JOC*Note*

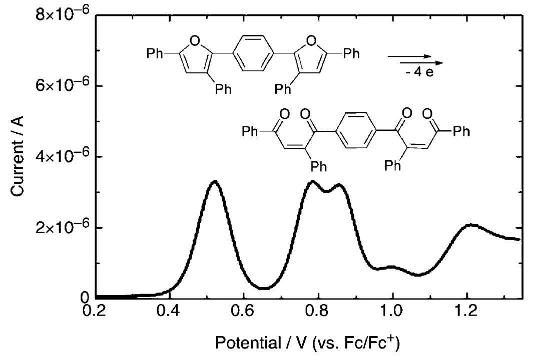
Sequential Electrochemical Oxidation of Alternating Benzene-Furan Oligomers

Cheng-Lan Lin,[§] Yi-Lin Wu,[§] Chang-Li Chen,[†]
Chih-Ming Chou,[§] and Tien-Yau Luh*,[§]

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, and Institute of Chemistry, Academia Sinica, Nangang, Taipei, Taiwan 115

tyluh@ntu.edu.tw

Received May 15, 2007



Electrochemical oxidation of pentaaryl **2** containing two furan moieties occurs sequentially to give diketone **8** after two-electron transfer. Further oxidation with another two-electron transfer gives the corresponding tetraketone **9**. Radical cation intermediate is detected by absorption spectroscopy. The radical intermediates of different regiochemistry have been shown to exhibit different oxidation potentials as revealed by the differential pulse voltammetry.

Alternating benzene-furan oligomers have recently been shown to display a range of interesting optoelectronic properties.[1−4] To illustrate, cyclophenes **1** exhibit extraordinary second-order nonlinear optical properties due to interaction between two twisted π systems involving the donor furan moiety and the double bond acceptor.[2] Pentaaryl **2** is known to be an efficient hole transporting material in an electroluminescent device.[3] Preliminary cyclic voltammetric examinations on **2** and related compounds suggest that the molecules undergo reversible redox processes.[3a,4] The oxidation potentials and the number of electron transfers in these alternating benzene-furan oligomers depend on the conjugation lengths.[4] The corresponding radical cation generated upon the first oxidation process might be relatively stable to facilitate the electron-transfer process in an electroluminescent sandwich device. The chemistry of radical cations derived from heteroaromatic oligoaryl is well-documented.[5−7] The presence of substituents at C_2 and C_5 positions seems to be essential to stabilize these radical cations, and hence, electrochemical promoted polymerization can be avoided.[8] In this paper, we report the details of the electrochemical oxidation of **2** and related furan-containing oligoaryls including the characterization of the corresponding radical cations.

We have previously shown that **2** exhibited a first reversible oxidation at 582 mV[9] and a second oxidation around 866 mV, as revealed by the cyclic voltammogram.[3a] During the course of this voltammetric investigation, a blue material was generated on the electrode surface and gradually diffused into the solution. The color persisted for at least several minutes in solution at ambient temperature. In situ spectro-electrochemical experiments were carried out. The potential was set at 582 mV to oxidize **2**, and a blue solution was obtained. In comparison with the absorption spectrum **2**, the new peaks at 570 and 630 nm were ascribed as the absorptions of the radical cation intermediate **5** (Figure 1). A similar blue solution was obtained when a CH_2Cl_2 solution of **2** was treated with a few drops of concentrated sulfuric acid, and the absorption spectrum of this mixture is

---

[§] National Taiwan University.

[†] Academia Sinica.

(1) For a review, see: Luh, T.-Y.; Lee, C.-F. *Eur. J. Org. Chem.* **2005**, 3875.

(2) Lin, H.-C.; Lin, W.-Y.; Bai, H.-T.; Chen, J.-H.; Jin, B.-Y.; Luh, T.-Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 897.

(3) (a) Zhang, L.-Z.; Chen, C.-W.; Lee, C.-F.; Wu, C.-C.; Luh, T.-Y. *Chem. Commum.* **2002**, 2336. (b) Wu, C.-C.; Hung, W.-Y.; Liu, T.-L.; Zhang, L.-Z.; Luh, T.-Y. *J. Appl. Phys.* **2003**, *93*, 5465.

