New Narrow-Bandgap Polymers Composed of [1,2,5]Thiadiazolo[3,4-*g*]quinoxaline and Aromatic Heterocycles

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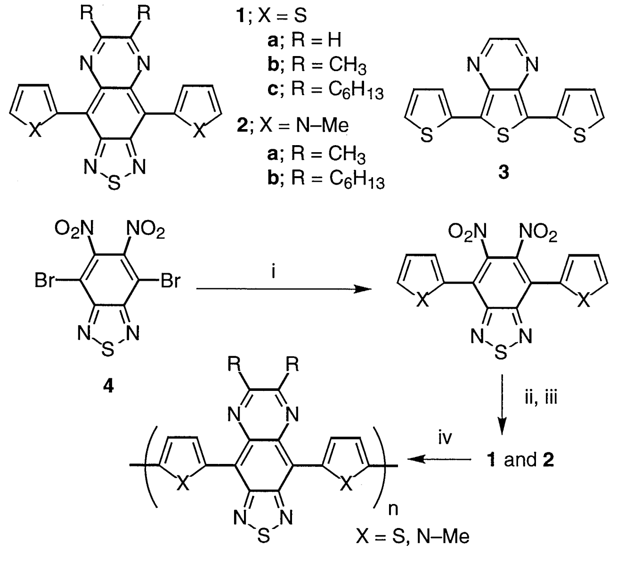
Polymers composed of [1,2,5]thiadiazolo[3,4-*g*]quinoxaline and either thiophene or *N*-methylpyrrole were synthesized by electrochemical polymerization and showed bandgaps of about 0.7 eV.

In the field of conjugated polymers, band structure engineering has grown important for the development of novel molecular devices. In particular, the design and preparation of narrow bandgap polymers are one of the subjects of intense interest,[1–11] because such polymers are expected to exhibit good intrinsic conductivities as well as characteristic nonlinear optical properties. So far two types of periodic copolymers have been proposed as promising candidates for narrow bandgap systems; one has a [*o*-quinoid unit-aromatic unit]$_n$ structure[3] and the other has a [donor unit-acceptor unit]$_n$ structure.[5,6] On the basis of these guidelines, we have now succeeded in the synthesis of monomers (**1**) consisting of a new class of *o*-quinoid-acceptor unit, [1,2,5]thiadiazolo[3,4-*g*]quinoxaline (**TDQ**), and various aromatic-donor units. We have already shown that copolymers composed of thieno[3,4-*b*]pyrazine (**TP**) and thiophene rings possess a bandgap of ~1 eV.[8] The MO calculations suggest that the **TDQ** unit has an appreciably small HOMO-LUMO separation[4] compared to the **TP** unit,[12] so that the polymers of **1** might exhibit a bandgap value below 1 eV. In addition, a notable advantage of **TDQ** over hitherto-known *o*-quinoid thiophenes is that this heterocycle has no peripheral hydrogen atom which would induce a nonplanar geometry of the polymer backbone due to the steric repulsion between adjacent units.[9]



Scheme 1. *Reagents and conditions*: i, $Bu_3Sn(C_4H_3X)$: X = S or N–Me, $PdCl_2(PPh_3)_2$, THF, reflux ; ii, Fe, AcOH, 30 °C; iii, 2,3-Dihydroxy-1,4-dioxane, $MeNO_2$, or $(RCO)_2$, AcOH, room temp. ; iv, electrochemical polymerization

Monomers **1** were synthesized from 4,7-dibromo-5,6-dinitro-2,1,3-benzothiadiazole[13] (**4**) as shown in Scheme 1. A few alkyl derivatives were also prepared in order to improve the processability of the corresponding polymers. The monomers with longer alkyl chains showed better solubility in common organic solvents such as THF and $CHCl_3$. The physical data of **1** and the related compounds are summarized in Table 1. The electronic spectra of **1** display 0.25~0.29 eV red shifts of the longest wavelength absorption band compared with that of **3**. The oxidation peak potentials of **1** are comparable to that of **3**, while the reduction ones are 0.26~0.33 V higher than that of **3** due to the higher electron-accepting ability of **TDQ** with respect to **TP**. These results confirm that monomers **1** have smaller HOMO-LUMO gaps and higher amphoteric redox properties (smaller differences between the redox potentials, E_{pa}–E_{pc}) compared to **3** as expected theoretically. The X-ray structure analysis of **1c** revealed that this compound has an almost

Table 1. The longest absorption maxima and redox potentials of monomers

Monomer	λmax/nm(eV)[a]	E_{pa}/V[b]	E_{pc}/V[b]	E_{pa}–E_{pc}/V
1a	604(2.05)	0.98	–0.72	1.80
1b	591(2.10)	1.04	–0.85	1.89
1c	593(2.09)	1.05	–0.81	1.86
2a	572(2.17)	0.86	–1.03	1.89
2b	571(2.17)	0.88	–0.99	1.87
3[c]	529(2.34)	0.97	–1.05	2.03

[a]In $CHCl_3$. [b]0.1 mol dm^{-3} Bu_4NClO_4 in PhCN, Pt electrode, scan rate 100 mVs^{-1}, V *vs.* SCE. [c]Reference 7.

