Synthesis of Novel Heteroquaterphenoquinones and Their Electrochemical, Structural, and Spectroscopic Characterization

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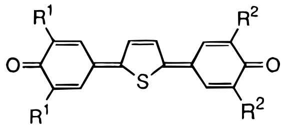
Novel heteroquaterphenoquinones, 5,5′-bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-5,5′-dihydro-2,2′-bithienyl (**3**) and its 2,2′-biselenienyl (**4**), 2,2′-bifuryl (**5**), and 2,2′-bi-*N*-methylpyrrolyl (**6**) analogues, were synthesized by a stepwise cross-coupling reaction or by a more convenient one-pot oxidative homocoupling reaction of heterocycle-substituted phenols. Despite a highly conjugation-extended system, the quinones **3**−**6** are very stable in the solid state and in solution in common organic solvents. These quinones undergo a reversible one-stage, two-electron reduction up to dianions and a two-stage, one-electron oxidation reaction up to dications. The E_1^{red} of these quinones increases with the increase in the aromaticity of the incorporated heterocycles. The E_1^{ox} of these quinones appears to be specified by the ionization potential of the incorporated heterocycles. Thus, the *N*-methylquinone **6** exhibiting the lowest E_1^{ox} value exhibits the smallest E_1^{sum} among the quinones **3**−**6**. The quinone **5** was revealed to exist in an unusual *O-cis* conformation in the solid state by X-ray crystallography, whereas the quinone **3** exists in an *S-trans* conformation in the solid state. The *cis* and *trans* isomers are interconvertible in solution in **3**−**5**, whereas only *N-trans* isomer was detected for **6** in ^{1}H NMR spectroscopy. The quinones **3**−**6** exhibit a very intense absorption maximum in the near-infrared region of 662−827 nm. Of these, the maximum absorption wave length of **6** shifts to a more bathochromic region by 149−165 nm than those of **3**−**5**. The quinones **3**−**6** can be used as dyestuffs in various fields for laser-driven high-density optical storage media.

A molecular design strategy to incorporate a thienylene group in constructing novel conjugation-extended π-electron systems was originally developed in quinarene chemistry in 1980.[1] During these 15 years, many new molecules incorporated with one or more five-membered heteroaromatics[2] have been designed and synthesized, thus contributing significantly to the development of novel aromatic compounds as well as functional materials of topical interest. We have recently designed and synthesized thienylene- or furylene-incorporated heteroterphenoquinones such as **1**[3] and **2**[4] and have clarified the fundamental aspects of these quinones. However, the compounds that belong to the quaterphenoquinone family were completely unknown until our first communication[5] on the synthesis of **3** was reported. *p*-Quaterphenoquinone itself constructed with four quinonoidal benzene rings would be too unstable to be synthesized owing to the significant contribution of its biradical structure to the ground state.[6] From our knowledge, incorporation of heterocyclic group(s) as an integral π-component appears to be very effective in stabilizing not only the closed-shell but also the open-shell π-electron systems. Such stabilization is not achieved by the incorporation of ethylene or phenylene group(s).[7] Consequently, the synthesis of heteroquaterphenoquinones now appears to be accessible, and therefore, these quinones may be ranked as very important compounds in the investigation of the unknown field of highly cunjugation-extended quinones, as well as related quinonoid compounds including doped heterocyclic oligomers[8] and doped heterocyclic polymers.[9] With this in mind, we have now synthesized novel heteroquaterphenoquinones **3**−**6** and have characterized their electrochemistry, structures, and spectroscopic properties, which are reported herein.

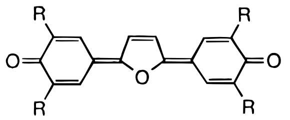


1a: R^1=R^2=H **1b**: R^1=R^2=Me

1c: R^1=R^2=Bu^t **1d**: R^1=H, R^2=Bu^t

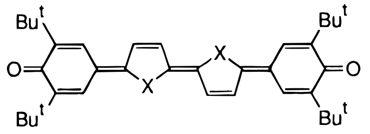
1e: R^1=Bu^t, R^2=SMe **1f**: R^1=Bu^t, R^2=Cl

1g: R^1=Bu^t, R^2=Br



2a: R=Me

2b: R=Bu^t



3: X=S **4**: X=Se

5: X=O **6**: X=NMe

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(1) Takahashi, K.; Takase, T.; Sakae, T. *Chem. Lett.* **1980**, 1485. Takahashi, K.; Sakae, T.; Takase, K. *Chem. Lett.* **1980**, 179.

(2) Takahashi, K. *J. Synth. Org. Chem. Jpn.* **1986**, *44*, 806. Takahashi, K. *Pure Appl. Chem.* **1993**, 127. Takahashi, K.; Tomitani, K. *J. Chem. Soc., Chem. Commun.* **1995**, 821. Takahashi, K.; Tarutani, S. *Adv. Mater.* **1995**, *7*, 639. Takahashi, K.; Nihira, T.; Akiyama, K.; Ikegami, Y.; Fukuyo, E. *J. Chem. Soc., Chem. Commun.* **1992**, 620. Ribou, A.-C.; Launey, J.-P.; Takahashi, K.; Nihira, T.; Tarutani, S.; Spangler, C. W. *Inorg. Chem.* **1994**, *33*, 1325. Yui, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1539. Rao, V. P.; Jen, A. K.-Y.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118. Kawai, S. H.; Gilat, S. L.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 1011.

(3) (a) Takahashi, K.; Suzuki, T.; Akiyama, K.; Ikegami, Y.; Fukazawa, Y. *J. Am. Chem. Soc.* **1991**, *113*, 4576. (b) Takahashi, K.; Sakai, T. *Chem. Lett.* **1993**, 157.

(4) Takahashi, K.; Gunji, A.; Akiyama, K. *Chem. Lett.* **1994**, 863.

(5) Takahashi, K.; Suzuki, T. *J. Am. Chem. Soc.* **1989**, *111*, 5483.

(6) Dimroth, K.; Umbach, W.; Blocher, K. H. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 620.

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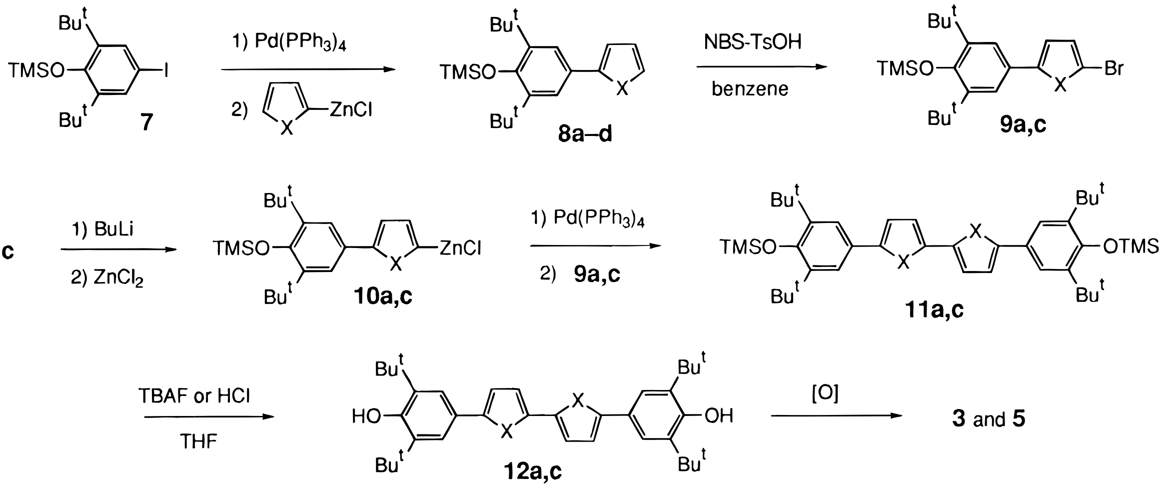
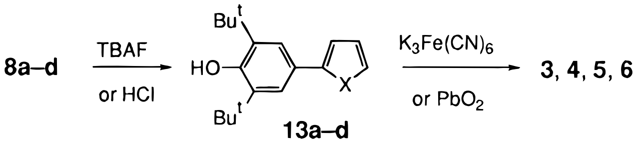
Scheme 1



a: X=S, **b**: X=Se, **c**: X=O, **d**: X=NMe

Scheme 2



a: X=S, **b**: X=Se, **c**: X=O, **d**: X=NMe

Interestingly, the dioxaquaterphenoquinone **5** has been proved to exist in an unusual *O-cis* bifurylene-type conformation in the solid state. Furthermore, it has also been revealed that the quinones **3**–**6** have a high potential for use as dyestuffs for diode laser or as electroconducting mediators for optoelectronics, since they exhibit an intense absorption maximum in the near-infrared (NIR) region and undergo amphoteric three-stage redox reactions.

Result and Discussion

Synthesis. Quinones **3**–**6** were synthesized through the route depicted in Schemes 1 and 2. Five-membered heterocycle-substituted (trimethylsiloxy)benzenes **8a**–**d** were synthesized in satisfactory yields by the reaction of iodobenzene derivative **7**[3a] with 2-furyl- or 2-thienylzinc chloride in the presence of 5 mol % of $Pd(PPh_3)_4$ generated *in situ* by treating $Cl_2Pd(PPh_3)_2$ with *i*-Bu_2-AlH_4. Zinc-metalated derivatives **10a**,**c**, prepared from lithiated **8a**,**c** and zinc chloride, were allowed to react with **9a**,**c**, prepared by NBS bromination of **8a**,**c**, in the presence of the Pd(0) catalyst, to produce **11a** and **11c** in 86 and 84% yields, respectively. The bis(silyloxy) derivatives **11a**,**c** were desilylated with 1 M HCl in THF or, more conveniently, with tetrabutylammonium fluoride (TBAF) in dry THF to give the corresponding bisphenols **12a** and **12c** in 90 and 96% yields, respectively. TBAF is superior to BBr_3 or HCl, since it is applicable to acid-sensitive compounds. Subsequent oxidation of **12a** and **12c** with potassium ferricyanide dissolved in aqueous KOH solution gave quinones **3** and **5** in 83.7 and 90.4% yields, respectively. Both **12a** and **12c** were oxidized more quickly with PbO_2 in dichloromethane to give **3** and **5** in 98.6 and 98% yields, respectively.

