JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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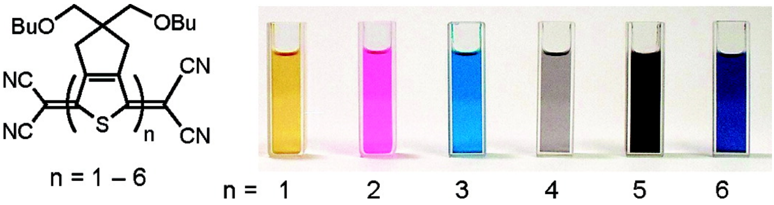
J. Am. Chem. Soc., **2005**, 127 (25), 8928-8929• DOI: 10.1021/ja051840m • Publication Date (Web): 07 June 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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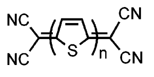
Extensive Quinoidal Oligothiophenes with Dicyanomethylene Groups at Terminal Positions as Highly Amphoteric Redox Molecules

Toshiaki Takahashi,[†] Ken-ichi Matsuoka,[†] Kazuo Takimiya,[†] Tetsuo Otsubo,*,[†] and Yoshio Aso[‡]

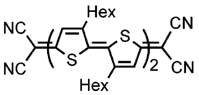
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University,
Higashi-Hiroshima 739-8527, Japan, and The Institute of Scientific and Industrial Research,
Osaka University, Ibaraki 567-0047, Japan

Received March 22, 2005; E-mail: otsubo@hiroshima-u.ac.jp

Extensively conjugated tetracyanothienoquinodimethanes are currently attracting much attention in terms of advanced molecular electronics materials. In 1974, the prototypical compound **1a** was developed as the first heteroquinoid analogue of tetracyanoquinodimethane (TCNQ) by Gronowitz and Uppström but found no use as an electron acceptor.[1] However, we later found that the bi- and terthienoquinoid homologues **1b** and **1c** formed conductive molecular complexes with TTF and TTT.[2] This finding led to the subsequent developments of their various derivatives as good electron acceptors.[2b,3] Furthermore, Higuchi and co-workers reported a large third-order nonlinear optical property for the quaterthienoquinoid derivative **2**.[4] Quite recently, Pappenfus and co-workers found an unusual ambipolar field-effect transistor performance for the terthienoquinoid derivative **3**.[5] Evidently, the tetracyanothienoquinodimethane systems have a great potential as optoelectronics materials, and their versatile functions are endowed with the extended thienoquinoidal conjugated structures. A great drawback of these compounds is, however, that they become insoluble in common solvents with quinoid extension. This solubility problem hampers further synthetic extension. We recently developed well-defined oligothiophenes **4**, where each thiophene unit is fused with a bis(butoxymethyl)cyclopentane ring.[6] This fused ring is quite helpful for solubilization, accordingly, allowing the formation of a series of extraordinarily long oligothiophenes up to the 96-mer. It has thus occurred to us that this structural modification would be also effective for the solubility problem of the thienoquinoid systems. Here we report the preparation and properties of a series of highly extensive thienoquinoid compounds **5a**−**f**.



1a–c (n = 1 – 3)



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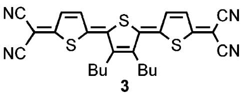

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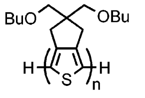
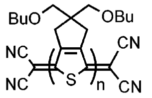
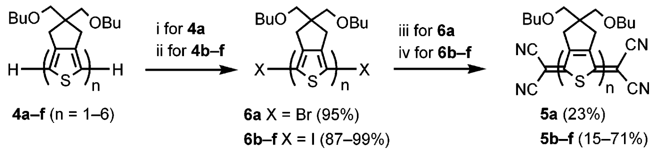


4 (n = up to 96)



5a–f (n = 1 – 6)

Scheme 1 [a]



[a] Reagents and conditions: (i) NBS, DMF, room temperature, 30 h; (ii) NIS, 4:1 DMF−$CHCl_3$, room temperature, 3−11 h; (iii) TCNEO, Cu, $BrCH_2CH_2Br$, reflux, 3.5 d; (iv) NaH, $CH_2(CN)_2$, $Pd(PPh_3)_4$, dppf, THF, reflux, 10−40 h then diluted HCl, air oxidation, room temperture, 0.5 h.

