ORGANIC
LETTERS

2005
Vol. 7, No. 20
4313−4316

Synthesis and Spectral Properties of a Highly Soluble Push–Pull Type of Quinoidal Thiophenes

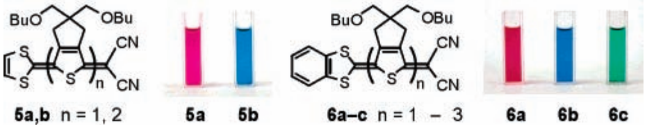
Toshiaki Takahashi,[†] Kazuo Takimiya,[†] Tetsuo Otsubo,*[,†] and Yoshio Aso[‡]

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, CREST, Japan Science and Technology Corporation (JST), Mihoga-oka, Ibaraki, Osaka 567-0047, Japan

otsubo@hiroshima-u.ac.jp

Received June 3, 2005

ABSTRACT



A series of push–pull quinoidal thiophenes 5a,b and 6a–c substituted with an electron-donating 1,3-dithiol-2-ylidene unit and an electron-withdrawing dicyanomethylene unit at the terminals is developed. They are highly soluble in common solvents and deeply colored with extension of the thienoquinoid skeleton.

The quinoidal compounds **1** and **2** initially developed by Gompper and co-workers are push−pull chromophores incorporated with a strong electron-donating group, 1,3-dithiol-2-ylidene, at one terminal and with a strong electron-withdrawing group, dicyanomethylene, at the other terminal, accordingly demonstrating a strong intramolecular charge-transfer transition in the visible region (Figure 1).[1] The optical properties of the chromophores are markedly influenced by the quinoid spacer.[2] Actually, we previously found that the biphenoquinoid system **3** shifted its CT absorption to the near-infrared region,[3] and the thienoquinoid system **4** showed a marked nonlinear optical property.[4] Thus, these types of compounds have a great application potential as optoelectronics materials. However, they become poorly soluble in common solvents with quinoid extension because the enhanced polar character strengthens intermolecular interactions. This is a serious drawback to their uses in wide applications. To circumvent the solubility problem, we have undertaken effective insulation of the thienoquinoid skeleton by fusion of a bis(butoxymethyl)cyclopentene ring into each thiophene unit.[5] Here, we would like to report the preparation and properties of compounds **5a**,**b** and **6a**−**c**, which behave as highly soluble push−pull thienoquinoid systems.

Compounds **5a**,**b** and **6a**,**b** were prepared starting with the bis(butoxymethyl)cyclopentene-fused thiophene **7a** or bithio-

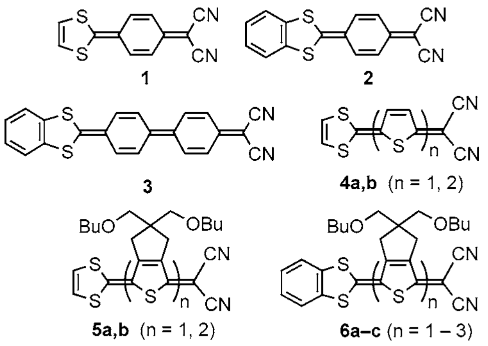


Figure 1.

[†] Hiroshima University.

[‡] Osaka University.

(1) Gompper, R.; Wagner, H.-U. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1437−1455.

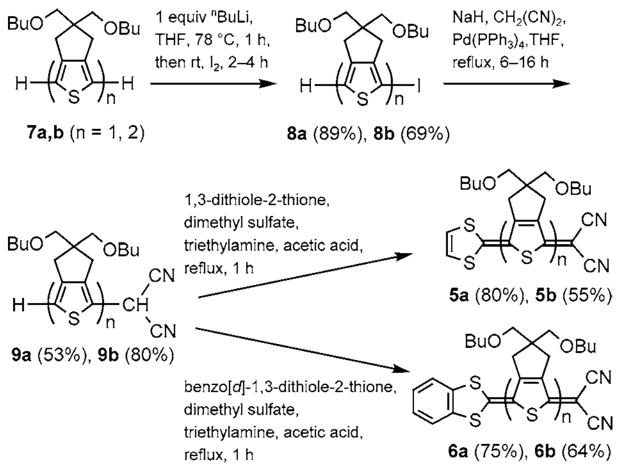
(2) Milián, B.; Ortí, E.; Hernández, V.; Navarrete, J. T. L.; Otsubo, T. *J. Phys. Chem. B* **2003**, *107*, 12175−12183.

(3) Inoue, S.; Aso, Y.; Otsubo, T. *Chem. Commun.* **1997**, 1105−1106.

