# A CONVENIENT SYNTHESIS OF HETEROQUATERPHENOQUINONES INCLUDING NOVEL NITROGEN- AND SELENIUM-CONTAINING QUINONES WITH CHARACTERISTIC PROPERTIES

Kazuko Takahashi* and Atsushi Gunji

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-77, Japan

Abstract – A series of heteroquaterphenoquinones including novel biselenieno- and bi-*N*-methylpyrrolo-quinonoid incorporated quinones have been synthesized by a novel one-pot oxidative homocoupling reaction of heterocycle-substituted phenols. Characteristic properties adequate for using as functional materials have been clarified.

Dyes with intense absorption at near infrared (NIR) regions are currently receiving attention for using as high density optical storage materials responsible for semiconductor lasers.[1] Highly amphoteric compounds are of special interest as a novel organic photoconducting mediator having both electron and hole transporting abilities.[2] Unfortunately a series of heteroterphenoquinones synthesized recently exhibit absorption bands at around 530−600 nm and showed relatively low amphotericities except a tellurium-containing derivative.[3,4] Therefore, more conjugation-extended heteroquaterphenoquinones may be candidates for such materials and will be used in various other fields of applied chemistry or applied physics. However, only sulfur and oxygen containing heteroquaterphenoquinones (1)[5] and (2)[6] have been known so far. Moreover, the reported synthetic methodologies for 1 and 2 are a little complicated and not always applicable to the synthesis of other quinones such as 4 which may exhibit unique and precise properties requested to the functional materials mentioned above. We have now found a convenient, short-step, and general method for the synthesis of a series of heteroquaterphenoquinones and in these efforts, we have created novel quinones (3) and (4), and clarified their electronic spectral and electrochemical properties.
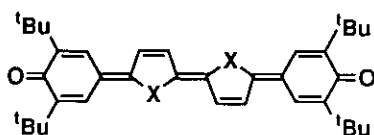
1: X=S,   2: X=O

3: X=Se,   4: X=NMe

The oxidative dimerization of phenols is an important tool for the synthesis of diphenoquinones, although the reaction is liable to give benzoquinones and aryloxy polymers as by-products depending on the oxidizing reagents.[7] In consequence, we have investigated one-electron oxidation of heterocycle-substituted phenols (8a−d) as shown in Scheme 1.
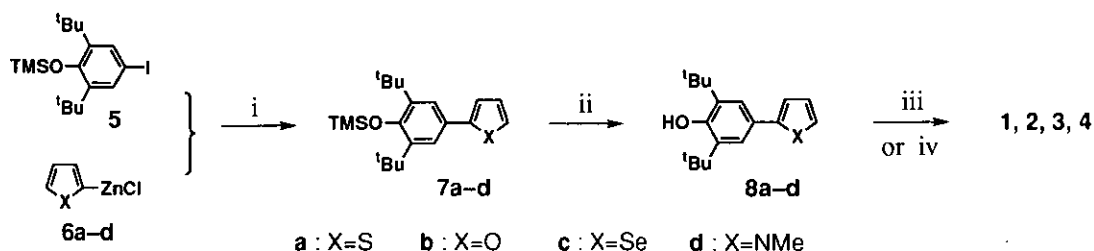
Scheme 1. i: 1.5 mol equiv. **6a—d**, 5.0 mol % Pd(PPh$_3$)$_4$, THF, room temperature, 1 h (for **7a, 7c, 7d**), 3 h (for **7b**); ii: 1.1 mol equiv. TBAF, THF, room temperature, 1 min (for **8a, 8b**), 20 min (for **8d**), 0 °C, 2 min (for **8c**); iii: 10 mol equiv. K$_3$Fe(CN)$_6$, benzene, room temperature, 4 h (for **8a**), 24 h (for **8c**), 51 h (for **8b**); iv: 10 mol equiv. PbO$_2$, CH$_2$Cl$_2$, room temperature, 30 min (for **8a—c**), 0 °C, 30 min (for **8d**).

