Available online at www.sciencedirect.com

Tetrahedron Letters

Tetrahedron Letters 47 (2006) 467–471

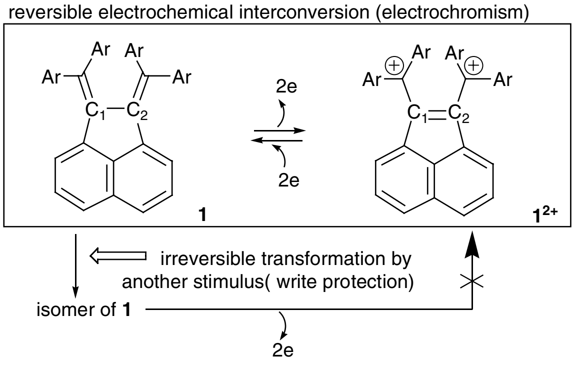
# The first stable tetraarylacenaphthenequinodimethanes exhibiting electrochromism with 'write-protect' option: preparation, highly deformed structure, and reversible interconversion with acenaphthylene-5,6-diyl dicationic dyes

Takanori Suzuki,[a,*] Shinichi Iwashita,[a] Tsuyoshi Yoshino,[a] Hidetoshi Kawai,[a]
Kenshu Fujiwara,[a] Masakazu Ohkita,[b] Takashi Tsuji,[a]
Kazunori Ono[c] and Masami Takenaka[c]

[a] *Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan*
[b] *Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan*
[c] *Asahi Kasei Electronic Co., Shioya, Hichiya, Hyuga 883-0062, Japan*

Received 26 October 2005; revised 9 November 2005; accepted 11 November 2005
Available online 28 November 2005

**Abstract**—Severely deformed title quinodimethanes [1,2-bis(diarylmethylene)acenaphthenes] **1** have been designed and prepared as novel electrochromic materials, which can be reversibly interconverted with the deeply colored dicationic dyes $\mathbf{1}^{2+}$ with acenaphthylene-1,2-diyl skeleton. The X-ray analysis of **1** revealed that the inner two aryl groups are forced to overlap in proximity, which can account for the facile electrocyclization process to the isomer. By combination of reversible electrochemical transformation with irreversible isomerization process, the present system provides a prototype for novel molecular response systems equipped with the 'write-protect' option.



**Scheme 1.** Electrochromism with the 'write-protect' option.

1,1,4,4-Tetraaryl-1,3-butadienes[1] (open-chain violenes[2]) consist of one of the representative classes of electrochromic systems,[3] that can be reversibly interconverted with the corresponding 2-butene-1,4-diyl dicationic dyes upon two-electron transfer. Annulation of π-system at 2,3-positions induces geometrical fixation of the diene unit in the *cis* form, thus forcing the two inner aryl groups to arrange in proximity. Such a severe steric hindrance endows the molecule with special reactivity as exemplified by facile electrocyclization of 7,7,8,8-tetraphenyl-*o*-quinodimethane, the short-lived strained hydrocarbon.[4] By combination of the reversible electrochemical interconversion with the irreversible transformation process by another stimulus, the novel molecular response system equipped with the 'write-protect' option[5] would be realized (Scheme 1). We have designed the title molecules as the most promising candidates for this purpose, which would be produced as persistent species. Although there are no reports on generating this class of highly congested compounds, we have succeeded in isolating the first members of 9,9,10,10-tetraarylacenaphthenequinodimethanes. Here,

---

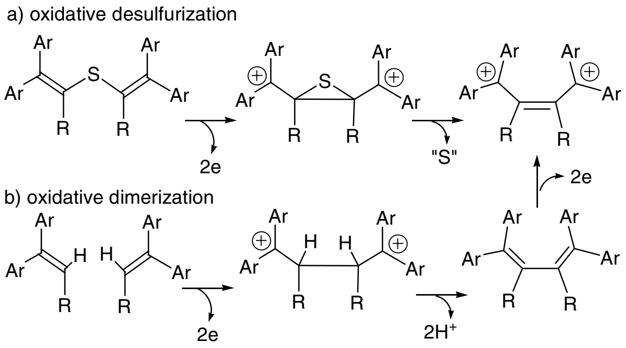
*Keywords*: Quinodimethane; Strained molecule; Steric hindrance; Redox system; Electrochromism; Dye; Dication; Acenaphthene; Electrocyclization.