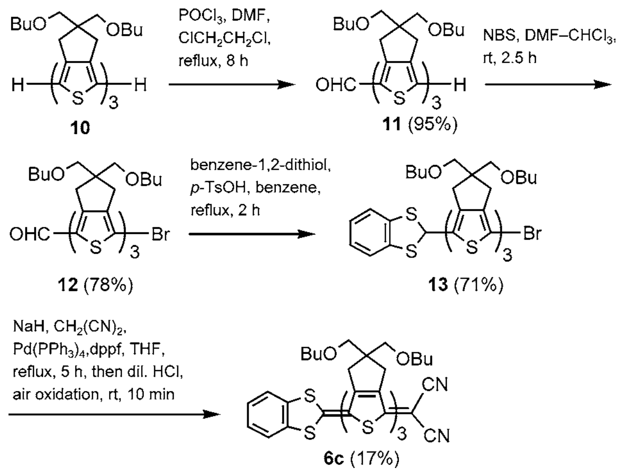
(4) Inoue, S.; Mikami, S.; Aso, Y.; Otsubo, T.; Wada, T.; Sasabe, H. *Synth. Met.* **1997**, *84*, 395−396.

10.1021/ol0513037 CCC: $30.25

Scheme 1. Synthesis of **5a**,**b** and **6a**,**b**



Scheme 2. Synthesis of **6c**



phene **7b**[5] according to the synthetic route shown in Scheme 1. Thus, treatment of **7a**,**b** with butyllithium in THF at −78 °C, followed by quenching with iodine at room temperature, gave the corresponding iodo derivatives **8a**,**b**, which were then subjected to a Pd(0)-promoted substitution reaction with sodium dicyanomethanide in refluxing THF according to the Takahashi method[6] to afford the dicyanomethyl derivatives **9a**,**b**. Finally, the coupling reaction between **9a**,**b** and 2-methylthio-1,3-dithiolium methyl sulfate in the presence of triethylamine in refluxing acetic acid according to the Gompper method[1] gave **5a**,**b**. Similar coupling of **9a**,**b** with 2-methylthiobenzo[*d*]-1,3-dithiolium methyl sulfate successfully gave the benzo-fused derivatives **6a**,**b**. All reactions proceeded in good to high yields.

We also attempted the same approach starting with the bis(butoxymethyl)cyclopentene-fused terthiophene **10**[5] for the synthesis of the terthienoquinoid homologues, but the final coupling was unsuccessful. We then exploited an alternative synthetic route to **6c**, as shown in Scheme 2. Thus, **10** was formylated by the Vilsmeier reaction in refluxing 1,2-dichloroethane, and the resulting **11** was then brominated with NBS at another terminal position to the derivative **12**. After the formyl group was converted into the thioacetal group by treatment with benzene-1,2-dithiol, the bromo group of **13** was converted into the dicyanomethyl group by the Takahashi method. During the workup with diluted hydrochloric acid, spontaneous air-oxidation occurred to give the desired **6c**.

All the compounds **5a**,**b** and **6a**−**c** were fully characterized by NMR, MS, IR, and elemental analyses. They are highly soluble in common solvents. The solubilities (>10^{-2} mol/L) of **5a**,**b** and **6a**−**c** in chloroform are much improved as compared to those of **4a** (2.3×10^{-3} mol/L) and **4b** (<10^{-5} mol/L). The molecular structure of **5b** was determined by an X-ray crystallographic analysis, as shown in Figure 2 (left). The π-conjugated skeleton of the molecule is completely flat, and the bithienoquinoid skeleton takes a *trans* conformation to avoid intramolecular sterical hindrance of the two fused rings. In the crystal packing, the molecules stack in a tangle of butoxymethyl groups, as shown in Figure 2 (right). However, the face-to-face distance of the π-backbone is ca. 3.7 Å far beyond normal interactions (3.4 Å) of conjugated π-systems. In addition, the shortest sulfur−sulfur distance is 3.69 Å, a little longer than van der Waals distance (3.6 Å), indicating little intermolecular interactions due to the incorporated skeletal sulfurs. Evidently, the pendant butoxymethyl groups block the intermolecular interactions of the π-backbone, being responsible for high solubility of the present push−pull system.

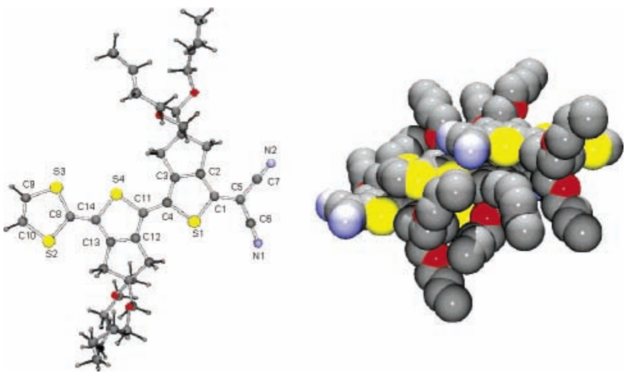


Figure 2. Molecular structure of **5b**; left top view, selected bond lengths: C5−C1, 1.403(10); C1−C2, 1.414(10); C2−C3, 1.381(10); C3−C4, 1.402(10); C4−C11, 1.392(9); C11−C12, 1.41(1); C12−C13, 1.357(10); C13−C14, 1.414(10); C14−C8, 1.380(9); C9−C10, 1.28(1) Å; right, stacking mode for three molecules of **5b** represented with the CPK model without hydrogen atoms.