Five-membered heterocycle-substituted trimethylsiloxybenzenes (**7a—d**), the precursors of phenols (**8a—d**), were synthesized in satisfactory yields (Table 1) by the reaction of organozinc chlorides (**6a—d**) with the iodobenzene derivative (**5**) in the presence of 5 mol% of Pd(PPh$_3$)$_4$ generated in situ by treating Cl$_2$Pd(PPh$_3$)$_2$ with i-Bu$_2$AlH.[8] The siloxybenzenes (**7a—d**) were desilylated with tetrabutylammonium fluoride (TBAF) in dry THF to give corresponding phenols (**8a—d**) in good yields. TBAF is superior to BBr$_3$ or HCl, since it is applicable to the compounds sensitive to the acids, such as **7d**. The oxidative coupling reaction of **8a—d** was examined with one-electron oxidizing agents, potassium ferricyanide and lead dioxide, because the oxidation reaction with these reagents can be carried out in relatively low temperature and basic or neutral conditions. Procedures for the oxidation are very easy.[9] The yields of quinones (**1**) and (**2**) are very high in both ferricyanide and PbO$_2$ oxidations. The yield of **3** is much better in the PbO$_2$ oxidation than in the ferricyanide oxidation. In the ferricyanide oxidation of **8b**, heteroterphenoquinone (**11**: 16%) and diphenoquinone (**12**: 6.8%) were obtained together with **2**. The lower yield in **2** can be attributed to the unfavorable aryloxy radical coupling affording **9** and **10** as intermediates for **11** and **12**, respectively. In common with the sensitive nature of pyrroles to oxidation with Fe(III) ion, oxidation of **8d** with potassium ferricyanide gave many uncharacterizable products.

Table 1. Yields (%) of heteroquaterphenoquinones and their synthetic precursors[a]

Entry	Silylether (i)		Phenol (ii)		Heteroquinone	K$_3$Fe(CN)$_6$ (iii)	PbO$_2$ (iv)
1	**7a** (X=S)	85.4	**8a** (X=S)	84.6	1	100	82.1
2	**7b** (X=O)	89.4	**8b** (X=O)	96.1	2	35.7	62.1
3	**7c** (X=Se)	75.3	**8c** (X=Se)	92.5	3	85.7	98.5
4	**7d** (X=NMe)	79.0	**8d** (X=NMe)	85.5	4	—	76.9

a Reaction conditions (i, ii, iii, and iv) are described in the caption to Scheme 1.
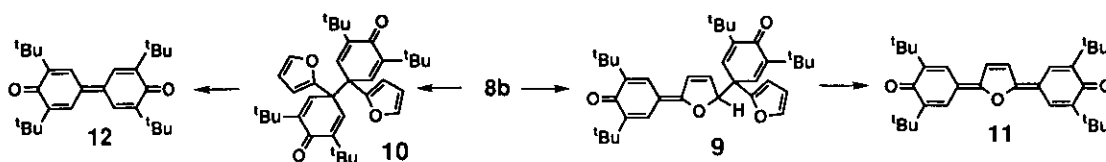
Scheme 2.

Table 2. Redox potentials[a], E_1^{sum} values, and absorption bands[b] of heteroquaterphenoquinones

Hetero-quinones	E_1^{ox}	E_{p1}^{ox}	E_{p2}^{ox}	ΔE_p^{ox}	E_1^{red}	E_1^{sum}	vis to NIR-Band			
							λ_{max}	ε_{max}	λ_{max}	ε_{max}
	V vs. SCE						nm	$mol^{-1}cm^{-1}$	nm	$mol^{-1}cm^{-1}$
1	+0.85	+0.91	+1.40	0.49	−0.43	1.28	678	31212	725 sh	11220
2	+0.83	+0.89	+1.49	0.60	−0.49	1.32	662	103322	730 sh	50118
3	+0.88	+0.94	+1.35	0.41	−0.45	1.33	665	97951	742 sh	12540
4	+0.47	+0.53	+1.18	0.65	−0.47	0.94	827	98658	—	—

a Potentials are measured by cyclic voltammetry in PhCN with 0.1 M $(n\text{-Bu})_4NClO_4$ at room temperature (scan rate, 50 mV/s). b Absorption spectra are measured in MeCN.