(4) (a) Chou, C.-M.; Chen, W.-Q.; Chen, C.-H.; Lin, C.-L.; Tseng, J.-C.; Lee, C.-F.; Luh, T.-Y. *Chem.—Asian J.* **2006**, *1*, 46. (b) Lee, C.-F.; Liu, C.-Y.; Song, H.-C.; Luo, S.-J.; Tseng, J.-C.; Tso, H.-H.; Luh, T.-Y. *Chem. Commun.* **2002**, 2824. (c) Lee, C.-F.; Yang, L.-M.; Hwu, T.-Y.; Feng, A.-H.; Tseng, J.-C.; Luh, T.-Y. *J. Am. Chem. Soc.* **2000**, *122*, 4992.

(5) Oligothiophenes: (a) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 2728. (b) Kasai, J. G. P.; Diaz, A.; Wu, R.; Tour, J. M. *Chem. Mater.* **1992**, *4*, 1097. (c) Elandaloussi, E. H.; Frère, P.; Richomme, P.; Orduna, J.; Garin, J.; Roncali, J. *J. Am. Chem. Soc.* **1997**, *119*, 10774. (d) van Haare, J. A. E. H.; Havinga, E. E.; van Dongen, J. L. J.; Janssen, R. A. J.; Cornil, J.; Brédas, J. L. *Chem.—Eur. J.* **1998**, *4*, 1509. (e) Chahma, M. C.; Myles, D. J. T.; Hicks, R. G. *Chem. Mater.* **2005**, *17*, 2672. (f) Sun, X. H.; Chan, C. S.; Wong, M. S.; Wong, W. Y. *Tetrahedron* **2006**, *62*, 7846. (g) Zade, S. S.; Bendikov, M. *Chem.—Eur. J.* **2007**, *13*, 3688.

(6) Oligopyrroles: (a) Davies, A. G.; Julia, L.; Yazdi, S. N. *J. Chem. Soc., Perkin Trans. 2* **1989**, 239. (b) Audebert, P.; Guyard, L.; Nguyen Dinh An, M.; Groenendaal, L.; Meijer, E. W. *Chem. Mater.* **1997**, *9*, 723. (c) Guyard, L.; Hapiot, P.; Neta, P. *J. Phys. Chem. B* **1997**, *101*, 5698. (d) van Haare, J. A. E. H.; van Boxtel, M.; Janssen, R. A. J. *Chem. Mater.* **1998**, *10*, 1166. (e) E, W.; Ohkubo, K.; Sanchez-Garcia, D.; Zhang, M.; Sessler, J. L.; Fukuzumi, S.; Kadish, K. M. *J. Phys. Chem. B* **2007**, *111*, 4320.

(7) Oligofurans: (a) Lazana, M. C. R. L. R.; Franco, M. L. T. M. B.; Herold, B. J. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1305. (b) Bachmann, R.; Gerson, F.; Gescheidt, G.; Vogel, E. *J. Am. Chem. Soc.* **1993**, *115*, 10286. (c) Lahti, M.; Ling, C. *J. Am. Chem. Soc.* **1994**, *116*, 8784. (d) Abaev, V. T.; Profatilova, I. A.; Butin, A. V.; Mel'chin, V. V.; Bumber, A. A. *Russ. J. Gen. Chem.* **2006**, *76*, 2037.

(8) Gandini, A.; Belgacem, M. N. *Prog. Polym. Sci.* **1997**, *22*, 1203. Zotti, G. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: Chichester, 1997; Vol. 2, Chapter 4.

(9) A symmetric redox pair was observed with $i_{pc}/i_{pa} \sim 1$, where i_{pc} and i_{pa} are cathodic and anodic peak currents, respectively.

(10) (a) Yokozawa, Y.; Miyashita, I. *J. Chem. Phys.* **1956**, *25*, 796. (b) Weissman, S. I.; De Boer, E. *J. Chem. Phys.* **1956**, *26*, 963. (c) Carrington, A.; Dravnieks, F.; Symons, M. C. R. *J. Chem. Soc.* **1959**, 947. (d) Lewis, I. C.; Singer, L. S. *J. Chem. Phys.* **1965**, *43*, 2712. (e) Hyde, J. S.; Brown, H. W. *J. Chem. Phys.* **1962**, *37*, 368. (f) Forbes, W. F.; Sullivan, P. D. *J. Am. Chem. Soc.* **1966**, *88*, 2862. (g) Reymond, A.; Fraenkel, G. K. *J. Phys. Chem.* **1967**, *71*, 4570. (h) Yang, G. C.; Pohland, A. E. *J. Phys. Chem.* **1972**, *76*, 1504. (i) Wang, H.; Kispert, L. D.; Sang, H. *J. Org. Chem.* **1988**, *53*, 5967. (j) Eberson, L.; Hartshorn, M. P.; Persson, O.; Radner, F. *Chem. Commun.* **1996**, 2105.