Compounds **5a**−**f** were prepared from the corresponding oligothiophenes **4a**−**f**, as shown in Scheme 1. Treatment of **4b**−**f** with 2 equiv of NIS in 4:1 DMF−chloroform at room temperature for 3−11 h gave the corresponding diiodo derivatives **6b**−**f** in excellent yields (87−99%). According to the Takahashi method,[7] **6b**−**f** were then subjected to Pd(0)-promoted coupling with sodium dicyanomethanide in refluxing tetrahydrofuran for 10−40 h, followed by air oxidation to give the quinoid oligothiophenes **5b**−**f**. The yield of **5b** was high (71%), but the yields of the higher homologues drastically decreased with chain extension down to 15% for **5f**. This approach could not be applied to the synthesis of the first member **5a**, because **4a** was less reactive to NIS, and the dibromothiophene **6a** instead obtained with NBS did not undergo the Takahashi reaction. Alternatively, **5a** was obtained in 23% yield by treating **6a** with tetracyanoethylene oxide in refluxing 1,2-dibromoethane for 3.5 d according to the Gronowitz protocol for the synthesis of **1a**.[1]

All the compounds **5a**−**f** as well as **6a**−**f** were characterized by NMR, MS, IR, and elemental analyses. They are highly soluble in common solvents, such as chloroform and THF; for example, the molar solubilities of **5a**−**f** in chloroform are $>10^{-2}$ mol/L. They are deeply colored in solid and solution phases and show pronounced color changes with quinoid extension. Figure 1 demonstrates the electronic absorption spectra of **5a**−**f** measured in THF, and Table 1 compares the wavelengths of the absorption bands. The strong absorption bands of **5a**, **5b**, and **5c** in the visible region are responsible for the respective solution colors yellow, magenta, and sky blue. This color-determining band for the higher homologues is red-shifted to the near-infrared region, and, as a result, the solution of **5d** is discolored to only a faint gray. Furthermore, the solutions of **5e** and **5f** are again deeply colored to dark brown and violet, respectively, owing to the following red-shifted absorption bands. In particular, the red-shift of the first excitation band of **5f** is very remarkable: the 0−0 transition peak appears at 1371 nm and the absorption edge extends to 1600 nm. It is worth noting that such dyes with absorptions beyond 1000 nm are very few among closed-shell organic compounds.[8−10]

To understand the origin of the deep coloration, the HOMO and LUMO levels of **5a**−**f** were examined by measuring their cyclic voltammograms in benzonitrile (Figure S1, Supporting Information). Table 1 also compares the half-wave reduction and oxidation potentials. Upon sweeping down to −1.0 V, the first member **5a** demonstrates two reversible one-electron reduction waves whose half-wave potentials are −0.09 and −0.65 V vs Ag/AgCl. The first wave of the second member **5b** shows a small cathodic shift, while the second wave shows a large anodic shift. In the third, **5c**, the two waves are combined at −0.28 V. In further higher homologues **5d**−**f**, the combined wave becomes sharper and is little by little

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[†] Hiroshima University.
[‡] Osaka University.

10.1021/ja051840m CCC: $30.25 © 2005 American Chemical Society

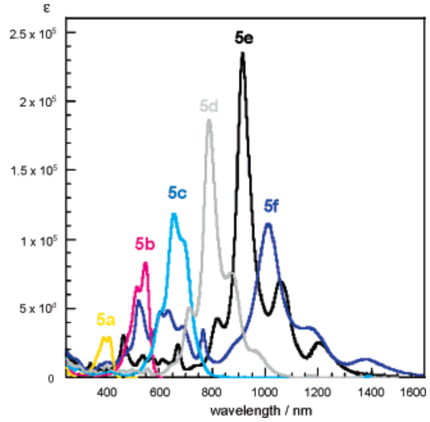


Figure 1. Electronic absorption spectra of **5a−f** in THF.