[*] Corresponding author. Tel./fax: +81 11 706 2714; e-mail: tak@sci.hokudai.ac.jp

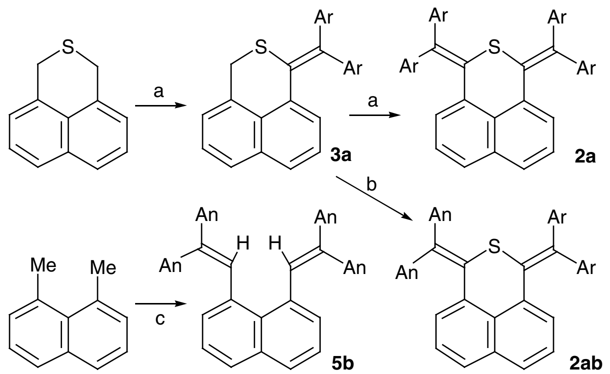
0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.11.059

we report the preparation and X-ray structure of the title electron donors **1**, and their redox properties and novel reactivities will be also disclosed.

Acenaphthylene-1,2-diyl bis(diarylmethyliums) **1**$^{2+}$ were selected as suitable precursors for the strained quinodimethanes **1**. Due to rotational flexibility about the $C^+$–$C_{1(\text{or }2)}$ bonds, dications **1**$^{2+}$ are free from the steric repulsion, which the neutral donors **1** suffer from.[6] To isolate the dications as stable salts, $p$-$Me_2NC_6H_4$ (**a**) and $p$-$MeOC_6H_4$ (anisyl; **b**) groups are chosen as electron-donating aryl substituents. The dication **1a**$^{2+}$ [$\lambda_{max}$ 714 ($\log\varepsilon$ 4.39) in MeCN] with four amino groups was isolated as a deep violet bis(triiodide) salt[8] in 85% yield by oxidative desulfurization of the bis(diarylethenyl)sulfide[9] derivative **2a**[8] with 3 equiv of iodine (Scheme 2a). The ring contractive formation of 1,2-disubstituted acenaphthylene is a very useful protocol since the sulfide donor **2a** is much less hindered and was easily derived from 2*H*,6*H*-naphtho[1,8-*cd*]thiin[10] via **3a**[8] (Scheme 3). However, the similar desulfurization[11] did not proceed for the donor containing the less electron-donating anisyl groups. Instead, a spiro compound **4ab**[8,12] was obtained in 80% yield upon oxidation of **2ab**[8] followed by hydrolysis.[13] Therefore, 1,8-bis(2,2-dianisylethenyl)naphthalene **5b**[8] was selected as the new precursor for dication **1b**$^{2+}$, which was prepared as outlined in Scheme 3. This electron donor may undergo oxidative C–C bond formation between the triarylethene units[14] followed by deprotonation[1,15] to furnish the dimethyleneacenaphthene skeleton, which is more easily oxidized than the starting diolefinic donor (Scheme 2b). In fact, oxidation of **5b** with 4 equiv of $NOBF_4$ proceeded smoothly to give the desired dication **1b**$^{2+}$. Due to its high sensitivity toward moisture, the crude product was first transformed into a stable dihydrofuran derivative **6b**,[8] which was isolated in 35% yield. Then, pure dication **1b**$^{2+}$ [$\lambda_{max}$ 592 ($\log\varepsilon$ 4.46) in $CF_3CO_2H$] was regenerated as a purple $BF_4^-$ salt[8] in 97% yield upon treatment of **6b** with $HBF_4$.