The oxidative dimerization of phenols is an important tool for the synthesis of diphenoquinones,[10] although this reaction is liable to give benzoquinones and aryloxy polymers as byproducts depending on the oxidizing reagents. We, therefore, investigated one-electron oxidation of heterocycle-substituted phenols. Thus, the siloxybenzene derivatives **8a**–**d** were desilylated with TBAF in dry THF to give the corresponding phenols **13a**–**d** in good yields. The oxidative dimerization reaction of **13a**–**d** with potassium ferricyanide or with PbO_2 proceeded smoothly, giving the corresponding heteroquaterphenoquinones **3**–**6** in fairly good yields. The yields of the quinones **3** and **4** are very high in both ferricyanide and PbO_2 oxidations. The yield of **5** is much better in the PbO_2 oxidation than in the ferricyanide oxidation. In the ferricyanide oxidation of **13c**, heteroterphenoquinone **2b** (16%) and tetra-*tert*-butyldiphenoquinone **16** (6.8%) were obtained as byproducts together with the main product **5**. Therefore, the lower yield of **5** can be attributed to the unfavorable aryloxy radical coupling affording **14** and **15** as intermediates for **2b** and **16**, respectively (Scheme 3).

True to the sensitive nature of pyrroles to oxidation with Fe(III) ion, reaction of **13d** with potassium ferricyanide was complicated and gave a number of uncharacterizable products. Nevertheless, the quinone **6**[11] was obtained in 76.9% yield by the PbO_2 oxidation of **13d**. Synthetic methodologies of this oxidative homocoupling reaction involve convenient and short-step reactions that can be manipulated quite easily and so are suitable for large-scale preparation. The quinones **3**–**6** are very

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[7] Yamashita, Y.; Kobayashi, Y.; Miyashi, T. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1052. Moore, A. J.; Bryce, M. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 157. Yamashita, Y.; Tanaka , S.; Tomura, M. *J. Chem. Soc., Chem. Commun.* **1993**, 652.

[8] Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 4437. Effenberger, F.; Würthner, F.; Steybe, F. *J. Org. Chem.* **1995**, *60*, 2082.

[9] Gleins, S.; Benz, M.; LeGoff, E.; Schindler, J. L.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 12519 and references cited therein. McCullough, R.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.

[10] Hains, A. H. In *Method for the Oxidation of Organic Compounds*; Academic Press, Inc.: London, Orlando, 1985; p 195 and references cited therein. Balogh, V.; Fetizon, M.; Golfier, M. *J. Org. Chem.* **1971**, *36*, 1339.

[11] Quinone **6** was not synthesized through the route described in Scheme 1.

Scheme 3

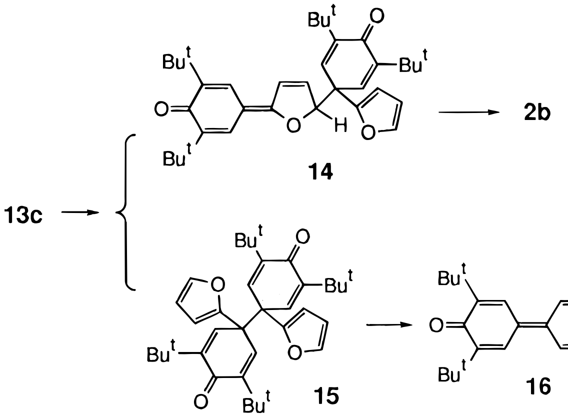


Table 1. Redox Potentials[a] and E_1^{sum} Values of Heteroquaterphenoquinones and Their Reference Quinones

quinone	E_1^{ox}	E_{p1}^{ox}	E_{p2}^{ox}	ΔE_p^{ox}	E_1^{red}	E_1^{sum}
3	+0.85	+0.91	+1.40	0.49	−0.43	1.28
4	+0.88	+0.94	+1.35	0.41	−0.45	1.33
5	+0.83	+0.89	+1.49	0.60	−0.49	1.32
6	+0.47	+0.53	+1.18	0.65	−0.47	0.94
1c	+1.23	+1.28			−0.47	1.70
2b	+1.25	+1.30			−0.54	1.79

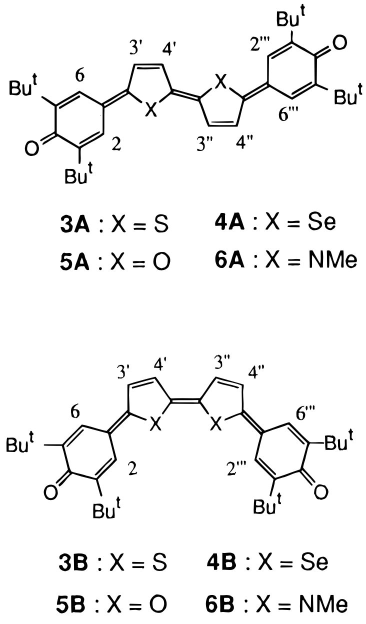
[a] Potentials (V *vs* SCE) are measured by cyclic voltammetry in PhCN with 0.1 M (*n*-Bu)4NClO4 at room temperature (scan rate, 50 mV/s).

stable in the solid state and soluble in nonpolar organic solvents such as tetrachloroethane, dichloromethane, benzene, and alkylcyclohexanes.

Electrochemistry. Quinones **3**−**6** were readily reduced with Na-metal in THF to the corresponding radical anions, which were confirmed by the ESR spectra showing seven splitting signals.[12] However, the cyclic voltammograms of **3**−**6** showed a reversible two-electron reduction wave in the range of −0.43−−0.49 V (Table 1), affording the corresponding dianions. This fact reveals that the difference between the first and second reduction potentials is small owing to the decrease in Coulomb repulsion in the corresponding dianion.

The E_1^{red} appears to increase with the increase in the aromaticity of the incorporated heterocycles, but the differences among the values of **3**−**6** are not large. The quinones **3**−**6** showed one-electron, two-step oxidation waves in the anodic direction corresponding to the formation of the radical cations and dications of these quinones. The E_1^{ox} values of **3** and **5** are significantly lower by 0.38 and 0.42 V than those of the corresponding heteroterphenoquinones **1c** and **2b**, respectively, whereas the E_1^{red} values of the former are more positive only by 0.04 and 0.05 V than those of the latter. Thus, the E_1^{sum} ($= E_1^{ox} + (-E_1^{red})$)[13] value, a measure to express the span of the oxidation and reduction potentials, is much smaller in heteroquaterphenoquinones than in heteroterphenoquinones. As can be seen in Table 1, the first oxidation potentials (E_1^{ox}) of the quinones **3**−**5** are in fairly the same range; nevertheless, the E_1^{ox} of the *N*-methylquinone **6** is very low. Thus, the E_1^{ox} values of these heteroquaterphenoquinones appear to be specified by the ionization potential of the incorporated heterocycles, because the ionization potential of pyrrole (8.2 eV) is significantly lower than those of thiophene (8.87 eV), selenophene (8.92 eV), and furan (8.89 eV). Reflecting the low oxidation potential, the *N*-methylquinone **6** exhibits the smallest E_1^{sum} among the quinones **3**−**6**, indicating that conjugation−extension with the *N*-methylpyrrole groups is markedly effective in enhancing the amphotericity.

Scheme 4



Structural Analysis. Conformational analysis of the heteroquaterphenoquinones **3**−**6** has become a very interesting subject of study because these quinones can be characterized as the smallest oligomers of organic conducting polymers such as doped polythiophenes, polyfurans, and polypyrroles. 2,2′-Bifuryl itself has been reported to exist in an *O-trans* planar conformation in the crystalline state[14] and predominantly in the *O-trans* isomer (78 ± 2)% in the liquid state.[15] Therefore, we first expected an *O-trans* conformation (**5A**) for the quinone **5** (Scheme 4).

However, contrary to our expectations, the X-ray crystallographic analysis revealed that the quinone **5** exists in the *O-cis* conformation (**5B**) in crystals (Figure 1).[16] The quinone **5** is an essentially planar molecule with torsion angles between the mean planes of the two rings: 1.90 ° (A−B), 4.77 ° (C−D), 5.29 ° (B−C), and 11.26 ° (A−D). The C12−O3 (1.239 Å) and the C26−O4 (1.234 Å) bonds are a little longer than the CO bond of *p*-benzoquinone (1.222 Å) and the three intercyclic bonds, C1−C9 (1.383 Å), C8−C23 (1.380 Å), and C4−C5 (1.372 Å), are longer than the standard double bond length (1.34 Å), which might be ascribed to the contribution of the dipolar structure to some extent to the ground state. The molecules form dimers with the center of symmetry at

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[12] The EPR spectrum was too broad to obtain the splitting constants.

[13] Nakasuji, K.; Yoshida, K.; Murata, I. *J. Am. Chem. Soc* **1982**, *104*, 1432; **1983**, *105*, 5136. Takahashi, K.; Ogiyama, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1197.

[14] Bambagiotti, M.; Castellucci, E.; Sbrana, G. *Spectrochim. Acta* **1974**, *30A*, 1413.

[15] Bellitto, L.; Petrongolo, C.; Veracini, C. A.; Bambogiotti, M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 314. Orti, E.; Sanchez-Marin, J.; Merchan, M.; Tomas, F. *J. Phys. Chem.* **1987**, *91*, 545.