10.1021/jo070999+ CCC: $37.00

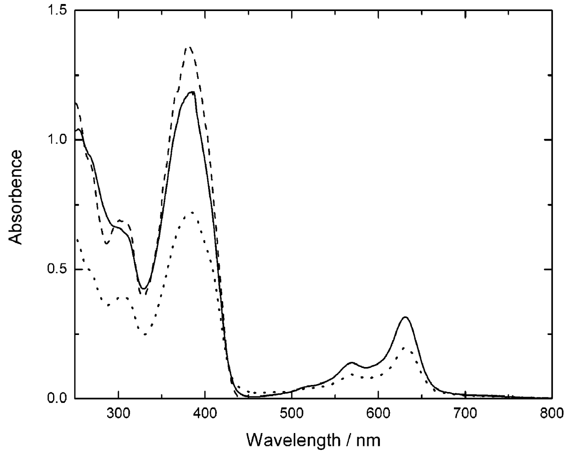
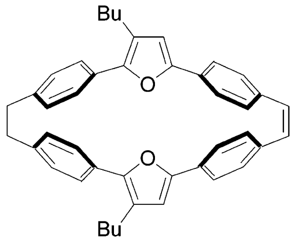
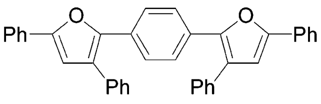


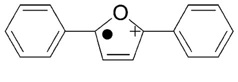
FIGURE 1. Absorption spectra of **2** and its derived radical cations **5**. Dashed line: the absorption spectrum of **2**. Solid line: radical cation **5** generated by applying a potential of 582 mV to a solution containing 10^{-4} M of **2** and 0.1 M Bu_4NPF_6. Dotted line: radical cation **5** generated by treatment of **2** in CH_2Cl_2 with a few drops of concentrated H_2SO_4.



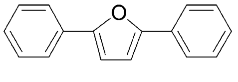
1



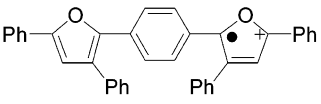
2



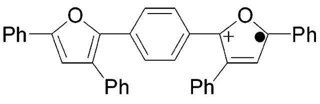
3



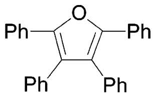
4



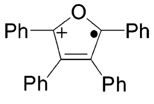
5a



5b



6



7

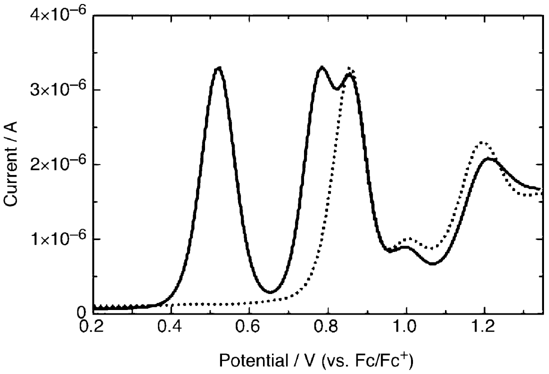
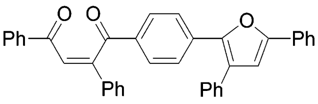


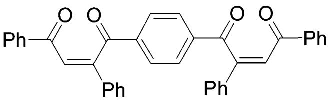
FIGURE 2. Differential pulse voltammograms 10^{-3} M of **2** (solid line) or **8** (dotted line) in CH_2Cl_2 solutions containing 0.1 M Bu_4NPF_6. Scan rate = 5 mV s^{-1}.

also shown in Figure 1. These strong acidic or related electrophilic conditions are known for the generation of aromatic radical cations.[7,10] Indeed, 2,5-diphenylfuran radical cation **3** generated from **4** in concentrated sulfuric acid has been genuinely characterized by electron spin resonance (ESR).[7a] Radical cation **5** generated either from electrolysis or from strong acid treatment of **2** exhibited a single peak without hyperfine splitting in the ESR spectra.[11,12] On the other hand, the radical cation **7** generated from the reaction of **6** with concentrated sulfuric acid gave the expected ESR spectrum with hyperfine splittings.[12] These results suggested that the radical cations would be easily accessible by one-electron oxidation of alternating benzene-furan oligoaryls and, hence, echoed our previous work using these compounds as efficient hole transporting materials.[3]