The synthetic method we used here will open many possibilities for the synthesis of a variety of the correlated quinones with different skeletal structures. Actually, quinones (**3**) and (**4**) are the first heterocycle-extended quinones incorporating selenium and nitrogen atoms, respectively.

Quinones (**3**) and (**4**)[10] exhibit a very intense absorption maximum in their electronic spectra (Table 2) accompanied by an absorption tail reaching to 850 nm for **3** and to 900 nm for **4**. These quinones are stable in the solid state and soluble in non-polar organic solvents such as tetrachloroethane, dichloromethane, benzene, and alkylcyclohexanes. Thus these quinones appear to have good physical and chemical properties for using as write-once-read-many (WORM) type diode laser optical storage media.[11]

Quinones (**3**) and (**4**) showed one-electron two-step oxidation waves in the anodic direction corresponding to the formation of the radical cations and dications of these quinones. As can be seen in Table 2, the first oxidation potential (E_1^{ox}) of the quinone (**3**) is in the fairly same range as those of quinones **1** and **2**, nevertheless the E_1^{ox} of N-methylquinone (**4**) is very low. This could be rationalized by the low ionization potential of the N-methylpyrrole moiety compared with those of thiophene, selenophene, and furan moieties of **1**−**3**. Quinones (**3**) and (**4**) were readily reduced with Na-metal to the corresponding radical anions, which was confirmed by ESR spectroscopy, but the cyclic voltammograms of **3** and **4** showed a reversible two-electron reduction wave affording corresponding dianions. The smallest E_1^{sum} ($=E_1^{ox} + (-E_1^{red})$)[12] of **4** originates in its low E_1^{ox} value, because the E_1^{red} value of **4** does not differ much from others. Thus, conjugation-extension with N-methylpyrrole groups is significant in enhancing the amphotericity. The high amphotericity of **4** can be attributed to the small HOMO-LUMO separation in **4**, which has been demonstrated by the bathochromic shift by 149−165 nm in the 1st excitation band of **4** compared with those of **1**−**3** (Table 2). In this regard the highly amphoteric qiunone (**4**) can be used as a novel photoinduced electroconducting mediator having both electron and hole transporting abilities. While the quinone (**2**) exists predominatingly in an O-cis conformation,[6] the N-methylquinone (**4**) exists in an N-trans conformation in solution and no N-cis isomer is detected from the ^{1}H nmr spectroscopy at the temperature range of −40 − +40 °C. The Se-trans conformation is more stable in **3** because the relative ratio of Se-trans to Se-cis at −40 °C is 1.42 : 1 in $CDCl_3$ solution. Quinones (**2**) and (**4**) with a rigid conformation exhibit a large ΔE_p^{ox} value, compared with the flexible quinones (**1**) and (**3**).

ACKNOWLEDGMENTS

REFERENCES AND NOTES

1. M. Emmelius, G. Pawlowski, and H. W. Vollmann, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1445 and references cited therein; M. Umehara, M. Abe, and H. Oba, *J. Synth. Org. Chem. Jpn.*, 1985, **43**, 334; J. Fabian and R. Zahradnik, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 677.

2. K. Y. Law, *Chem. Rev.*, 1993, **93**, 449 and references therein; Y. Yamaguchi, H. Tanaka, and M. Yokoyama, *J. Chem. Soc., Chem. Commun.*, 1990, 222; W. D. Gill, *J. Appl. Phys.*, 1972, **43**, 5033.