[16] X-ray data for the crystallographic analysis of quinone **5** have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

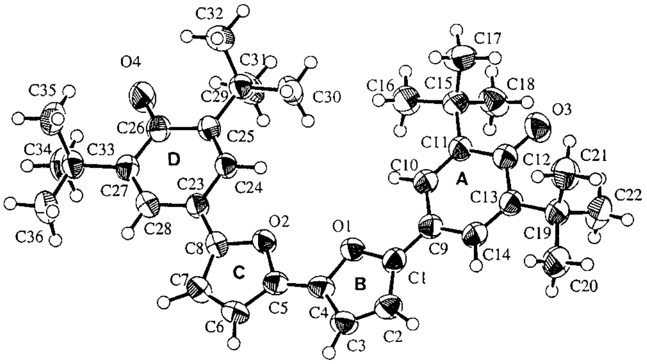

Figure 1. Molecular structure of **5**, showing an *O-cis* bifuran conformation.

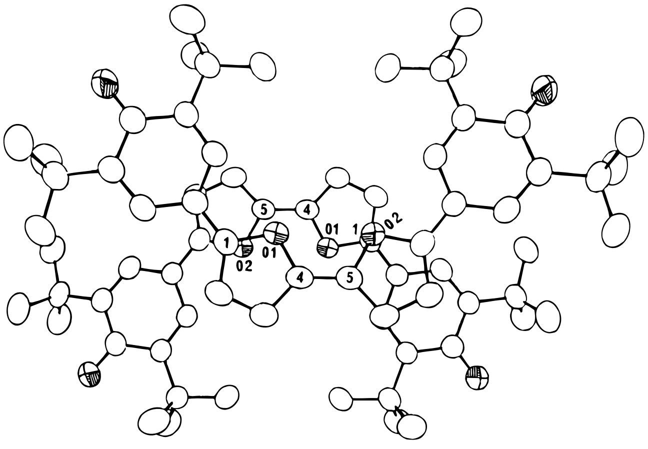

Figure 2. Overview of the dimeric molecular structure of **5**.

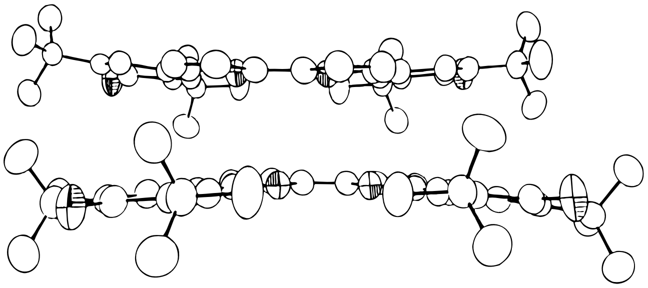

Figure 3. Side view of the dimeric molecular structure of **5**.

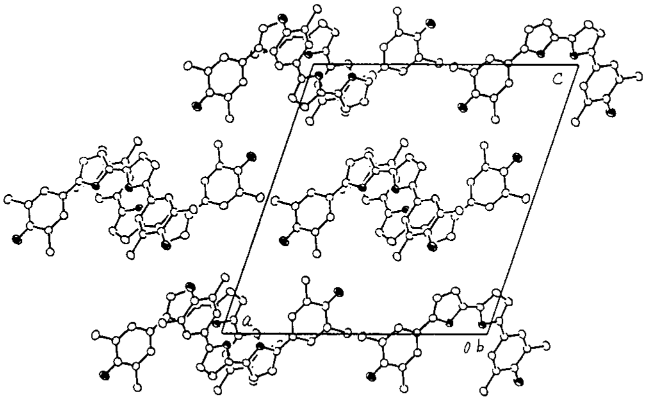

Figure 4. Crystal structure of **5** viewed along the *b*-axis.

the midpoint of the dimer. The overview and side view are shown in Figures 2 and 3, respectively. Interestingly, in the paired molecules, the shortest intermolecular atom−atom distance of 3.33 Å is observed between the C1 and O2 of one molecule and the O2 and C1 of the other molecule, respectively. The intermolecular contacts may be attributed to the dipole−dipole interaction between the electron-poor C1 atom and the electron-rich O2 atom, since the C1 is the *exo*-methylene carbon of the *p*-benzoquinonemethide moiety. Similar intermolecular contacts are also observed between the O1 atom and the C4−C5 bond of one molecule and the C4−C5 and the O1 atom of the other molecule (O1−C5: 3.48 Å, O1−C4: 3.50 Å), respectively. The C4 and C5 atoms are also electron poor, owing to the inductive effect of the neighboring oxygen atom. This type of overlapping mode advantageously avoids the steric hindrance of the *tert*-butyl groups (Figure 2); nevertheless, all the *tert*-butyl groups are a little warped out of the molecular plane to achieve the favorable contacts in the central bifuryl rings (Figure 3). The crystal structure is shown in Figure 4.

Table 2. Coalescence Temperatures and Energy Barriers for the *Cis*−*Trans* Isomerization and *Trans:Cis* Ratio of Heteroquaterphenoquinones

quinone	T_c (°C)	$\Delta G^{\ddagger a}$ (Kcal mol^{-1})	*trans:cis*[b]
3	10	13.4	2.23:1
4	40	15.3	1.42:1
5	50	16.7	1:2.67
6			100:0

[a] Obtained from the ^{1}H NMR spectral changes of H-4′,3″ and H-3′,4″ in CDCl$_3$. [b] At −40 °C in CDCl$_3$.

This is the first report dealing with the crystallographic structure of a quaterphenoquinone analogue. Moreover, compound **5** is the first example of a stable *O-cis* 2,2′-bifuryl derivative. The *O-cis* isomer (**5B**) and the *O-trans* isomer (**5A**) are interconvertible around room temperature in solution. Conformational fixation occurred, and each isomer was detected separately by ^{1}H NMR spectra[17] in the CDCl$_3$ solution below −40 °C (Table 2), revealing the relative ratio of **5A** to **5B** at this temperature to be 1:2.67. Therefore, the *O-cis* isomer (**5B**) is more stable than the *O-trans* isomer (**5A**). The coalescence temperature T_c and the rotational barrier ($\Delta G^{\ddagger}$) obtained from the spectral changes of H-4′,3″ and H-3′,4″ protons are listed in Table 2. These dynamic NMR parameters cannot be applied to the rotation about the intercyclic bond between the six-membered and furan rings, since the chemical shifts of H-2,2‴ and H-6,6‴ are nearly invariant with temperature change, although the signals broaden around the T_c.

By the dynamic ^{1}H NMR spectroscopic method, we have also clarified that the dithiaquaterphenoquinone **3**, in contrast to **5**, exists predominantly in an *S-trans* conformation (**3A**) in CDCl$_3$ solution; i.e., the relative ratio of **3A** to **3B** at −40 °C is 2.23:1,[15] while **3A** and **3B** are in equilibrium with each other at higher temperature. The energy barrier for the isomerization ($\Delta G^{\ddagger}$) is lower in **3** than in **5** (Table 2). This might be due in part to the aromatic stabilization of the biradical transition state that may be larger in **3**, incorporating a bithienyl moiety, than in **5**, incorporating a bifuryl moiety. From the ratio of **4A** to **4B**, it is indicated that the *Se-trans* isomer (**4A**) is more stable than the *Se-cis* isomer (**4B**) in **4**.

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[17] The assignment of the ^{1}H NMR signals was made on the basis of the following evidence: The ^{1}H NMR resonance of H-2 (H-2‴) of **5B** appeared at a lower field than that of **5A** owing to the anisotropic effect of the oxygen atom in the furan rings: the positive NOE's were detected between H-6 (H-6‴) and H-3′ (H-4″) in **5A**, **3A**, and **3B**. The H-3′ (H-4″) proton of *trans* isomers always exhibited a downfield chemical shift relative to that of *cis* isomers: the electron-attracting effect of the carbonyl group of the remote six-membered ring may be stronger in *trans* isomers than in *cis* isomers.

Table 3. Maximum Absorption Wavelengths and ν_{CO} Frequencies of Heteroquaterphenoquinones

	VIS to NIR-Band^a				
quinone	λ_{max} (nm)	ϵ_{max} (mol^{-1} cm^{-1})	λ_{max} (nm)	ϵ_{max} (mol^{-1} cm^{-1})	$\nu_{CO}{}^b$ (cm^{-1})
3	678	31 212	725 sh	11 220	1566
4	665	97 951	742 sh	12 540	1577
5	662	103 322	730 sh	50 118	1582
6	827	98 658			1560

^{a} Absorption spectra are measured in CH_3CN. ^{b} Measured in KBr disk.

The X-ray crystallographic analysis of dithiaquaterphenoquinone **3** also reveals that the molecule has indeed an *S-trans* conformation, although the poor quality of the crystals precluded a full crystal structure analysis of **3**.

It is not clear at this stage why the *O-cis* conformer (**5B**) is more stable than the *O-trans* isomer (**5A**) in **5**, but evidence in hand suggests that oligofurans as well as polyfurans[9,18] might have an *O-cis* type of helical structures[19] in a doped state or in a conjugated state, in contrast to doped oligothiophenes as well as polythiophenes existing in an *S-trans* conformation.[20]

The *N*-methyl quinone **6** exists in an *N-trans* conformation (**6A**) in solution, and no *N-cis* isomer (**6B**) was detected from the ^{1}H NMR spectroscopy at the temperature range of −30 to +40 °C. In addition to the steric strain between the *N*-methyl groups, the *N-cis* isomer can be destabilized by the Coulomb repulsion between the two proximate electropositive *N*-methyl groups because the dipolar resonance structure contributes significantly to the ground state of **6**: that is revealed by the fairly low CO frequency at 1560 cm^{-1} in the IR spectrum (Table 3) and the low ^{1}H NMR chemical shift ($\delta = 3.84$) of the *N*-methyl groups of **6**.

