27** (1.1 g, 74%): MS *m/z* 329 (M^+-$C_{12}H_{25}$); ^1H NMR δ 0.87 (t, J=6.6 Hz, 6H), 1.1-1.9 (m, 38H), 1.5 (m, 2H),

1.8 (m, 1H), 1.9 (m, 1H), 3.31 (dt, J=9.1, 4.8 Hz, 1H), 3.51 (dt, J=9.1, 6.8 Hz, 1H), 4.33 (t, J=6.6 Hz, 1H), 7.06(d, J=3.2 Hz, 1H), 7.16 (dd, J=5.6, 3.2 Hz, 1H), 7.91 (dd, J=5.6, 0.7 Hz, 1H).

5-(1-Dodecyloxytridecyl)-2,2'-biselenophene (**28**)
Yield 70% from **26** analogously to **27**; yellow oil; MS *m/z* 628 (M^+); ^1H NMR δ 0.87 (t, J=6.6 Hz, 6H), 1.25 (m, 38H), 1.50 (m, 2H), 1.65 (m, 1H), 1.86 (m, 1H), 3.31 (dt, J=9.1, 6.8 Hz, 1H), 3.51 (dt, J=9.1, 6.8 Hz, 1H), 4.33 (t, J=6.6 Hz, 1H), 6.95 (d, J=4.0 Hz, 1H), 7.08 (d, J=4.0 Hz, 1H), 7.21 (m, 2H), 7.84 (dd, J=5.1, 1.7 Hz, 1H).

2-(1-Dodecyloxytridecyl)-5-tributylstannylselenophene (**29**)
Yield 95% from tributylstannylation of **27**; pale yellow oil; MS *m/z* 729 (M^+-C_4H_9); ^1H NMR δ 0.75-1.90 (m, 75H), 3.44 (dt, J=9.2, 6.8 Hz, 1H), 3.45 (dt, J=9.2, 7.1 Hz, 1H), 4.47 (t, J=6.8 Hz, 1H), 7.17 (d, J=3.4 Hz, 1H), 7.30 (d, J=3.4 Hz, 1H).

5-(1-Dodecyloxytridecyl)-5'-tributylstannyl-2,2'-biselenophene (**30**)
Yield 70% from tributylstannylation of **28**; brown oil; MS *m/z* 916 (M^+); ^1H NMR δ 0.75-1.90 (m, 75H), 3.44 (dt, J=9.2, 6.8 Hz, 1H), 3.45 (dt, J=9.2, 6.8 Hz, 1H), 4.47 (t, J=6.8 Hz, 1H), 6.94 (d, J=3.9 Hz, 1H), 7.07 (d, J=3.9 Hz, 1H), 7.17 (m, 1H), 7.32 (m, 1H).

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