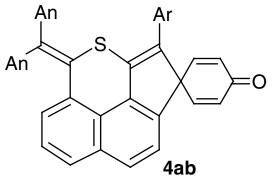


**Scheme 2.** Two synthetic approaches toward the hindered dications.

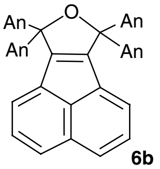


(Ar = $p$-$Me_2NC_6H_4$; An = $p$-$MeOC_6H_4$ )

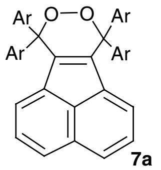
**Scheme 3.** Preparation of precursors. Reagents and conditions: (a) (i) $n$-BuLi for **3a**, $t$-BuLi for **2a**, (ii) $Ar_2C{=}O$, (iii) TsOH (94% for **3a**, 36% for **2a**); (b) (i) $t$-BuLi, (ii) $An_2C{=}O$, (iii) TsOH (42%); (c) (i) $n$-BuLi/TMEDA, (ii) $An_2C{=}O$, (iii) ClCOOMe/DMAP (34%).



**4ab**



**6b**



**7a**

(Ar = $p$-$Me_2NC_6H_4$; An = $p$-$MeOC_6H_4$)

According to the X-ray analysis of **1a**$^{2+}(I_3^-)_2$,[12] the dication in crystal is $C_2$-symmetric, with the separation of 3.14 Å between two carbenium centers (Fig. 1). Electrostatic repulsion seems the major reason for the out-of-plane deviation of exocyclic carbons ($C^+$) from the acenaphthylene unit (torsion angle of 13.7° for $C^+$–$C_1$–$C_2$–$C^+$). Diarylmethylium units are twisted by 45.6° against the acenaphthylene skeleton in the same direction. Thus, the two inner aryl groups are arranged in parallel (dihedral angle 0°) with the closest C–C contact of 3.24 Å. On the other hand, rotation about the $C^+$–$C_1$ bond seems rapid in solution as shown by the $C_{2v}$-symmetric $^1H$ NMR spectrum in $CD_3CN$. The dication **1b**$^{2+}$ also gave only one set of signals for the four anisyl groups in the $^1H$ NMR spectrum.

Upon treatment of **1b**$^{2+}(BF_4^-)_2$ with Zn powder, purple color disappeared gradually to give reddish-orange crystals [$\lambda_{max}$ 398 ($\log\varepsilon$ 4.10) in MeCN] in isolated yield of

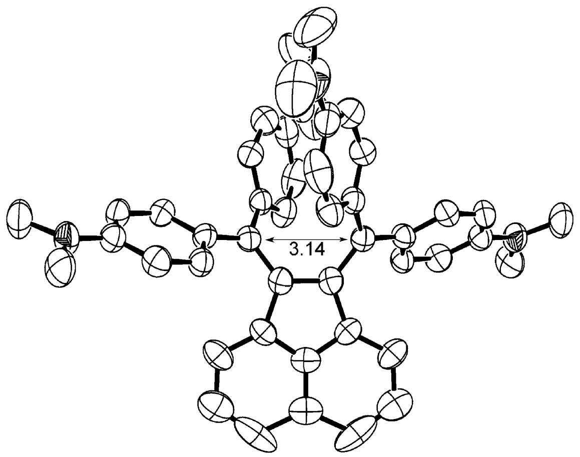


**Figure 1.** Molecular structure of **1a**$^{2+}$ determined by X-ray analysis of the bis(triiodide) salt at 15 °C. The dication is located on the crystallographic twofold axis. Hydrogen atoms are omitted for clarity.