When the oxidation potential of the in situ spectroelectrochemical experiments was set at 950 mV, a colorless solution was observed. It seems likely that stepwise oxidations of **2** may be well-resolved so that different products may be selectively formed by controlling different oxidation potentials. In order to scrutinize the actual mode of the electrochemical oxidation of **2**, differential pulse voltammetry was employed. As shown in Figure 2, there were three stages of oxidation between 200 and 950 mV in the oxidation of **2** and two additional weak oxidation peaks at 1005 and 1196 mV. Potentiostatic bulk electrolyses were carried out at different oxidation stages. When the applied potential was at 700 mV, diketone **8** was obtained in 90% yield.[13] The structure of **8** was unambiguously proved by X-ray crystallography. On the other hand, when a 1100 mV potential was applied, tetraketone **9** was isolated in 92% yield.



8



9

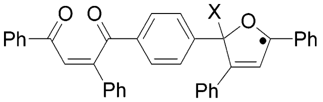
As can be seen from Figure 2, the first two-electron oxidations (with potentials at 523 and 785 mV) might be responsible for the formation of **8**. The potentials at 1005 and 1196 mV could contribute to the oxidation of **8** to afford **9**. Since the furan moiety in **10** is unsymmetrical, the radical might reside on two different carbon atoms (**10a** and **10b**, where X could be any nucleophile in the medium). Owing to the presence of the carbonyl substituent in **10**, it seems likely that the oxidation potential for **10a** might be lower than that for **10b** because the cation thus generated from **10b** would have conjugative interaction with the electron-withdrawing carbonyl group. It is noteworthy that the two-electron oxidation of **8** gave a similar profile in the differential pulse voltammetry in the higher potential region (0.7−1.4 V), and the results are compared in Figure 2.

---

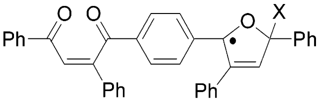
(11) Presumably, **5** may contain more than one radical center (e.g., **5a** and **5b**), and the hyperfine signals may have added up to a smooth curve due to significant overlappings.

(12) See Supporting Information.

(13) A range of solvents (CH_2Cl_2, THF, or THF/EtOH) was used for electrolysis, and the yields of **8** were similar. Presumably, trace amount of water in the solvent may be responsible for the formation for the diketones, although we cannot completely rule out the formation of diketones from the workup procedure. See: (a) Torii, S.; Tanaka, H.; Ogo, H.; Yamasita, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1079. (b) Torii, S.; Tanaka, H.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2783.

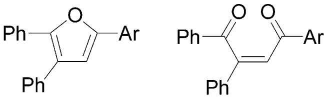


10a



10b

The oxidations of teraryls **11** and **12** were also examined. Diketones **13** and **14** were obtained in 91 and 92% yield, respectively. In addition, both **11** and **12** exhibited differential pulse voltammetry profiles similar to that of **8** (Figure 3). Again, unsymmetrical furan moiety in these substrates would generate radicals located at C_2 or C_5 in the furan ring, exhibiting different oxidation potentials. When a symmetrical substrate **6** was employed, two oxidation waves appeared at 745 and 1210 mV. Unlike the cases described above, only one kind of radical cation **7** would be produced in the first oxidation. Consequently, there would be only one oxidation potential in the second electron-transfer process.



Ar		
4-$MeO_2CC_6H_4$	**11**	**13**
Ph	**12**	**14**

Electrochemical oxidation of furan rings has been extensively used for the preparation of a range of 2,5-dimethoxy-2,5-dihydrofurans and related compounds.[14,15] In the present study, we have demonstrated the clean electrochemical oxidation of the furan moiety in oligoaryls leading to the corresponding ene-diones in excellent yield. In particular, when the oligoaryl contained more than one furan moiety, sequential oxidations took place to give ene-dione and then bis-ene-dione. The radical species of different regiochemistry have been shown to exhibit different oxidation potentials as revealed by the differential pulse voltammetry. The radical cations generated from these oligoaryls were fairly stable and were characterized by absorption spectra as well as by ESR. These results are consistent with our earlier reports that furan-containing oligoaryls, in particular **2**, are useful hole transporting materials for optoelectronic applications.