Table 1. Electronic Absorption Maxima, Half-Wave Redox Potentials, and Nitrile Vibrational Frequencies of 5a−f

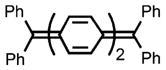
compd	λ_{max}/nm[a]	$E_{1/2}{}^{red}$/V[b]	$E_{1/2}{}^{ox}$/V[b]	ν_{CN}/cm^{-1} [c]
5a	392, 412 (4.47)	−0.09, −0.65	*d*	2226.1
5b	518, 548 (4.99)	−0.21, −0.46	*d*	2214.5
5c	596 sh, 657 (5.06), 696	−0.28	+1.18	2206.8
5d	715, 788 (5.27), 872, 966 sh	−0.21	+0.80, +1.45[e]	2201.0
5e	820, 913 (5.45), 1058, 1203	−0.16	+0.55, +1.05	2199.1
5f	1012 (5.05), 1169, 1371	−0.12	+0.38, +0.78	2195.3

[a] Measured in THF. For the most intense peak, the molar absorption coefficient in logarithmic units is given in parentheses. [b] Voltammetric conditions: RE, Ag/AgCl; WE, Pt; solvent, PhCN; SE, Bu_4NPF_6. [c] Measured on KBr disk. [d] No oxidation wave below 1.5 V. [e] Irreversible.

shifted to higher potentials. On the other hand, in the anodic sweeping up to +1.5 V, **5a** and **5b** show no oxidation waves. For **5c**, however, an oxidation wave appears as a result of the increasing quinoidal extension. For **5d−f**, not only the first oxidation wave but also the second one are observed. It is thus understandable that marked extension of the thienoquinoidal part makes these higher homologues highly amphoteric redox systems.[11]

The first excitation bands of **5a−f** may be formally represented as an intramolecular charge-transfer transition from the thienoquinoidal moiety to the dicyanomethylene moiety, supported by the red shifts of the absorption bands in polar solvents (Table S1, Supporting Information). The increasing polar structures of **5a−f** with quinoid extension are corroborated by consecutive low-frequency shifts of the nitrile vibrational frequencies (see Table 1).[12]

We have noticed that, although the first excitation bands of **5a−e** steadily grow up with chain extension, the band of **5f** in the near-infrared region decreases when compared to that of **5e**, and instead, the second band in the visible region increases. Electronic spectra at variable temperatures (Figure S2) and in different solvents (Figure S3) revealed that another species is involved in equilibrium with the thienoquinoid species **5f**. Increasing temperatures and less polar solvents favor the fraction showing the visual band. Interestingly, the NMR spectra of **5e** and even **5f** showed no signals due to the tetracyanothienoquinodimethane and cyclopentane carbons, though definite signals assignable to the pendant butoxy carbons are observed (Figure S4). This means the contribution of radical species on the π-skeletons. Actually, in contrast to ESR silence for **5a−d**, a broad signal at $g = 2.0033$ was observed in the chloroform solutions of **5e** and **5f** (Figure S5). Although **5e** and **5f** are stable in solid, they are moderately sensitive to air in solution. Considering these results as well as Chichibabin's hydrocarbon **7** with an unusually large amount of biradical character,[13] we have speculated that a biradical species **8** exists in the equilibrium mixture. The fractions of **8e** and **8f** are estimated on the basis of the ESR intensities to be 2.8% and 29%, respectively. The increasing fraction of **8f** is caused by stabilization due to a gain of large aromaticity from the increasing thienoquinoid rings.[14]



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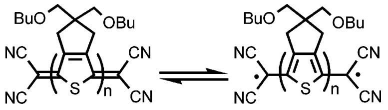

5e,f **8e,f**

In conclusion, we have succeeded in the development of a series of extensive quinoidal oligothiophenes **5a−f** with high solubilities in common solvents. They are highly amphoteric redox systems, which show strong electronic absorptions in the visible to near-infrared region. The higher homologues **5e**,**f** exist as equilibrium mixtures with the biradical species **8e**,**f**.