83%. The $C_2$-symmetry of the product was suggested by its $^1$H NMR, showing the double bond character for the $C_{exo}$–$C_{1(\text{or } 2)}$ bond. Two of the four MeO signals exhibit a downfield shift by 0.17 ppm from the other two, suggesting that these protons are close to the shielding region of another aromatic ring. By the low-temperature X-ray analysis, its structure was finally confirmed to be the severely deformed quinodimethane **1b** (Fig. 2). The striking feature is the large torsion angles around the $C_1$–$C_2$ bond (45.8° for $C_{exo}$–$C_1$–$C_2$–$C_{exo}$ and 16.2° for $C_{8a}$–$C_1$–$C_2$–$C_{2a}$, respectively) despite the rigid five-membered ring structure of the acenaphthene skeleton. The $C_{exo}$–$C_{1(\text{or } 2)}$ bond length [1.363(4) Å] is similar to that in hexaarylbutadienes.[14a] So that, the strain was released by twisting the double bond but not by expanding it. The two inner aryl groups are forced to overlap in a face-to-face manner with the interplanar separation of 3.38 Å (dihedral angle 17.7°) and the closest C–C contact of 3.22 Å. Repulsion between these aryl groups must be the major reason for large twisting angle of 23.5° of the exocyclic double bonds. Upon reduction of $\mathbf{1a}^{2+}(I_3^-)_2$ with Zn, another quinodimethane **1a**[8] with four amino groups was obtained as deep red crystals [$\lambda_{max}$ 456sh (log $\varepsilon$ 4.06) in $CH_2Cl_2$] in 94% yield. Due to the very high electron-donating properties (vide infra), **1a** is less stable under air with gradual transformation into endoperoxide **7a**[8,12] probably via some open-shell species. Due to formation of such paramagnetic species, $^1$H NMR spectrum of **1a** is too featureless to give structural information, but other spectral data (IR, HR-MS) are in accord with this structural assignment.

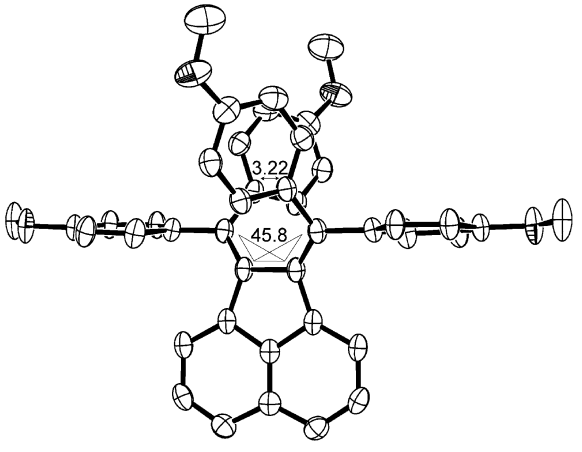


**Figure 2.** Molecular structure of **1b** determined by X-ray analysis of the $CH_2Cl_2$ solvated crystal at −120 °C. The quinodimethane is located on the crystallographic twofold axis. Hydrogen atoms are omitted for clarity.

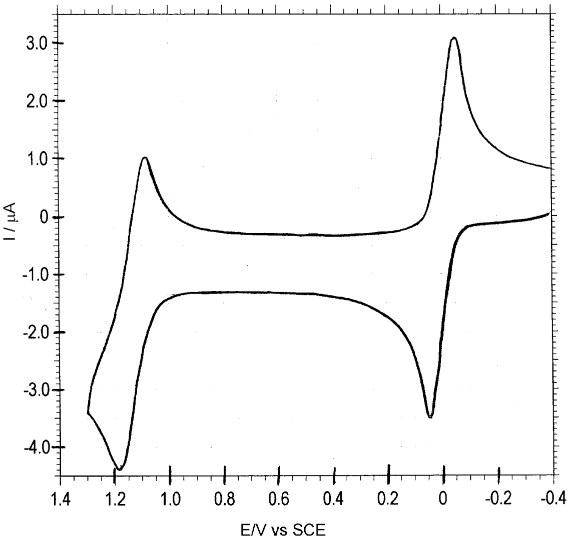


**Figure 3.** Cyclic voltammogram of **1a** ($E/V$ vs SCE) measured in $CH_2Cl_2$ containing 0.1 mol dm$^{-3}$ $n$-$Bu_4NBF_4$ (scan rate 100 mV s$^{-1}$). A pair of peaks at +1.13 V are assigned to the oxidation process of $[(4\text{-}Me_2NC_6H_4)_2C^+]$ moieties in $\mathbf{1a}^{2+}$ to give $\mathbf{1a}^{4+}$.