Owing to the extensively π-conjugated structures, they are deeply colored in both solid and solution phases. The solution colors consecutively vary from red for **5a** and **6a**, blue for

---

(5) Izumi, T.; Kobashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2003**, *125*, 5286−5287.

(6) (a) Uno, M.; Seto, K.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 932−933. (b) Uno, M.; Seto, K.; Masuda, M.; Ueda, W.; Takahashi, S. *Tetrahedron Lett.* **1985**, *26*, 1553−1556.

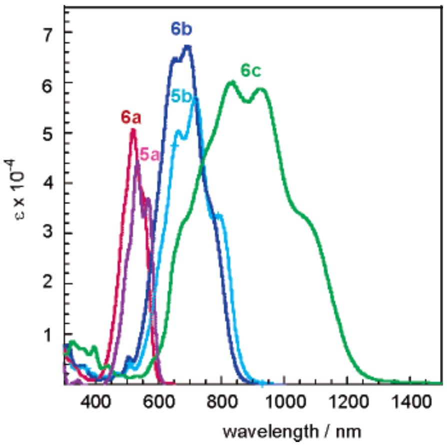


Figure 3. Electronic absorption spectra of **5a**,**b** and **6a**−**c** in THF.

Table 1. Electronic Absorption Data,[a] Redox Potentials,[b] and Nitrile Vibrational Frequencies of **5a**,**b** and **6a**−**c**[c]

	λ_{max}/nm	E_{pc}/V	$E_{1/2}^{ox}$/V	ν_{CN}/cm^{-1}
5a	532 (4.64), 567 (4.57)	−1.12	+0.91	2203
5b	663 (4.70), 718 (4.76), 791 (4.53)	−0.82	+0.45, +1.19	2195
6a	520 (4.71), 555 sh	−1.04	+1.05	2207
6b	646 sh, 691 (4.83), 780 sh	−0.77, −1.35	+0.55, +1.26	2197
6c	837 (4.78), 927 (4.77), 1070 sh	−0.57, −1.15	+0.24, +0.87	2178

[a] Measured in THF. Molar extinction coefficients are given in logarithmic unit in parentheses. [b] Voltammetric conditions: RE, Ag/AgCl; WE, Pt; solvent, benzonitrile; SE, $^{n}Bu_4NPF_6$; scan rate, 100 mV/s. [c] Measured on KBr disk.

5b and **6b**, to green for **6c**, depending on chain extension. Figure 3 demonstrates the electronic absorption spectra of **5a**,**b** and **6a**−**c** measured in THF, which are characterized by strong charge-transfer absorption bands in the visible region, responsible for deep coloration. Table 1 summarizes the absorption data. Consistent with the color changes, the absorption bands are steadily shifted to longer wavelength and much enhanced with the thienoquinoidal extension. A comparison between the absorption bands of **4a** (λ_{max} 549 and 588 nm) and **5a** (λ_{max} 532 and 567 nm) indicates that the fused cyclopentene ring of **5a** causes a blue shift of the charge-transfer band. The electronic spectra of the benzo derivatives **6a** and **6b** are essentially similar to the respective ones of **5a** and **5b** but for small blue shifts and hyperchromic shifts. In particular, it is worth noting that the absorption band of **6c** is remarkably red-shifted to the near-infrared region, and its absorption edge extends to nearly 1300 nm. It thus affords another example for rare near-infrared dyes with closed-shell electronic structures.[3,7,8]

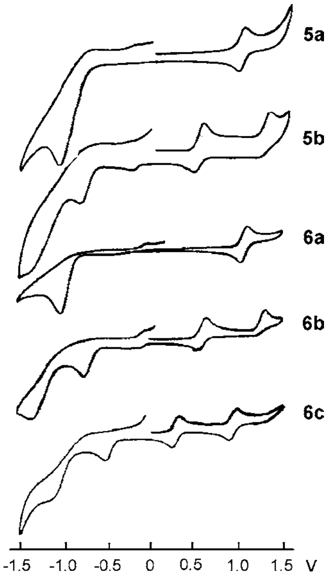


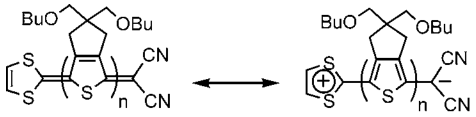
Figure 4. Cyclic voltammograms of **5a**,**b** and **6a**−**c** in benzonitrile.