Acknowledgment. The authors sincerely thank Dr. Kenji Komaguchi for ESR measurement. This research was supported by a Grant-in-Aid for Scientific Research, Priority Areas of Molecular Conductors, No. 15073218, from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Experimental procedures and characterization data of **5a−f** and **6a−f**, ^{13}C NMR spectra of **5e**,**f**, absorption data of **5a−f** in different solvents, absorption spectrum of **5f** at variable temperatures and in different solvents, cyclic voltammograms of **5a−f**, and ESR spectra of **5d−f**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Gronowitz, S.; Uppström, B. *Acta Chem. Scand. B* **1974**, *28*, 981−985.
(2) (a) Yui, K.; Aso, Y.; Otsubo, T.; Ogura, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1816−1817. (b) Yui, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1539−1546.
(3) (a) Yui, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Chem. Lett.* **1988**, 1179−1182. (b) Yui, K.; Ishida, H.; Aso, Y.; Otsubo, T.; Ogura, F.; Kawamoto, A.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1547−1555. (c) Ishida, H.; Yui, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2828−2835. (d) Fujii, M.; Aso, Y.; Otsubo, T.; Ogura, F. *Synth. Met.* **1993**, *56*, 2136−2139. (e) Yoshida, S.; Fujii, M.; Aso, Y.; Otsubo, T.; Ogura, F. *J. Org. Chem.* **1994**, *59*, 3077−3081.
(4) Higuchi, H.; Nakayama, T.; Koyama, H.; Ojima, J.; Wada, T.; Sasabe, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2363−2377.
(5) (a) Pappenfus, T. M.; Chesterfield, R. J.; Frisbie, C. D.; Mann, K. R.; Casado, J.; Raff, J. D.; Miller, L. L. *J. Am. Chem. Soc.* **2002**, *124*, 4184−4185. (b) Pappenfus, T. M.; Raff, J. D.; Hukkanen, E. J.; Burney, J. R.; Casado, J.; Drew, S. M.; Miller, L. L.; Mann, K. R. *J. Org. Chem.* **2002**, *67*, 6015−6024. (c) Chesterfield, R. J.; Newman, C. R.; Pappenfus, T. M.; Ewbank, P. C.; Haukaas, M. H.; Mann, K. R.; Miller, L. L.; Frisbie, C. D. *Adv. Mater.* **2003**, *15*, 1278−1282.
(6) Izumi, T.: Kobashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2003**, *125*, 5286−5287.
(7) Uno, M.; Seto, K.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 932−933.
(8) Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79−82.
(9) Inoue, S.; Aso, Y.; Otsubo, T. *Chem. Commun.* **1997**, 1105−1106.
(10) (a) Fabian, J.; Zahradník, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 677−694. (b) Fabian, J.; Nakazumi, H.; Matsuoka, M. *Chem. Rev.* **1992**, *92*, 1197−1226.
(11) Takahashi and Suzuki reported that thienoquinoid-inserted diphenoquinones showed amphoteric behaviors, but the absorption bands are below 900 nm. Takahashi, K.; Suzuki, T. *J. Am. Chem. Soc.* **1989**, *111*, 5483−5485.
(12) Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442−2443.
(13) Montgomery, L. K.; Huffman, J. C.; Jurczak, E. A.; Grendze, M. P. *J. Am. Chem. Soc.* **1986**, *108*, 6004−6011 and references therein.
(14) (a) Rebmann, A.; Zhou, J.; Schuler, P.; Rieker, A.; Stegmann, H. B. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1615−1617. (b) Hoogmartens, I.; Adriaensens, P.; Vanderzande, D.; Gelan, J.; Quattrocchi, C.; Lazzaroni, R.; Brédas, J. L. *Macromolecules* **1992**, *25*, 7347−7356.

JA051840M