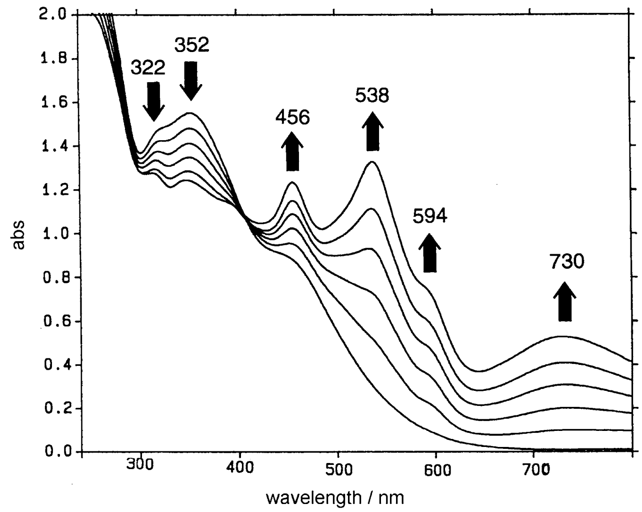
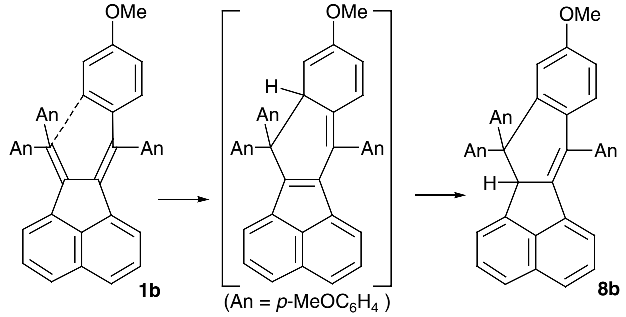


**Figure 4.** Changes in UV–vis spectra of **1a** (3.5 mL, 7.6 × 10$^{-5}$ mol dm$^{-3}$ in $CH_2Cl_2$) upon constant-current electrochemical oxidation (30 μA at 1 min interval). $n$-$Bu_4NBF_4$ (0.05 mol dm$^{-3}$) was used as an electrolyte.

Quinodimethane **1a** with four amino groups is a very strong electron donor and undergoes 2e-oxidation at +0.01 V in $CH_2Cl_2$ (Fig. 3), which is much less positive than that for the representative donor, $N,N,N',N'$-tetramethyl-$p$-phenylenediamine (+0.24 V), measured under the similar conditions.[16a] Redox interconversion between **1a** and $\mathbf{1a}^{2+}$ could be achieved electrochemically, thus demonstrating electrochromic response with vivid change in color from red to deep violet (Fig. 4). The isosbestic point in the spectroelectrogram indicates negligible steady-state concentration of the intermediary cation radical,[17] which is suitable for constructing the reversible electrochromic system as a result of suppressing the side reactions from the reactive open-shell species.[18] In the preparative-scale experiment, $\mathbf{1a}^{2+}(I_3^-)_2$ was regenerated and isolated in 97% yield upon treatment of **1a** with 3 equiv of iodine. Dication $\mathbf{1b}^{2+}$ with four anisyl groups was also regenerated as moisture-sensitive $I_3^-$ salt in quantitative yield upon oxidation of **1b** [$E^{ox}$ +0.61 V (2e) in MeCN].[16b]

The detailed examination on the isomerization reactions of **1a** was hampered by the susceptibility toward oxygen,