Experimental Section

General. Furan-containing oligoaryls **2**, **6**, **11**, and **12** were prepared according to literature procedures.[3a,4]

General Procedures of Potentiostatic Bulk Electrolyses. The bulk electrolysis was carried out using a tube-shaped Pt-web (52 mesh, diameter 1.5 cm and height 1.5 cm) working electrode, a Pt foil counter electrode, and a Ag/Ag^+ (10 mM $AgNO_3$) reference electrode. Substrate was dissolved in THF solution (50 mL) containing Bu_4NPF_6 (0.1 M) as the supporting electrolyte. The electrolytic solution was stirred continuously throughout the electrolysis process. A constant applying potential (vs Fc/Fc^+) was employed, and the electrochemical oxidation was stopped when a steady-state current response was reached near zero. The charge consumption was calculated by integrating the current−time curve.

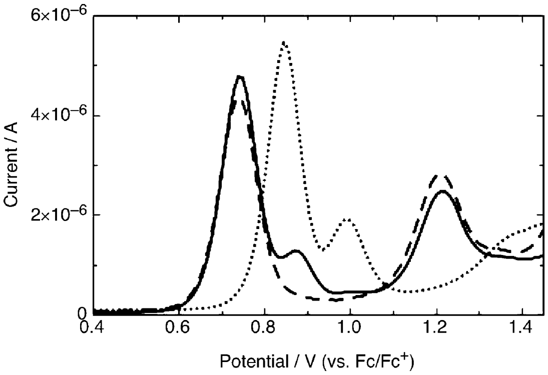


FIGURE 3. Differential pulse voltammograms 10^{-3} M of **11** (dotted line), **12** (solid line), or **6** (dashed line) in CH_2Cl_2 solutions containing 0.1 M Bu_4NPF_6. Scan rate = 5 mV s^{-1}.

The electrolyte was evaporated in vacuo, and the crude product was obtained after workup.

Electrochemical Oxidation of Pentaaryl 2. According to the general procedure, a THF solution (50 mL) containing 0.1 M Bu_4NPF_6 and **2** (137 mg, 0.27 mmol) was electrolyzed at 700 mV, and the charge consuming 49.7 Coulombs was calculated. The electrolyte was evaporated in vacuo, and the residue was triturated with ether. The ethereal solution was evaporated in vacuo, and the residue was chromatographed on silica gel (CH_2Cl_2/hexane 2:1) to afford **8** (127 mg, 90%) as a yellowish powder: mp 209−210 °C (ether/pentane); ^1H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 1 H), 7.28−7.50 (m, 16 H), 7.56−7.63 (m, 4 H), 7.66 (d, J = 8.4 Hz, 2 H), 7.74 (d, J = 8.4 Hz, 2 H), 7.89 (d, J = 7.6 Hz, 2 H), 7.99 (d, J = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.3, 121.0, 124.1, 125.6, 127.25, 127.33, 127.8, 128.0, 128.7, 128.80, 128.86, 128.9, 129.0, 129.3, 130.1, 130.8, 133.4, 133.9, 134.4, 134.8, 135.5, 137.4, 146.6, 153.5, 156.3, 188.2, 196.7; IR (KBr) ν 1663, 1660, 1655 cm^{-1}; HRMS (FAB) calcd for $C_{38}H_{27}O_3$ (M + 1) 531.1960; found 531.1965.

In a similar manner, a THF solution (50 mL) containing 0.1 M Bu_4NPF_6 and **2** (135 mg, 0.27 mmol) was electrolyzed at 1100 mV, and the charge consuming 113.9 Coulombs was calculated. After workup and chromatographic separation (silica gel, hexane/ethyl acetate 3:1), **9** (132 mg, 92%) was isolated as a white powder: mp 235−236 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.47 (m, 10 H), 7.54−7.58 (m, embodied a doublet at 7.55, J = 7.2 Hz, 6 H), 7.61 (s, 2 H), 7.95 (d, J = 7.2 Hz, 4 H), 7.80 (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.2, 127.3, 128.7, 128.8, 129.1, 129.4, 131.0, 133.6, 134.3, 137.1, 139.2, 156.2, 188.1, 196.8; IR (KBr) ν 1670, 1655 cm^{-1}; HRMS (FAB) calcd for $C_{38}H_{27}O_4$ (M + 1) 547.1909; found 547.1917;