3. a) K. Takahashi, T. Suzuki, K. Akiyama, Y. Ikegami, and Y. Fukazawa, *J. Am. Chem. Soc.*, 1991, **113**, 4576; b) K. Takahashi, A. Gunji, and K. Akiyma, *Chem. Lett.*, 1994, 863; c) K. Takahashi and T. Sakai, *Chem. Lett.*, 1993, 157.

4. R. Tamura, Y. Nagata, H. Shimizu, A. Matsumoto, N. Ono, A. Kamimura, and K. Hori, *Adv. Mater.*, 1993, 719.

5. K. Takahashi and T. Suzuki, *J. Am. Chem. Soc.*, 1989, **111**, 5483.

6. K. Takahashi, A. Gunji, K. Yanagi, and M. Miki, *Tetrahedron Lett.*, 1995, **36**, 8055.

7. A. H. Haines, *Method for the oxidation of organic compounds*, Academic press 1985, p. 195; V. Balogh, M. Fe'tizon, and M. Golfier, *J. Org. Chem.*, 1971, **36**, 1339.

8. Preparations of **7b**−**d** were performed under a similar procedure for **7a** described in reference [3a].

9. *Ferricyanide Oxidation*: To a solution of **8a**−**c** in benzene were added 0.1 mol dm^{-3} aqueous KOH solution and then 10 mol equiv. of potassium ferricyanide at room temperature and the mixture was stirred vigorously for 4 h (for **8a**), 51 h (for **8b**), and 24 h (for **8c**). After usual work-up, quinones (**1**−**3**) were purified by chromatography (SiO_2-1:1 haxane-CH_2Cl_2). *Lead Dioxide Oxidation*: To a solution of **8a**−**d** in CH_2Cl_2 was added 10 mol equiv. of PbO_2 and the mixture was stirred vigorously for 30 min at room temperature (for **8a**−**c**) or at 0 °C (for **8d**) in N_2 atmosphere. After removal of PbO_2 by filtration, the residual reaction mixture was purified by chromatography (SiO_2-1:1 hexane:CH_2Cl_2).

10. The structures of **3** and **4** were confirmed by their elemental analysis, mass spectrometry, and ^1H nmr spectroscopy. Selected physical data for **3**: deep green powder, mp 263−264 °C; DEI-ms: m/z (%) 670 (M^++2, 80), 668 (M^+, 100); ^1H nmr (600 MHz, $CDCl_3$): δ 1.36 (s, 36H, *t*-Bu), 6.99 (br. s, 2H, H-2,2'''), 7.41 (br s, 2H, H-6,6'''), 7.59 (br s, 2H, H-3',4''), 7.35 (br s, 2H, H-4',3''); FTir (KBr): 2956−2870, 1577 (C=O), 1477, 1452, 1356, 1325, 1255, 1136, 1103, 1086, 1022, 978 cm^{-1}; uv/vis/NIR (CH_3CN): λ_{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); HRms (70 eV, DEI): calcd for $C_{36}H_{44}O_2Se_2$ [M^+] 668.1672, found 668.1669; for **4**: deep green crystals, mp 222−223 °C; EI-ms: m/z (%) 568 (M^++2, 100), 566 (M^+, 5); ^1H nmr (600 MHz, $CDCl_3$): δ 1.40 (s, 36H, *t*-Bu), 3.84 (s, 6H, NMe), 7.03 (br s, 4H, H-3',4'' and H-4',3''), 7.40 (br s, 4H, H-2,2''' & H-6,6'''); FTir (KBr): 2952−2864, 1560 (C=O), 1500, 1450, 1354, 1336, 1107, 1092, 1020, 991, 811 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); HRms (70 eV, DEI): calcd for $C_{38}H_{52}O_2N_2$ [M^+] 568.4029, found 568.4034.

11. The details of optical writing with diode laser will be reported in more special journals.

12. K. Nakasuji, K. Yoshida, and I. Murata, *J. Am. Chem. Soc.*, 1982, **104**, 1432; *idem, ibid.*, 1983, **105**, 5136.