**Scheme 4.** Pericyclic reactions of **1b** to **8b**.

however, the anisyl derivative **1b** was found to undergo facile electrocyclization followed by hydrogen shift (Scheme 4). The rearranged product **8b**[8,12] with the dihydronaphtho[2,3-*a*]acenaphthylene skeleton was isolated in 97% yield as a yellow solid after irradiation by a Xe lamp ($\lambda > 300$ nm) for 3.5 h in the solid state.[19] Intimate arrangement of the inner two aryl groups in **1** is favored for the pericyclic reaction to occur as in the case of tetraphenyl-*o*-quinodimethane.[4a] In contrast to easy oxidation of **1b** to **1b**$^{2+}$, the isomer **8b** is a much weaker electron donor [$E^{\text{ox}}$ + 1.00 V (irrev.) in MeCN][16b] and was no longer transformed into **1b**$^{2+}$ upon oxidation.

In summary, we could demonstrate that the newly designed quinodimethanes **1** with a severely deformed geometry can be reversibly interconverted with the dicationic dyes **1**$^{2+}$, and the strained geometry for the tetraarylbutadiene unit in **1** makes the irreversible isomerization to occur within the easily accessible conditions. Since the rearranged product can no longer give the dication **1**$^{2+}$ upon oxidation, the present system can be considered as a new prototype for the electrochromic system with the 'write-protect' option, for which electric potential and light work as the independent input signals.

## Acknowledgements

This work was supported by the Ministry of Education, Science, and Culture, Japan (Nos. 15350019 and 17655012 to T.S.). We thank Professor Tamotsu Inabe (Hokkaido University) for use of the X-ray structure analysis system. MS spectra were measured by Mr. Kenji Watanabe and Dr. Eri Fukushi at the GC–MS and NMR Laboratory (Faculty of Agriculture, Hokkaido University).

## Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 283278–283283. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

ORTEP drawings of **4ab**, **6b**, **7a**, and **8b** and selected spectral data for new compounds are given as a pdf file. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.11.059.