Electrochemical Oxidation of 11. According to the general procedure, a THF solution (50 mL) containing 0.1 M Bu_4NPF_6 and **11** (150 mg, 0.42 mmol) was electrolyzed at 1100 mV, and the charge consuming 102.1 Coulombs was calculated. After workup and chromatographic separation on silica gel (CH_2Cl_2/hexane 2:1), **13** was obtained (143 mg, 91%) as a white powder: mp 114−115 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3 H), 7.41−7.50 (m, 5 H), 7.57−7.61 (m, 3 H), 7.67 (s, 1 H), 7.99 (d, J = 7.8 Hz, 2 H), 8.03 (d, J = 8.4 Hz, 2 H), 8.09 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.5, 121.1, 127.1, 128.3, 128.5, 128.6, 129.2, 129.9, 130.8, 133.4, 133.7, 134.2, 136.9, 139.1, 155.8, 166.0, 187.9, 196.6; IR (KBr) ν1722, 1674, 1651, cm^{-1}; HRMS (FAB) calcd for $C_{24}H_{19}O_4$ (M + 1) 371.1283; found 371.1292.

Electrochemical Oxidation of 12. According to the general procedure, a THF solution (50 mL) containing 0.1 M Bu_4NPF_6 and **12** (152 mg, 0.51 mmol) was electrolyzed at 950 mV, and the charge consuming 94.1 Coulombs was calculated. After workup and chromatographic separation on silica gel (CH_2Cl_2/hexane 1:1), **14**

---

(14) (a) Fry, A. J. *Synthetic Organic Electrochemistry*; Wiley: New York, 1988. (b) Yoshida, K. *Electrooxidation in Organic Chemistry: The Role of Cation Radicals as Synthetic Intermediates*; Wiley: Chichester, 1984.

(15) (a) Nad, S.; Roller, S.; Haag, R.; Breinbauer. *Org. Lett.* **2006**, *8*, 403. (b) Tajima, T.; Fuchigami, T. *Chem.—Eur. J.* **2005**, *11*, 6192. (c) Kokoh, K. B.; Belgsir, E. M. *Tetrahedron Lett.* **2002**, *43*, 229. (d) Medeiros, M. J.; Montenegro, M. I. *J. Electroanal. Chem.* **1990**, *290*, 155. (e) Shono, T.; Matsumura, Y.; Hamaguchi, H. *J. Chem. Soc., Chem. Commun.* **1977**, 712. (f) Ross, S. D.; Frinkelstein, M.; Uebel, J. J. *J. Org. Chem.* **1969**, *34*, 1018.

was obtained (144 mg, 90%) as a white powder: mp 126−127 °C (lit.[16] 128−129 °C).

In situ Spectro-electrochemical Absorption Spectra. A 1 mm quartz cell equipped with a Pt-web working electrode (52 mesh), a Pt wire counter electrode, and a Ag wire reference electrode was employed to acquire the absorption spectra of the intermediate from electrolysis. A solution containing **2** (10^{-4} M) and Bu_4NPF_6 (0.1 M) in CH_2Cl_2 (3 mL) was electrolyzed at different applying potentials, and the absorption spectra were recorded.

Differential Pulse Voltammetry. The electrochemical cell equipped with a Pt disc working electrode (diameter 2 mm), a Pt coil counter electrode, and a Ag/Ag^+ (0.01 M $AgNO_3$) reference was used under argon atmosphere for measuring differential pulse voltammetry of a CH_2Cl_2 solution (5 mL) containing Bu_4NPF_6 (0.1 M) and the substrate.

ESR Measurements. ESR spectra were recorded on a Bruker E580 or a Bruker EMX X-band digital ESR spectrometer, both of which are equipped with a TE102 cavity. Spectra processing and simulation were performed with Bruker WIN-ESR and SimFonia Software. Electrochemical or chemical oxidation methods were used to in situ generate radicals for ESR measurements. For the electrochemical one, the experiments were carried out in an electrochemical ESR cell with a PC-controlled potentiostat CHI611C (CH Instruments, Inc.) using a Ag/Ag^+ reference electrode and Pt wires as the working and counter electrode. For in situ chemical oxidation, a few drops of concentrated sulfuric acid were added into a CH_2Cl_2 solution of the sample in the resonator of the ESR spectrometer. The spectra are shown in Figures S1 and S2 in the Supporting Information.

Acknowledgment. This work was supported by the National Science Council and the National Taiwan University of the Republic of China. We thank Professor Sunney I. Chan for helpful discussions, and Dr. Jason Lee for assistance in ESR measurements.

Supporting Information Available: NMR spectra of **8**, **9**, and **13**, ESR spectra of radical cations **5** and **7**, and the X-ray crystal structure of **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO070999+

---

[16] Trisler, J. C.; Aaron, C. S.; Frye, J. L.; Park, J. Y. *J. Org. Chem.* **1968**, *33*, 1077.