Application for Functional Materials. The importance of dyestuffs exhibiting an intense absorption maximum in the visible or NIR region has been documented extensively in recent years because these dyes can be used in high-density optical storage materials for semiconductor lasers.[21] The quinones **3**−**6** exhibit a very intense absorption maximum at 662−827 nm in their electronic spectra (Table 3) accompanied by an absorption tail extending to 850 nm for **3**−**5** and to 950 nm for **6**. The maximum absorption wavelength of **6** shifts to a more bathochromic region by 149−165 nm compared with those of **3**−**5**. This evidence corresponds to the small HOMO−LUMO separation, namely, the high amphotericity of **6** mentioned before. Moreover, the dithiaquaterphenoquinone **3** can be made into a thin film showing an intense and broad absorption band in the range of 600−850 nm. The films reflect 35% of incident light intensity at 780 nm.[22] Thus, the quinone **3** as well as other quinones **4**−**6** appear to have good physical and chemical properties for practical use as write-once-read-many (WORM)-type diode laser optical storage media.[23]

The quinones **3**−**6** have a high utility potential for novel light-induced electroconducting mediators for organic solar cells or for electrophotographic printing systems.[24] Owing to their amphoteric redox properties, the quinones **3**−**6** may have both electron- and hole-transporting abilities.[25] Moreover, the NIR dyestuffs **3**−**6** could be used for novel CGL pigments of the next multimedia generation for digital xerography involving laser scanning and digital printing.

Moreover, the quinones **3**−**6** appear to be useful for multicolor switching electrochromic dyes,[26] since remarkable and reversible color changes are observed in the process of their electrochemical redox reactions. These quinones are potentially applicable to various other fields of molecular electronics or optoelectronics, detailed investigations of which are now in progress.

Conclusion. In this paper, we have reported the successful synthesis of a series of the heteroquaterphenoquinones **3**−**6** incorporating two five-membered heterocyclic quinonoid moieties by an advantageous method using Pd-catalyzed cross-coupling reactions or by an oxidative homocoupling reaction of heterocycle-substituted phenols. We have investigated electrochemical properties, structures, and spectroscopic properties of the heteroquinones **3**−**6** and have clarified that there is a considerable difference in redox potentials, conformational structures, and absorption spectroscopic properties among the quinones with different central heteroatoms. The *N*-methyl quinone **6** exhibits a very low oxidation potential of +0.47 V, and the quinone **5** exists in an unusual *O-cis* conformation in the solid state. The synthetic methodologies reported here involve a convenient and short-step reaction that can be manipulated quite easily and are suitable for large-scale preparation at low cost. Therefore, some of these heteroquinones exhibiting an intense absorption band in a NIR region have high utility potential as NIR dyestuffs for next-generation, high-density optical storage materials for diode lasers and materials for OPC systems.

Experimental Section

General Procedures. All melting points are uncorrected. Chemical shift assignments were confirmed through spin decoupling and two-dimensional carbon−proton chemical shift correlation experiments and NOE experiments in some cases. The sample solution for an electrolysis was prepared using a vacuum line system.

2-(3,5-Di-*tert*-butyl-4-(trimethylsiloxy)phenyl)selenophene (8b). Under a nitrogen atmosphere, a hexane solution of *n*-BuLi (1.61 M, 0.95 mL, 1.53 mmol) was added dropwise to a solution of selenophene (200 mg, 1.53 mmol) in dry ether (6 mL) at room temperature, and the resulting solution was stirred at the same temperature for 5 min and then refluxed for 15 min. After the solution was cooled to 0 °C, to it was added a solution of anhydrous $ZnCl_2$ (208 mg, 1.53 mmol) in

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(18) Ohsawa, T.; Kaneto, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1984**, *23*, L663. Yoshino, K.; Hayashi, S.; Sugimoto, R. *Jpn. J. Appl. Phys.* **1984**, *23*, L899.

(19) Garnier, F.; Tourillon, G.; Barraud, J. Y.; Dexpert, H. J. *Mater. Sci.* **1984**, *161*, 51. Cui, C. X.; Kertesz, M. *Phys. Rev. B* **1989**, *40*, 9661. Yang, R.; Dalsin, K. R.; Evans, D. F.; Christensen, L.; Hendrickson, W. A. *J. Phys. Chem.* **1989**, *93*, 511.

(20) Mo, Z.; Lee, K. B.; Kobayashi, M.; Heeger, A. J.; Wudl, F. *Macromolecules* **1985**, *18*, 1972. Wragai, K.; Hotta, S. *Synth. Met.* **1991**, *41*, 519. Hotta, S.; Waragai, K. *J. Mater. Chem.* **1991**, *1*, 835.

(21) Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1445 and references cited therein. Umehara, M.; Abe, M.; Oba, H. *J. Synth. Org. Chem. Jpn.* **1985**, *43*, 334. Fabian, J.; Zahradnik, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 677. Keil, D.; Hartmann, H. *Liebigs Ann. Chem.* **1995**, 979.

(22) The reflectivity was measured by A. Hirose at Mitsui Toatsu Chemicals, Inc., Yokohama, Japan, to whom the authors are indebted.

(23) Optical writing with a diode laser proved the clear pit forming character for a film of the dye **3**. The details of these characteristics for optical storage media will be reported in other journals together with those for the quinones **4**−**6**.

(24) Law, K. Y.*Chem. Rev.* **1993**, *93*, 449 and references cited therein. Yamaguchi, Y.; Tanaka, H.; Yokoyama, M. *J. Chem. Soc., Chem. Commun* **1990**, 222. Carter, F. L. *Molecular Electronic Devices*; Marcel Dekker, New York, 1982. Alxandru, L.; Hopper, M. A. *Mater. Microlichogr.* **1984**, *22*, 435.

(25) Gill, W. D. *J. Appl. Phys.* **1972**, *43*, 5033.

(26) Ueno, T.; Hirai, Y.; Tani, C. *J. Appl. Phys.* **1985**, *24*, L178.

dry THF (6 mL), and the resulting mixture was stirred at the same temperature for 60 min, yielding 2-selenophene-zinc chloride solution. On the other hand, Pd(0)-catalyst was prepared by adding a toluene solution of DIBAH (1.5 M, 78 μL, 0.117 mmol) to a suspension of PdCl$_2$(PPh$_3$)$_2$ (41 mg, 0.058 mmol) in dry THF (6 mL), followed by stirring for 15 min. To the Pd(0)-catalyst suspension were added a solution of 1-(trimethylsiloxy)-2,6-di-*tert*-butyl-4-iodobenzene (**7**) (475 mg, 1.17 mmol) in dry THF (6 mL) and the above-prepared 2-selenophene-zinc chloride solution. After being stirred for 1 h at room temperature, the reaction mixture was poured into water, acidified with 1 N HCl, and extracted with ether, and the ether extract was washed (water, then brine), dried (Na$_2$SO$_4$), and evaporated (reduced pressure). The residue was chromatographed twice on silica gel (hexane), affording **8b** as white crystals (514 mg, 1.26 mmol, 75.3%): mp 52−53 °C; IR (KBr) 2956−2845 (m), 1463 (m), 1415 (s), 1362 (w), 1259 (s), 1230 (s), 1207 (s), 1119 (w), 914 (s), 845 (s), 758 (w), 681 (m) cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 0.43 (s, 9H, SiMe), 1.44 (s, 18H, *t*-Bu), 7.29 (dd, 1H, $J = 5.6$, 3.8 Hz, SelH-4′), 7.34 (dd, 1H, $J = 3.8$, 1.1 Hz, SelH-3′), 7.45 (s, 2H, ArH-2,6), 7.86 (dd, 1H, $J = 5.6$, 1.1 Hz, SelH-5′); ^{13}C NMR (150 MHz, CDCl$_3$) δ 3.92 (SiMe), 31.15 (C*Me*), 35.15 (*C*Me), 123.96 (SelC-3′), 124.15 (ArC-2,6), 128.54 (ArC-1), 128.63 (SelC-5′), 130.45 (SelC-4′), 141.23 (ArC-3,5), 151.97 (SelC-2′), 153.17 (ArC-4); MS (DEI) *m/z* (rel intensity) 410 (M$^+$ + 2, 25), 409 (M$^+$ + 1, 29), 408 (M$^+$, 100), 393 (22), 312 (35), 297 (28), 263 (22); HRMS calcd for C$_{21}$H$_{32}$OSiSe 408.1388, found 408.1391.