## References and notes

1. Hünig, S.; Kemmer, M.; Wenner, H.; Barbosa, F.; Gescheidt, G.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Peters, K. *Chem. Eur. J.* **2000**, *6*, 2618.
2. Deuchert, K.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 875.
3. (a) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism: Fundamentals and Applications*; VCH: Weinheim, Germany, 1995; (b) Hünig, S.; Aldenkortt, S.; Bäuerle, P.; Briehn, C. A.; Schäferling, M.; Perepichka, I. F.; Stalke, D.; Walfort, B. *Eur. J. Org. Chem.* **2002**, 1603; (c) Ito, S.; Inabe, H.; Morita, N.; Ohta, K.; Kitamura, T.; Imafuku, K. *J. Am. Chem. Soc.* **2003**, *125*, 1669.
4. (a) Quinkert, G.; Wiersdorff, W.-W.; Finke, M.; Opitz, K.; von der Harr, F.-G. *Chem. Ber.* **1968**, *101*, 2302; (b) Iwashita, S.; Ohta, E.; Higuchi, H.; Kawai, H.; Fujiwara, K.; Ono, K.; Takenaka, M.; Suzuki, T. *Chem. Commun.* **2004**, 2076; (c) Paul, T.; Boese, R.; Steller, I.; Bandmann, H.; Gescheidt, G.; Korth, H.-G.; Sustmann, R. *Eur. J. Org. Chem.* **1999**, 551.
5. Suzuki, T.; Takahashi, H.; Nishida, J.; Tsuji, T. *Chem. Commun.* **1998**, 1331.
6. Sterically hindered terphenoquinones have been designed as novel molecular switches, which were prepared from the less hindered precursors by redox reactions (Ref. 7).
7. (a) Kurata, H.; Tanaka, T.; Oda, M. *Chem. Lett.* **1999**, 749; (b) Kurata, H.; Takehara, Y.; Kawase, T.; Oda, M. *Chem. Lett.* **2003**, 538.
8. Selected data for new compounds are given in the Supplementary data.
9. Suzuki, T.; Yoshino, T.; Nishida, J.; Ohkita, M.; Tsuji, T. *J. Org. Chem.* **2000**, *65*, 5514.
10. Guttenberger, H. G.; Bestmann, H. J.; Dickert, F. L.; Jørgensen, F. S.; Snyder, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 159.
11. Stuedel, Y.; Stuedel, R.; Wang, M. W. *Chem. Eur. J.* **2002**, *8*, 217.
12. *Crystal data of dication salt* **1a**$^{2+}$(I$_3^-$)$_2$:C$_{46}$H$_{46}$N$_4$I$_6$, *M* 1440.35, monoclinic *C*2/*c* (No. 15), $a = 18.465(2)$, $b = 20.120(2)$, $c = 14.077(1)$ Å, $\beta = 97.544(4)°$, $V = 5184.6(8)$ Å$^3$, $D_c$ ($Z = 4$) = 1.845 g cm$^{-3}$, $T = 288$ K, $\mu = 36.31$ cm$^{-1}$. The final *R* value is 0.072 for 3283 independent reflections with $I > 3\sigma I$ and 354 parameters. Esds for bond lengths and angles are 0.02–0.03 Å and 0.7–2° for nonhydrogen atoms of **1a**$^{2+}$. *Crystal data of quinodimethane* **1b**·*CH$_2$Cl$_2$ solvate*: C$_{43}$H$_{36}$O$_4$Cl$_2$, *M* 687.66, monoclinic *P*2/*c* (No. 13), $a = 10.841(2)$, $b = 11.726(2)$, $c = 13.876(2)$ Å, $\beta = 102.276(1)°$, $V = 1723.6(5)$ Å$^3$, $D_c$ ($Z = 2$) = 1.325 g cm$^{-3}$, $T = 153$ K, $\mu = 2.33$ cm$^{-1}$. The final *R* value is 0.094 for 2425 independent reflections with $I > 2\sigma I$ and 227 parameters. Esds for bond lengths and angles are 0.003–0.006 Å and 0.1–0.4° for nonhydrogen atoms of **1b**. *Crystal data of spiro compound* **4ab**·*ether$_{0.5}$ solvate*: C$_{44}$H$_{38}$O$_{3.5}$NS, *M* 668.85, triclinic *P*1 bar (No. 2), $a = 11.162(2)$, $b = 11.843(1)$, $c = 14.518(2)$ Å, $\alpha = 71.087(6)$, $\beta = 80.961(4)$, $\gamma = 86.335(4)°$, $V = 1738.3(4)$ Å$^3$, $D_c$ ($Z = 2$) = 1.278 g cm$^{-3}$, $T = 273$ K, $\mu = 1.37$ cm$^{-1}$. The final *R* value is 0.089 for 4009 independent reflections with $I > 4\sigma I$ and 437 parameters. Esds for bond lengths and angles are 0.005–0.01 Å and 0.3–0.9° for nonhydrogen