It was actually confirmed by cyclic voltammetry that the color-determining absorption bands of **5a**,**b** and **6a**−**c** are identified as intramolecular charge-transfer transitions because their transition energies are roughly equal to the HOMO−LUMO gaps estimated from the differences between the first oxidation and first reduction waves (see Figure 4 for their cyclic voltammograms and Table 1 for their redox potential data). In addition, it has turned out that their marked red shifts, that is, reductions of the HOMO−LUMO gaps, are ascribable to increasing bipolar structures. The cyclic voltammograms of **5a**,**b** and **6a**−**c** demonstrate amphoteric redox waves in the scan sweeping region between +1.5 and −1.5 V vs Ag/AgCl, and the amphotericity becomes eminent with increasing thienoquinoid conjugation. Compound **5a** shows a reversible oxidation wave with $E_{1/2}$ = +0.91 V corresponding to one-electron oxidation of the 1,3-dithiol-2-ylidene unit and an irreversible reduction wave with E_{pc} = −1.12 V corresponding to one-electron reduction of the dicyanomethylene unit. On the other hand, **5b** shows a negative shift of the oxidation wave to $E_{1/2}$ = +0.45 V and a positive shift of the reduction wave to E_{pc} = −0.82 V. In addition, the second quasi-reversible oxidation wave is observed at +1.19 V. The voltammograms of **5a** and **5b** are essentially similar to those of **6a** and **6b**, respectively, although both oxidation and reduction waves tend to be a little shifted to higher potentials. The first and second oxidation waves of **6c** appear at further lower potentials +0.24 and +0.87 V, respectively, and the second oxidation wave becomes reversible. The reduction wave also shows a further positive shift to E_{pc} = −0.57 V, and the second irreversible reduction wave appears at E_{pc} = −1.15 V. Evidently, the extension of the central thienoquinoid con-

---

(7) Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79−82.

(8) (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.



5

14

Figure 5.

jugation induces high amphotericity. Presumably, it is because both oxidation and reduction states are stabilized by a gain of large aromaticity from the thienoquinoid rings.

One may suppose that an increase in the thienoquinoid rings accelerates the increasing contribution of the zwitterionic form, that is, **14** for **5**, to the resonance structure in the ground state (Figure 5). This was actually corroborated by examination of the nitrile vibrational frequencies, which are little by little shifted to lower wavenumbers with the thienoquinoid extension (see Table 1). Evidently, extension of the quinoidal skeleton strengthens their push–pull characters.[2]

The polar structures of these push–pull compounds can be also supported by the solvent effects of the charge-transfer bands. As seen from the peak positions measured in different solvents in Table 2, the absorption bands of all compounds are red-shifted with solvent polarities. In any case, the solvatochromism has a good correlation with the π^* scale of solvent polarity defined by Taft et al. (see Figure S1).[9] This means that these compounds still favor the quinoid form rather than the zwitterionic form in the ground state.

Table 2. Solvent Effects of the Absorption Bands (nm) of **5a**,**b** and **6a**–**c**[a]

	hexane	toluene	THF	$CHCl_3$	C_6H_5Cl	PhCN
5a	505	527	532	530	533	540
5b	659	698	718	714	719	730
6a	497	515	520	522	524	530
6b	646	679	691	698	700	715
6c	838	887	927	932	940	950

[a] Since the absorption bands are structured, only the most intense peaks are indicated. The π^* values of solvents: hexane, −0.08; toluene, 0.54; THF, 0.58; chloroform, 0.58; chlorobenzene, 0.71; benzonitrile, 0.90.

In conclusion, we have succeeded in the development of novel push–pull type of thienoquinoid compounds **5a**,**b** and **6a**–**c**, which assume deep colors and show amphoteric redox waves, depending on thienoquinoid extension. In addition, they have beneficial properties of good processability and thin film formation. Thus, these chromophores are suitable candidates for advanced materials applicable to optoelectronic fields, such as near-infrared dyes and nonlinear optics.

Acknowledgment. This research was partly supported by Grants-in-Aid of Scientific Research (Category A, No. 17205006 and Priority Areas of Molecular Conductors, No. 15073218) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Synthetic experimental details and characterization data for compounds **5a**,**b** and **6a**–**c**, X-ray crystal data and crystallographic information file (CIF) of **5b**, solvent dependency of the absorption bands of **5a**,**b** and **6a**–**c** with π^* scales. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0513037

---

(9) (a) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027–6038. (b) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877–2887. (c) Catalán, J. *J. Org. Chem.* **1997**, *62*, 8231–8234.