2-(3,5-Di-*tert*-butyl-4-(trimethylsiloxy)phenyl)furan (8c). Under nitrogen atmosphere, a pentane solution of *t*-BuLi (1.54 M, 3.48 mL, 5.56 mmol) was added dropwise to a solution of furan (379 mg, 5.56 mmol) in dry ether (7 mL) maintained at −20 °C. The resulting solution was then allowed to warm to 0 °C and stirred further for 80 min. The reaction mixture was then added to a solution of anhydrous ZnCl$_2$ (758 mg, 5.56 mmol) in dry THF (7 mL) at 0 °C, and the resulting mixture was stirred at the same temperature for 90 min, yielding 2-furylzinc chloride in solution. On the other hand, Pd(0)-catalyst was prepared by adding a hexane solution of DIBAH (1.0 M, 371 μL, 0.371 mmol) to a suspension of PdCl$_2$(PPh$_3$)$_2$ (130 mg, 0.185 mmol) in dry THF (7 mL), followed by stirring for 15 min. To the Pd(0)-catalyst suspension were added a solution of **7** (1.50 g, 3.71 mmol) in dry THF (14 mL) and the above-prepared 2-furylzinc chloride solution. After being stirred for 3 h at room temperature, the resulting mixture was worked up as usual, and the crude reaction product was chromatographed on silica gel (hexane), affording **8c** as white crystals (1.14 g, 3.32 mmol, 89.4%): mp 79−82 °C; IR (KBr) 3030−2871 (m), 1433 (m), 1412 (s), 1363 (m), 1263 (w), 1238 (s), 1201 (m), 1122 (m), 1014 (m), 943 (s), 918 (s), 887 (m), 847 (s), 766 (m), 731 (m) cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.42 (s, 9H, SiMe), 1.44 (s, 18H, *t*-Bu), 6.43 (dd, 1H, $J = 3.5$, 0.8 Hz, FurH-4′), 6.51 (dd, 1H, $J = 2.0$, 3.5 Hz, FurH-3′), 7.42 (dd, 1H, $J = 0.8$, 2.0 Hz, FurH-5′), 7.57 (s, 2H, ArH-2,6); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 3.88 (SiMe), 31.29 (C*Me*), 35.26 (*C*Me), 103.20 (FurC-3′), 111.42 (FurC-4′), 121.77 (ArC-2,6), 123.33 (ArC-1), 141.22 (FurC-4′), 141.26 (ArC-3,5), 152.97 (ArC-4), 155.02 (FurC-2′); MS (DEI) *m/z* (rel intensity) 346 (M$^+$ + 2, 9), 345 (M$^+$ + 1, 33), 344 (M$^+$, 100), 329 (32), 273 (6), 73 (17); HRMS calcd for C$_{21}$H$_{32}$O$_2$Si 344.2171, found 344.2168.

2-(3,5-Di-*tert*-butyl-4-(trimethylsiloxy)phenyl)-*N*-methylpyrrole (8d). Under nitrogen atmosphere, TMEDA (775 μL, 5.14 mmol) and then a hexane solution of *n*-BuLi (1.60 M, 3.21 mL, 5.14 mmol) were added dropwise to a solution of *N*-methylpyrrole (167 mg, 2.05 mmol) in dry ether (8 mL) at room temperature, and the resulting solution was stirred at room temperature for 30 min. To the resulting lithiated *N*-methylpyrrole solution was added a solution of anhydrous ZnCl$_2$ (700 mg, 5.14 mmol) in dry THF (8 mL) at room temperature, and the reaction mixture was stirred at the same temperature for 1 h, yielding (2-(*N*-methylpyrrolyl))zinc chloride in solution. On the other hand, a toluene solution of DIBAH (1.01 M, 125 μL, 0.187 mmol) was added to a suspension of PdCl$_2$(PPh$_3$)$_2$ (66 mg, 0.0934 mmol) in dry THF (6 mL), and the mixture was stirred for 10 min. To the Pd(0)-catalyst suspension were added a solution of **7** (755 mg, 1.87 mmol) in dry THF (8 mL) and the above-prepared (2-(*N*-methylpyrrolyl))zinc chloride solution. After being stirred for 1 h at room temperature, the resulting mixture was worked up as usual, and the crude reaction product was chromatographed twice on silica gel (hexane:CH$_2$Cl$_2$ = 1:1), affording **8d** as colorless oil (579 mg, 1.88 mmol, 79%): IR (neat) 2954−2871 (m), 1485 (w), 1464 (w), 1444 (w), 1410 (s), 1362 (w), 1315 (w), 1259 (s), 1232 (s), 1122 (w), 926 (s), 889 (s), 850 (s), 775 (m), 756 (w), 706 (m) cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 0.43 (s, 9H, SiMe), 1.43 (s, 18H, *t*-Bu), 3.65 (s, 3H, *N*Me), 6.17 (dd, 1H, $J = 3.5$, 1.9 Hz, PyrrH-3′), 6.19 (dd, 1H, $J = 3.5$, 2.7 Hz, PyrrH-4′), 6.69 (dd, 1H, $J = 2.6$, 1.9 Hz, PyrrH-5′), 7.27 (s, 2H, ArH-2,6); ^{13}C NMR (150 MHz, CDCl$_3$) δ 3.92 (SiMe), 31.26 (SiMe), 31.26 (C*Me*), 34.98 (NMe), 35.17 (*C*Me), 107.44 (PyrrC-4′), 107.57 (PyrrC-3′), 122.74 (PyrrC-5′), 125.22 (ArC-1), 126.39 (ArC-2,6), 135.50 (PyrrC-2′), 140.48 (ArC-3,5), 152.30 (ArC-4); MS (DEI) *m/z* (rel intensity) 359 (M$^+$ + 2, 8), 358 (M$^+$ + 1, 31), 357 (M$^+$, 100), 342 (7), 286 (6), 73 (40); HRMS calcd for C$_{22}$H$_{35}$ONSi 357.2488, found 357.2488.

2-Bromo-5-(3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl)thiophene (9a). To a solution of **8a** (500 mg, 1.386 mmol) in CHCl$_3$ (10 mL) were added acetic acid (10 mL) and NBS (247 mg, 1.386 mmol), and the reaction mixture was stirred for 30 min at room temperature. To this was added water, the mixture was extracted with ether, and the ether extract was washed (water, then brine) and dried (Na$_2$SO$_4$). After evaporation under reduced pressure, the residue was chromatographed on silica gel (hexane), and the product obtained was recrystallized from MeOH to give **9a** as colorless needles (600 mg, 1.365 mmol, 98.5%): mp 110−112 °C; IR (KBr) 3060−2800 (m), 1448 (m), 1408 (m), 1392 (w), 1360 (w), 1320 (w), 1256 (s), 1234 (s), 1200 (m), 1120 (m), 918 (s), 884 (w), 840 (s), 792 (w), 758 (w) cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.43 (s, 9H, SiMe), 1.43 (s, 18H, *t*-Bu), 6.92 (d, 1H, $J = 3.8$ Hz, ThiH-3′), 6.99 (d, 1H, $J = 3.8$ Hz, ThiH-4′), 7.39 (s, 2H, ArH-2,6); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 3.93 (SiMe), 31.17 (C*Me*), 35.22 (*C*Me), 109.84 (ThiC-5′), 122.00 (ThiC-3′), 123.48 (ArC-2,6), 125.90 (ArC-1), 130.61 (ThiC-4′), 141.51 (ArC-3,5), 147.09 (ThiC-2′), 153.44 (ArC-4); MS (EI) *m/z* (rel intensity) 441 (M$^+$ + 3, 17), 440 (M$^+$ + 2, 77), 439 (M$^+$ + 1, 14), 438 (M$^+$, 64), 425 (11), 423 (13), 73 (100).

2-Bromo-5-(3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl)furan (9c). To a solution of **8c** (85.5 mg, 0.248 mmol) in anhydrous benzene (20 mL) were added successively NBS (44.2 mg, 0.248 mmol) and a catalytic amount (ca. 3 mg) of *p*-toluenesulfonic acid, and the resulting solution was refluxed for 35 min under nitrogen atmosphere. The reaction mixture was filtered, and to the filtrate was added saturated aqueous Na$_2$SO$_3$ solution. The mixture was extracted with benzene, and the benzene extract was washed (water, then brine) and dried (Na$_2$SO$_4$). After evaporation under reduced pressure, the residue was chromatographed on silica gel (hexane) to give **9c** as colorless crystals (88.9 mg, 0.211 mmol, 85.0%). The compound **9c** is somewhat unstable and turns to pale brown on standing, so that it should be used to the next reaction soon after chromatographic purification: ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.42 (s, 9H, SiMe), 1.44 (s, 18H, *t*-Bu), 6.34 (d, 1H, $J = 3.4$ Hz, FurH-3′), 6.46 (d, 1H, $J = 3.4$ Hz, FurH-4′), 7.50 (s, 2H, ArH-2,6); ^{13}C NMR (150 MHz, CDCl$_3$) δ 3.84 (SiMe), 31.17 (C*Me*), 35.21 (*C*Me), 105.58 (FurC-4′), 113.11 (FurC-3′), 120.11 (FurC-5′), 121.43 (ArC-2,6), 122.32 (ArC-1), 141.31 (ArC-3,5), 153.26 (ArC-4), 156.90 (FurC-2′); MS (EI) *m/z* (rel intensity) 425 (M$^+$ + 3, 31), 424 (M$^+$ + 2, 100), 423 (M$^+$ + 1, 30), 422 (M$^+$, 96), 409 (11); HRMS calcd for C$_{21}$H$_{31}$O$_2$SiBr 422.1277, found 422.1274.

5,5′-Bis(3,5-di-*tert*-butyl-4-(silyloxy)phenyl)-2,2′-bithiophene (11a). A hexane solution of *n*-BuLi (1.64 M, 0.312 mL, 0.512 mmol) was added dropwise to a solution of **8a** (185 mg, 0.512 mmol) in dry ether (3 mL) at 0 °C, and the resulting solution was stirred for 1 h at the same temperature under argon atmosphere. This was then added dropwise into a solution of anhydrous ZnCl$_2$ (70 mg, 0.512 mmol) in dry THF (3 mL), and the reaction mixture was stirred for further 1 h to give **10a** in THF solution. On the other hand, a hexane solution of DIBAH (1 M, 0.034 mL, 0.034 mmol) was added to a suspension of $PdCl_2(PPh_3)_2$ (12 mg, 0.017 mmol) in dry THF (3 mL), and the mixture was stirred for 10 min at room temperature. To the suspension of Pd(0)-catalyst were added dropwise a solution of **9a** (150 mg, 0.341 mmol) in dry THF (6 mL) and the THF solution of the above-prepared THF solution of **10a**. The reaction mixture was stirred for 1 h at room temperature, poured into water, acidified with 1 N HCl, and extracted with ether. The ether extract was washed (water, then brine) and dried (Na_2SO_4). After evaporation under reduced pressure, the residue was chromatographed on silica gel (hexane:CH_2Cl_2 = 95:5) to give **11a** as pale yellow crystals (160 mg, 0.222 mmol, 65.2%): mp 262−267 °C; IR (KBr) 3000−2800 (m), 1466 (w), 1452 (w), 1416 (s), 1394 (w), 1362 (w), 1258 (s), 1220 (s), 1120 (m), 912 (s), 880 (m), 840 (s), 792 (m), 780 (m), 768 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.44 (s, 18H, SiMe),1.45 (s, 36H, *t*-Bu), 7.11 (d, 2H, J = 4.0 Hz, ThiH-3′,4″), 7.13 (d, 2H, J = 4.0 Hz, ThiH-4′,3″), 7.50 (s, 4H, ArH-2,2‴,6,6‴); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 3.94 (SiMe), 31.16 (C*Me*), 35.21 (*C*Me), 122.50 (ThiC-3′,4″), 123.38 (ArC-2,2‴,6,6‴), 123.93 (ThiC-4′,3″), 126.25 (ArC-1,1‴), 135.84 (ThiC-5′,2″), 141.31 (ArC-3,3‴,5,5‴), 143.86 (ThiC-2′,5″), 153.87 (ArC-4,4‴); MS (FD) *m/z* (rel intensity) 721 (M$^+$ + 3, 10), 720 (M$^+$ + 2, 39), 719 (M$^+$ + 1, 60), 718 (M$^+$, 100), 647 (6), 646 (16).