atoms of **4ab**. *Crystal data of dihydrofuran* **6b**: $C_{42}H_{34}O_5$, $M$ 618.73, triclinic $P$1bar (No. 2), $a = 9.986(2)$, $b = 11.304(2)$, $c = 14.806(2)$ Å, $\alpha = 82.121(8)$, $\beta = 74.449(7)$, $\gamma = 85.727(8)°$, $V = 1593.6(5)$ Å$^3$, $D_c$ $(Z = 2) = 1.289$ g cm$^{-3}$, $T = 153$ K, $\mu = 0.84$ cm$^{-1}$. The final $R$ value is 0.038 for 5009 independent reflections with $I > 3\sigma I$ and 424 parameters. Esds for bond lengths and angles are 0.002 Å and 0.1° for nonhydrogen atoms. *Crystal data of endoperoxide* **7a**·*acetone solvate*: $C_{49}H_{52}N_4O_3$, $M$ 744.97, monoclinic $P2_1/n$ (No. 14), $a = 10.071(8)$, $b = 15.792(5)$, $c = 26.744(5)$ Å, $\beta = 95.47(3)°$, $V = 4233(3)$ Å$^3$, $D_c$ $(Z = 4) = 1.169$ g cm$^{-3}$, $T = 296$ K, $\mu = 0.73$ cm$^{-1}$. The final $R$ value is 0.112 for 3634 independent reflections with $I > 3\sigma I$ and 481 parameters. Esds for bond lengths and angles are 0.009–0.01 Å and 0.7–1° for nonhydrogen atoms of **7a**. *Crystal data of isomer* **8b**·*ether*$_{0.5}$ *solvate*: $C_{44}H_{39}O_{4.5}$, $M$ 639.79, monoclinic $P2_1/c$ (No. 14), $a = 10.818(3)$, $b = 19.545(5)$, $c = 15.827(4)$ Å, $\beta = 93.121(1)°$, $V = 3341.3(1)$ Å$^3$, $D_c$ $(Z = 4) = 1.272$ g cm$^{-3}$, $T = 293$ K, $\mu = 0.81$ cm$^{-1}$. The final $R$ value is 0.059 for 2003 independent reflections with $I > 3\sigma I$ and 427 parameters. Esds for bond lengths and angles are 0.006–0.008 Å and 0.4–0.6° for nonhydrogen atoms of **8b**.

13. Mono(diarylmethylene)naphthothiin **3a** also gave the similar spiro compound upon oxidation followed by hydrolysis.
14. (a) Suzuki, T.; Higuchi, H.; Ohkita, M.; Tsuji, T. *Chem. Commun.* **2001**, 1574; (b) Higuchi, H.; Ohta, E.; Kawai, H.; Fujiwara, K.; Tsuji, T.; Suzuki, T. *J. Org. Chem.* **2003**, *68*, 6605; (c) Ohta, E.; Higuchi, H.; Kawai, H.; Fujiwara, K.; Suzuki, T. *Org. Biomol. Chem.* **2005**, *3*, 3024.
15. (a) Hascoat, P.; Lorcy, D.; Robert, A.; Carlier, R.; Tallec, A.; Boubekeur, K.; Batail, P. *J. Org. Chem.* **1997**, *62*, 6086; (b) Ohta, A.; Yamashita, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1761.
16. (a) Redox potentials in $CH_2Cl_2$ were measured with 0.1 mol dm$^{-3}$ $n$-$Bu_4NBF_4$ as a supporting electrolyte. The values are reported in $V$ versus SCE (scan rate 100 mV s$^{-1}$). Ferrocene undergoes 1e-oxidation at +0.53 V under the similar conditions; (b) Redox potentials in MeCN were measured with 0.1 mol dm$^{-3}$ $Et_4NClO_4$ as a supporting electrolyte. The values are reported in $V$ versus SCE (scan rate 100 mV s$^{-1}$). Ferrocene undergoes 1e-oxidation at +0.37 V under the similar conditions. The first oxidation potential of **1a** is +0.05 V under these conditions although the peaks are rather broad due to its lower solubility than in $CH_2Cl_2$.
17. Suzuki, T.; Higuchi, H.; Tsuji, T.; Nishida, J.; Yamashita, Y.; Miyashi, T. In *Chemistry of Nanomolecular Systems, Chapter 1: Dynamic Redox Systems*; Nakamura, T., Matsumoto, T., Tada, H., Sugiura, K., Eds.; Springer: Heidelberg, 2003; p 3.
18. Hünig, S.; Kemmer, M.; Wenner, H.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Gescheid, G. *Chem. Eur. J.* **1999**, *5*, 1969.
19. Irradiation of **1b** in benzene ($\lambda > 300$ nm; 0.5 h, 50% conversion) also afforded **8b** as a major component along with a small amount of unidentifiable by-products.