5,5′-Bis(3,5-di-*tert*-butyl-4-(silyloxy)phenyl)-2,2′-bifuran (11c). Under nitrogen atmosphere, a pentane solution of *t*-BuLi (1.57 M, 202 mL, 0.316 mmol) was added dropwise into a solution of **8c** (109.0 mg, 0.316 mmol) in dry ether (3 mL) at −40 °C, and the resulting solution was stirred for 60 min at the same temperature. To this was added dropwise a cooled (0 °C) THF solution of anhydrous $ZnCl_2$ (43 mg, 0.316 mmol), and the resulting solution was stirred for 60 min at −40 °C to give organozinc chloride **10c** in solution. On the other hand, a Pd(0)-catalyst was prepared by treating $Cl_2Pd(PPh_3)_2$ (7.4 mg, 0.0105 mmol) in dry THF (5 mL) with DIBAH in hexane (1.5 M, 14 μL, 0.021 mmol). To this were added sequentially under argon atmosphere a solution of **9c** (88.9 mg, 0.211 mmol) in dry THF (5 mL) and the above-prepared THF solution of **10c**. The reaction mixture was warmed to room temperature and stirred for 1 h at room temperature. After a usual workup the crude reaction product was chromatographed on silica gel (hexane) to give **11c** as colorless crystals (121.4 mg, 0.177 mmol, 83.7%): mp 183−184 °C; IR (KBr) 2958−2879 (w), 1473 (w), 1410 (s), 1362 (w), 1250 (s), 1203 (w), 1122 (w), 1018 (w), 930 (m), 849 (s), 773 (m) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.43 (s, 18H, SiMe), 1.47 (s, 36H, *t*-Bu), 6.60 (d, 2H, J = 3.3 Hz, FurH-3′,4″), 6.66 (d, 2H, J = 3.3 Hz, FurH-4′,3″), 7.63 (s, 4H, ArH-2,2‴,6,6‴); ^{13}C NMR (150 MHz, $CDCl_3$) δ 3.87 (SiMe), 31.20 (C*Me*), 35.22 (*C*Me), 105.17 (FurC-3′,4″), 106.79 (FurC-4′,3″), 121.61 (ArC-2,2‴,6,6‴), 122.91 (ArC-1,1‴), 141.25 (ArC-3,3‴,5,5‴), 145.45 (FurC-5′,2″), 153.03 (ArC-4,4‴), 153.93 (FurC-2′,5″); MS (DEI) *m/z* (rel intensity) 688 (M$^+$ + 2, 25), 687 (M$^+$ + 1, 59), 686 (M$^+$, 100), 621 (13), 620 (26), 488 (10), 487 (24); HRMS calcd for $C_{42}H_{62}O_4Si_2$ 686.4187, found 686.4191.

5,5′-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,2′-bithiophene (12a). (a) To a solution of **11a** (142.3 mg, 0.198 mmol) in dry THF (20 mL) was added a 1.0 M THF solution of TBAF (435 μL, 0.435 mmol) at 0 °C, and the reaction mixture was stirred for 30 s. Water was added, and the mixture was extracted with CH_2Cl_2. After usual workup, the crude reaction product was chromatographed on silica gel (hexane:CH_2Cl_2 = 2:1) to give **12a** as orange crystals (112.7 mg, 0.196 mmol, 99.1%): mp 279−282 °C; IR (KBr) 3600 (m), 3000−2800 (m), 1420 (s), 1300 (w), 1234 (m), 1224 (m), 1140 (m), 1118 (w), 876 (w), 786 (m), 698 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (s, 36H, *t*-Bu), 5.30 (s, 2H, OH), 7.09 (d, 2H, J = 3.8 Hz, ThiH-3′,4″), 7.13 (d, 2H, J = 3.8 Hz, ThiH-4′,3″), 7.42 (s, 4H, ArH-2,2‴,6,6‴); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 30.25 (C*Me*), 34.42 (*C*Me), 122.41 (ThiC-3′,4″), 122.83 (ArC-2,2‴,6,6‴), 123.94 (ThiC-4′,3″), 125.73 (ArC-1,1‴), 135.74 (ThiC-5′,2″), 136.44 (ArC-3,3‴,5,5‴), 144.18 (ThiC-2′,5″), 153.79 (ArC-4,4‴); MS (EI) *m/z* (rel intensity) 576 (M$^+$ + 2, 18), 575 (M$^+$ + 1, 41), 574 (M$^+$, 100), 57 (18).

(b) To a solution of **11a** (60 mg, 0.0834 mmol) in THF (11 mL) was added 12 N HCl (1 mL). After being stirred for 17 h at room temperature, the reaction mixture was evaporated under reduced pressure. Water was added, and the mixture was extracted with ether. The ether extract was washed (water, then brine), dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel (hexane:ether = 95:5) to give **12a** as pale orange needles (26 mg, 0.0452 mmol, 54.2%).

5,5′-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,2′-bifuran (12c). A 1.0 M THF solution of TBAF (166 mL, 0.166 mmol) was added to a solution of **11c** (51.9 mg, 0.0755 mmol) in dry THF (8 mL) at 0 °C, and the resulting solution was stirred for 30 s at room temperature. After addition of water, the reaction mixture was extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed twice (brine), dried (Na_2SO_4), and evaporated under reduced pressure, and the residue was chromatographed on silica gel (hexane:CH_2Cl_2 = 1:6) to afford **12c** as colorless crystals (39.5 mg, 0.0728 mmol, 96.3%): mp 229−230 °C; IR (KBr) 3622 (m), 2958−2875 (m), 1425 (s), 1365 (w), 1311 (w), 1236 (s), 1151 (m), 1093 (w), 1018 (m), 885 (m), 775 (m), 702 (w) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.50 (s, 36H, *t*-Bu), 5.30 (s, 2H, OH), 6.58 (d, 2H, J = 3.4 Hz, FurH-3′,4″), 6.65 (d, 2H, J = 3.4 Hz, FurH-4′,3″), 7.56 (s, 4H, ArH-2,2‴,6,6‴); ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.25 (C*Me*), 34.40 (*C*Me), 104.85 (FurC-3′,4″), 106.75 (FurC-4′,3″), 120.96 (ArC-2,2‴,6,6‴), 122.36 (ArC-1,1‴), 136.26 (ArC-3,3‴,5,5‴), 145.36 (FurC-5′,2″), 153.64 (ArC-4,4‴), 154.12 (FurC-2′,5″); MS (DEI) *m/z* (rel intensity) 544 (M$^+$ + 2, 15), 543 (M$^+$ + 1, 39), 542 (M$^+$, 100); HRMS calcd for $C_{36}H_{46}O_4$ 542.3396, found 542.3398.

5,5′-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-5,5′-dihydro-2,2′-bithiophene (3). (a) Under nitrogen atmosphere, PbO_2 (148 mg, 0.0619 mmol) was added to a solution of **12a** (35.6 mg, 0.0619 mmol) in dry benzene (30 mL), and the reaction mixture was stirred vigorously at room temperature for 30 min. After removal of the surplus PbO_2 by filtration through Celite, the filtrate was evaporated under reduced pressure, and the residue was chromatographed on silica gel (CH_2Cl_2) to give **3** as shining deep green crystals (34.9 mg, 0.0609 mmol, 98.6%): mp 268 °C; IR (KBr) 2950−2860 (w), 1632 (w), 1566 (s), 1444 (m), 1360 (m), 1326 (m), 1258 (w), 1140 (w), 1110 (m), 1022 (m), 872 (m), 796 (m), 704 (m) cm^{-1}; UV/vis/NIR (CH_3CN) λ_{max} nm (log ϵ) 725 sh (4.05), 678 (4.50), 620 (4.15), 428 (3.62), 263 (3.63); ^{1}H NMR (400 MHz, $CDCl_3$, −40 °C) for **3A** δ 7.23 (d, 2H, J = 2.4 Hz, ArH-6,6‴), 7.41 (d, 2H, J = 2.4 Hz, ArH-2,2‴), 7.52 (d, 2H, J = 5.5 Hz, ThiH-3′,4″), 7.55 (d, 2H, J = 5.5 Hz, ThiH-4′,3″); for **3B** δ 7.23 (d, 2H, J = 2.4 Hz, ArH-6,6‴), 7.37 (d, 2H, J = 5.5 Hz, ThiH-3′,4″), 7.41 (d, 2H, J = 2.4 Hz, ArH-2,2‴), 7.65 (d, 2H, J = 4.8 Hz, ThiH-4′,3″); δ 1.33, 1.35 (each s, 36H, *t*-Bu of **3A**, **3B**); MS (FD) *m/z* (rel intensity) 572 (M$^+$, 100). (b) To a solution of **12a** (24 mg, 0.0417 mmol) in CH_2Cl_2 (20 mL) were added a 0.1 M aqueous KOH solution (40 mL) and then potassium ferricyanide (137 mg, 0.416 mmol) at room temperature, and the mixture was stirred vigorously for 3 h. The reaction mixture was extracted with CH_2Cl_2, and the extract was washed (water, then brine), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane:CH_2Cl_2 = 1:1) to afford **3** as deep green crystals (20 mg, 0.0349 mmol, 83.7%).

5,5′-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-5,5′-dihydro-2,2′-bifuran (5). (a) In a manner similar to (a) for **3**, a solution of **12c** (38.4 mg, 0.708 mmol) in dry benzene (30 mL) was treated with PbO_2 (169 mg, 0.708 mmol) to give **5** as a deep green solid (37.7 mg, 0.069 mmol, 98.0%): mp 247−248 °C; IR (KBr) 2954−2873 (w), 1582 (s), 1525 (s), 1454 (w), 1419 (w), 1360 (m), 1255 (w), 1196 (m), 1173 (s), 1119 (m), 1093 (w), 914 (s) cm^{-1}; UV/vis/NIR (CH_3CN) λ_{max} nm (log ϵ) 730 sh (4.69), 662 (5.01), 601 sh (4.63), 402 (4.57), 381 (4.47), 357 (4.46), 334 (4.44), 280 (4.30); ^{1}H NMR (400 MHz, $CDCl_3$, −40 °C) for **5A** δ 7.26 (d, 2H, J = 2.4 Hz, ArH-6,6‴), 7.38 (d, 2H, J = 4.8 Hz, FurH-3′,4″), 7.52 (d, 2H, J = 4.8 Hz, FurH-4′,3″), 7.61 (d, 2H, J = 2.4 Hz, ArH-2,2‴); for **5B** δ 7.24 (d, 2H, J = 2.4 Hz, ArH-6,6‴), 7.28 (d, 2H, J = 5.2 Hz, FurH-3′,4″), 7.32 (d, 2H, J = 5.2 Hz, FurH-4′,3″), 7.78 (d, 2H, J = 2.4 Hz, ArH-2,2‴); δ 1.34, 1.36, 1.37 (72H, *t*-Bu, of **5A, 5B**); MS (DEI) *m/z* (rel intensity) 542 (M$^+$ + 2, 100), 541 (M$^+$ + 1, 53), 540 (M$^+$, 93), 483 (12); HRMS calcd for $C_{36}H_{44}O_4$ 540.3239, found 542.3246. (b) In a manner similar to (b) for **3**, a solution of **12c** (27.0 mg, 0.0498 mmol) in CH_2Cl_2 (20 mL) was treated with a 0.1 M aqueous KOH solution (40 mL) and potassium ferricyanide (164 mg, 0.498 mmol) at room temperature for 30 min. Pure **5** was obtained as shining deep green crystals (24.3 mg, 0.045 mmol, 90.4%) after chromatography on silica gel ($CHCl_3$). Quinone **5** is somewhat unstable to silica gel, so that slow elution of column chromatography should be avoided.

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)thiophene (13a). (a) To a solution of **8a** (90 mg, 0.249 mmol) in acetonitrile (11 mL) was added 12 N HCl (1 mL), and the mixture was stirred at room temperature for 1 h. After the solvent was evaporated under reduced pressure, water was added to the residue and the mixture was extracted with ether. The ether extract was washed (water, then brine), dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel (hexane) to give **13a** as colorless crystals (65 mg, 0.225 mmol, 90.5%): mp 54−55 °C; IR (CCl_4) 3640 (m), 3000−2850 (s), 1446 (m), 1420 (s), 1394 (w), 1362 (w), 1318 (m), 1236 (m), 1214 (w), 1156 (m), 1120 (w), 880 (w), 736 (s), 690 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.48 (s, 18H, *t*-Bu), 5.25 (s, 1H, OH), 7.04 (dd, 1H, *J* = 5.0, 3.6 Hz, ThiH-4′), 7.16 (dd, 1H, *J* = 3.6, 1.3 Hz, ThiH-3′), 7.19 (dd, 1H, *J* = 5.0, 1.3 Hz, ThiH-5′), 7.41 (s, 2H, ArH-2,6); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 30.24 (C*Me*), 34.38 (*C*Me), 121.87 (ThiC-3′), 123.24 (ArC-2,6), 123.51 (ThiC-5′), 125.99 (ArC-1), 127.77 (ThiC-4′), 136.33 (ArC-3,5), 145.74 (ThiC-2′), 153.68 (ArC-4); MS (EI) *m/z* (rel intensity) 289 (M^+ + 1, 12), 288 (M^+, 100), 273 (68), 57 (17).

(b) To a solution of **8a** (150 mg, 0.416 mmol) in dry THF (5 mL) was added a 1.0 M THF solution of TBAF (458 μL, 0.458 mmol) at room temperature, and the resulting solution was stirred for 1 min at room temperature. Water was added, and the mixture was extracted with CH_2Cl_2. The extract was washed twice (brine), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane) to afford **13a** as colorless needles (101.5 mg, 0.352 mmol, 84.6%).

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)selenophene (13b). In a manner similar to (b) for **13a**, a 1.0 M THF solution of TBAF (499 μL, 0.499 mmol) was added at 0 °C into a solution of **8b** (185.0 mg, 0.454 mmol) in dry THF (35 mL), and the resulting solution was stirred for 2 min at 0 °C. After a workup similar to (b) for **13a**, the reaction product was chromatographed on silica gel (hexane:CH_2Cl_2 = 4:1) and then further recrystallized from acetonitrile, providing pure **13b** as colorless crystals (93.2 mg, 0.285 mmol, 62.9%): mp 55−56 °C; IR (KBr) 3631 (m), 2964−2873 (m), 1460 (w), 1429 (s), 1394 (w), 1366 (w), 1308 (m), 1238 (s), 1205 (m), 1142 (s), 1120 (m), 1025 (w), 881 (w), 822 (w), 685 (m) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.49 (s, 18H, *t*-Bu), 5.30 (s, 1H, OH), 7.30 (p dd, 1H, *J* = 3.6, 3.6 Hz, SelH-4′), 7.32 (d, 1H, *J* = 3.6 Hz, SelH-3′), 7.39 (s, 2H, ArH-2,6), 7.87 (d, 1H, *J* = 5.5 Hz, SelH-5′); ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.21 (C*Me*), 34.32 (*C*Me), 123.58 (ArC-2,6), 123.91 (SelC-3′), 127.99 (ArC-1), 128.59 (SelC-5′), 130.43 (SelC-4′), 136.28 (ArC-3,5), 152.20 (SelC-2′), 153.75 (ArC-4); MS (DEI) *m/z* (rel intensity) 338 (M^+ + 2, 24), 337 (M^+ + 1, 31), 336 (M^+, 100), 334 (81), 321 (37); HRMS calcd for $C_{18}H_{24}OSe$ 336.0992, found 336.0997.

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)furan (13c). In a manner similar to (b) for **13a**, a 1.0 M THF solution of TBAF (135 μL, 0.135 mmol) was added at room temperature into a solution of **8c** (42.3 mg, 0.123 mmol) in dry THF (15 mL), and the resulting solution was stirred for 30 s at room temperature. After a workup similar to that for **13a**, the reaction products were chromatographed on silica gel (hexane:CH_2Cl_2 = 4:1) to afford **13c** as colorless crystals (32.1 mg, 0.118 mmol, 96.1%): mp 82.5−84.5 °C; IR (KBr) 3637 (m), 2958−2973 (m), 1421 (s), 1365 (w), 1311 (m), 1236 (s), 1149 (s), 1014 (m), 931 (w), 885 (m), 800 (w), 733 (m), 700 (w) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.49 (s, 18H, *t*-Bu), 5.28 (s, 1H, OH), 6.45 (dd, 1H, *J* = 3.3, 1.8 Hz, FurH-4′), 6.50 (dd, 1H, *J* = 3.3, 0.8 Hz, FurH-3′), 7.43 (dd, 1H, *J* = 1.8, 0.8 Hz, FurH-5′), 7.51 (s, 2H, ArH-2,6); ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.24 (C*Me*), 34.37 (*C*Me), 102.87 (FurC-3′), 111.41 (FurC-4′), 121.04 (ArC-2,6), 122.66 (ArC-1), 136.18 (ArC-3,5), 141.11 (FurC-5′), 153.53 (ArC-4), 155.04 (FurC-2′); MS (DEI) *m/z* (rel intensity) 273 (M^+ + 1, 20), 272 (M^+, 100), 258 (10), 257 (53); HRMS calcd for $C_{18}H_{24}O_2$ 272.1777, found 272.1775.

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*N*-methylpyrrole (13d). In a manner similar to (b) for **13a**, a 1.0 M THF solution of TBAF (476 μL, 0.477 mmol) was added at room temperature into a solution of **8d** (155.0 mg, 0.433 mmol) in dry THF (5 mL), and the resulting solution was stirred for 20 min at at room temperature. After a workup similar to that for **13a**, the reaction product was chromatographed on silica gel (hexane:CH_2Cl_2 = 1:1) to afford **13d** as colorless crystals (105.8 mg, 0.371 mmol, 85.5%): mp 112−113 °C; IR (KBr) 3597 (s), 2964−2873 (m), 1185 (m), 1446 (m), 1417 (m), 1363 (w), 1300 (m), 1234 (m), 1140 (m), 1084 (w), 889 (m), 771 (w), 715 (s), 679 (w) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.46 (s, 18H, *t*-Bu), 3.63 (s, 3H, *N*Me), 5.23 (s, 1H, OH), 6.15 (dd, 1H, *J* = 3.5, 1.8 Hz, PyrrH-3′), 6.19 (p dd, 1H, *J* = 3.1, 3.1 Hz, PyrrH-4′), 6.76 (p dd, 1H, *J* = 2.3, 2.3 Hz, PyrrH-5′), 7.19 (s, 2H, ArH-2,6); ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.31 (C*Me*), 34.37 (*C*Me), 34.85 (*N*Me), 107.40 (PyrrC-4′), 107.60 (PyrrC-3′), 122.58 (PyrrC-5′), 124.53 (ArC-1), 125.83 (ArC-2,6), 135.65 (ArC-3,5), 135.65 (PyrrC-2′), 153.00 (ArC-4); MS (EI) *m/z* (rel intensity) 286 (M^+ + 1, 23), 285 (M^+, 100), 270 (7), 132 (5), 131 (7), 113 (4); HRMS calcd for $C_{19}H_{27}ON$ 285.2093, found 285.2093.

Ferricyanide Oxidation of 13a To Afford 3. To a solution of **13a** (67 mg, 0.232 mmol) in benzene (4 mL) were added a 0.1 M aqueous KOH solution (8 mL) and then potassium ferricyanide (764 mg, 2.52 mmol) at room temperature, and the resulting mixture was stirred vigorously for 4 h at the same temperature. The reaction mixture was extracted with benzene, and the benzene extract was washed (water, then brine), dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel (hexane:ether = 3:2) to afford **3** as deep green crystals (67 mg, 0.116 mmol, quant).

Ferricyanide Oxidation of 13b To Afford 4. In a manner similar to that for **3**, a solution of **13b** (56.1 mg, 0.167 mmol) in benzene (10 mL) was combined with a 0.1 M aqueous KOH solution (20 mL), and then potassium ferricyanide (551 mg, 1.67 mmol) was added. The mixture was stirred vigorously at room temperature for 24 h. After addition of water, the reaction mixture was extracted with benzene. After a workup similar to that for **3**, the reaction product was chromatographed on silica gel (hexane:CH_2Cl_2 = 1:1) to afford **4** as green crystals (47.8 mg, 0.0717 mmol, 85.7%): mp 263−264 °C; IR (KBr) 2956−2870 (m), 1577 (s), 1477 (w), 1452 (s), 1387 (w), 1356 (s), 1325 (s), 1255 (m), 1200 (w), 1136 (m), 1103 (m), 1086 (m), 1022 (m), 978 (m), 887 (m), 854 (m), 810 (w), 785 (w), 688 (w) cm^{-1}; UV/vis/NIR (CH_3CN) $\lambda_{\max}$ nm (log ε) 742 sh (4.21), 665 (4.99), 605 sh (4.52), 555 sh (3.98), 448 sh (3.74), 387 (3.92), 327 sh (3.86); ^{1}H NMR (400 MHz, $CDCl_3$, −40 °C) for **4A** δ 1.32 (s, 36H, *t*-Bu), 6.98 (d, 2H, *J* = 2.5 Hz, ArH-2,2‴), 7.21 (d, 2H, *J* = 5.9 Hz, SelH-4′,3″), 7.41 (d, 2H, *J* = 2.5 Hz, ArH-6,6‴), 7.67 (d, 2H, *J* = 5.9 Hz, SelH-3′,4″); for **4B** δ 1.32 (s, 36H, *t*-Bu), 6.94 (d, 2H, *J* = 2.5 Hz, ArH-2,2‴), 7.41 (d, 2H, *J* = 2.5 Hz, ArH-6,6‴), 7.54 (d, 2H, *J* = 6.0 Hz, SelH-4′,3″), 7.58 (d, 2H, *J* = 6.0 Hz, SelH-3′,4″); MS (DEI) *m/z* (rel intensity) 670 (M^+ + 2, 80), 669 (M^+ + 1, 36), 668 (M^+, 100), 667 (73), 665 (28), 664 (27); HRMS calcd for $C_{36}H_{44}O_2Se_2$ 668.1672, found 668.1669.

Ferricyanide Oxidation of 13c To Afford 5. In a manner similar to **3**, a solution of **13c** (32.2 mg, 0.118 mmol) in benzene (4 mL) was combined with a 0.1 M aqueous KOH solution (8 mL), and then potassium ferricyanide (389 mg, 1.18 mmol) was added. The mixture was stirred vigorously at room temperature for 51 h. After the addition of water, the reaction mixture was extracted with $CHCl_3$. After a workup similar to that for **3**, the reaction product was chromatographed on silica gel ($CHCl_3$) to afford **5** as green crystals (11.4 mg, 0.0211 mmol, 35.7%).

PbO_2 Oxidation of 13a To Afford 3. PbO_2 (297 mg, 1.24 mmol) was added to a solution of **13a** (35.8 mg, 0.124 mmol) in dry CH_2Cl_2 (5 mL). The resulting mixture was stirred vigorously at room temperature for 30 min under nitrogen atmosphere. After removal of the surplus PbO_2 by filtration through Celite, the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane:CH_2Cl_2 = 1:1) to give **3** (29.1 mg, 0.051 mmol, 82.1%).

PbO_2 Oxidation of 13b To Afford 4. PbO_2 (665 mg, 2.78 mmol) was added to a solution of **13b** (93.2 mg, 0.278 mmol) in dry CH_2Cl_2 (5 mL). The resulting mixture was allowed to react and worked up in a manner similar to that described for the PbO_2 oxidation of **13a**. The crude product was purified through a silica gel column (hexane:$CHCl_3$ = 1:1) to afford **4** as deep green crystals (91.3 mg, 0.137 mmol, 98.5%).

PbO_2 Oxidation of 13c To Afford 5. PbO_2 (448 mg, 1.87 mmol) was added at 0 °C to a solution of **13c** (51.0 mg, 0.187 mmol) in dry CH_2Cl_2 (5 mL). The resulting mixture was allowed to react and worked up in a manner similar to that described for the PbO_2 oxidation of **13a**. The crude product was purified through a silica gel column (CH_2Cl_2) to afford **4** as deep green crystals (31.7 mg, 0.0587 mmol, 62.6%).

PbO_2 Oxidation of 13d To Afford 6. PbO_2 (338 mg, 1.41 mmol) was added to a solution of **13d** (40.3 mg, 0.141 mmol) in dry CH_2Cl_2 (4 mL). After a workup similar to that described for the PbO_2 oxidation of **13a**, the crude product was purified through a silica gel column (CH_2Cl_2, and then CH_2Cl_2:MeOH = 10:1) to afford **6** as deep green crystals (30.8 mg, 0.0543 mmol, 77.0%): mp 222−223 °C; IR (KBr) 2952−2864 (w), 1597 (w), 1560 (s), 1500 (s), 1450 (w), 1354 (m), 1336 (s), 1254 (w), 1107 (m), 1092 (s), 1020 (m), 991 (m), 881 (m), 777 (w), 727 (w) cm^{-1}; UV/vis/NIR (CH_3CN) λ_{max} nm (log ϵ) 827 (4.99), 455 sh (3.77), 396 (3.88), 338 (4.11), 290 (4.01); ^1H NMR (600 MHz, $CDCl_3$, −40 °C) for **6A:** δ 1.36 (s, 18H, *t*-Bu), 1.38 (s, 18H, *t*-Bu), 3.86 (s, 6H, *N*Me), 7.09 (d, 2H, J = 5.0 Hz, PyrrH-4′,3″), 7.27 (d, 2H, J = 5.0 Hz, PyrrH-3′,4″), 7.37 (s, 2H, ArH-6,6‴), 7.40 (s, 2H, ArH-2,2‴); MS (EI) m/z (rel intensity) 568 (M^+ + 2, 100), 567 (M^+ + 1, 16), 566 (M^+, 5), 284 (14); HRMS calcd for $C_{38}H_{52}O_2N_2$ 568.4029, found 568.4034.

Single-Crystal X-ray Structure Determination. The crystals of **5** belong to a monoclinic system with the following cell dimensions: a = 16.865(2) Å, b = 11.100(3) Å, c = 17.942(1) Å, β = 108.725(9)°, and V = 3180.8(6) Å^3. The space group is $P2_1/n$ and Z = 4. The empirical formula, molecular weight, and calculated density are $C_{36}H_{44}O_4$, 540.74, and 1.129 g/cm^3, respectively. The three-dimensional X-ray data were collected by the use of graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å) on a Rigaku AFC7R automatic four-circle diffractometer up to a maximum 2θ of 120.1°. The intensity data of 5022 independent reflections were collected, and 3023 with $I > 2.5\ \sigma(I)$ were used in the present X-ray analysis. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Full-matrix least-squares refinement converged to a conventional R factor of 0.041, R_w factor of 0.051. The standard deviation of an observation of unit weight was 1.73. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.13 and −0.14 e^-/ Å^3, respectively. All calculations were performed on a Silicon Graphics Indigo workstation using the teXsan crystallographic package [teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985, 1992)]. The crystals of **3** belong to a monoclinic system with the following cell dimensions: a = 11.168(9) Å, b = 19.570(4) Å, c = 17.643(3) Å, β = 101.55(1)°, and V = 3777.7(10) Å^3. The space group is $P2_1/n$ and Z = 4. The empirical formula, molecular weight, and calculated density are $C_{36}H_{44}O_2S_2$, 572.86, and 1.007 g/cm^3, respectively. The three-dimensional X-ray data were collected by the use of graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) on a Rigaku AFC5R automatic four-circle diffractometer up to a maximum 2θ of 58°. The intensity data of 2225 were used in the present X-ray analysis. All calculations were performed by micro Vax computer using the teXsan crystallographic package.

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Supporting Information Available: Copies of ^1H NMR spectra for all new compounds (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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