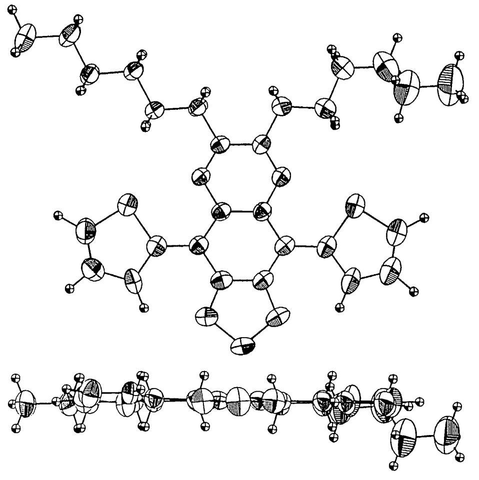


Figure 1. Molecular structure of **1c**.

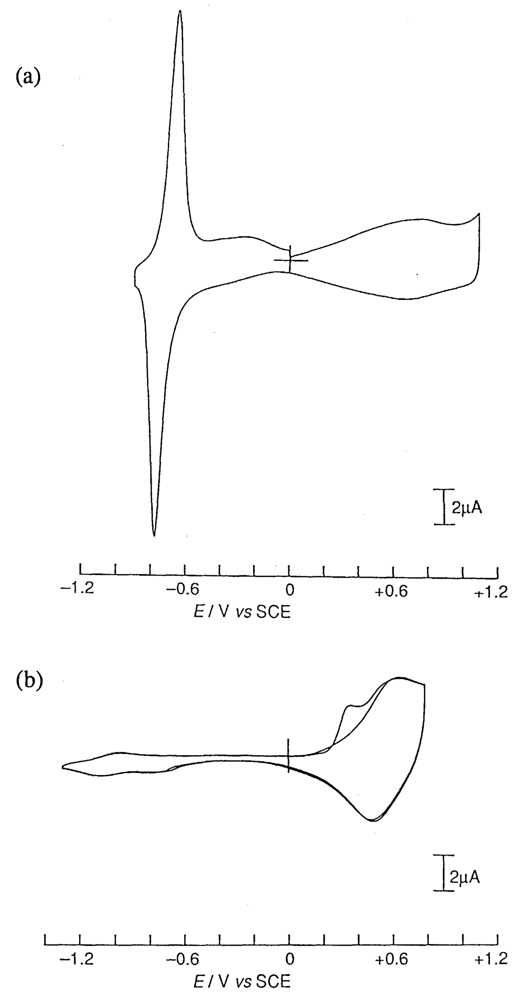


Figure 2. Cyclic voltammograms of (a) poly(**1a**) and (b) poly(**2a**) on Pt in 0.1 mol dm^{-3} Bu_4NClO_4 in PhCN, scan rate 10 mVs^{-1}.

coplanar conformation similarly to **3**[7] (Figure 1).[14] The dihedral angles between **TDQ** and thiophene rings are 8.6 and 1.7°.

Polymers of **1** were prepared on a Pt disk electrode and an indium tin oxide (ITO) glass electrode by anodic oxidation of monomers and were obtained as green-black films.[15] These polymers were stable to air, and insoluble in organic solvents despite the introduction of long alkyl chains. All the polymers of **1** exhibited both p- and n-doping processes. The former showed a broad wave, and the latter displayed a sharp wave (Figure 2a). The difference between p- and n-doping onset potentials of poly(**1a**), the electrochemical bandgap, was about 0.6 eV. The absorption spectra of neutral poly(**1**) on ITO glasses showed optical bandgaps of about 0.7 eV. These findings indicate that use of **TDQ** as an accepting unit is effective in reducing the bandgaps.

Furthermore, we have synthesized the *N*-methylpyrrole derivatives (**2**). *N*-Methylpyrrole has a higher HOMO level (−8.87 eV) compared with thiophene (−9.54 eV), and therefore the copolymerization of **TDQ** and pyrrole units can be expected to induce more effective intrachain CT interactions, leading to lower energy gaps compared with those of the thiophene derivatives, *i.e.* E_g< 0.7 eV. However, the spectral and electrochemical data (Table 1) indicate that monomers **2** have slightly larger HOMO-LUMO separations compared to **1**. In consistence with this, the absorption spectra of neutral poly(**2**) indicated bandgaps of about 0.7 eV, which is comparable to those of poly(**1**). Moreover, cyclic voltammograms of polymers of **2** hardly exhibited n-doping process (Figure 2b). These results can be attributed to the nonplanar conformation due to the steric repulsion between **TDQ** and the *N*-methyl group.[16] In contrast, the monomers consisting of free 1*H*-pyrrole units are predicted to have a coplanar structure by the MO calculations. Consequently, the key point of reducing bandgap values based on the effective intrachain CT interactions between **TDQ** and pyrrole units is the introduction of free 1*H*-pyrrole units into polymer backbone instead of *N*-methylpyrroles. Work along this line is now in progress.

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References and Notes

1 F. Wudl, M. Kobayashi, and A. J. Heeger, *J. Org. Chem.*, **49**, 3382 (1984); M. Kobayashi, N. Colaneri, M. Boysel, F. Wudl, and A. J. Heeger, *J. Chem. Phys.*, **82**, 5717 (1985).

2 J. L. Brédas, *Synth. Met.*, **17**, 115 (1987).

3 J. Kürti, P. R. Surján, and M. Kertesz, *J. Am. Chem. Soc.*, **113**, 9865 (1991).

4 J. P. Ferraris and T. L. Lambert, *J. Chem. Soc., Chem. Commun.*, **1991**, 1268.

5 E. E. Havinga, W. ten Hoeve, and W. Wynberg, *Synth. Met.*, **55–57**, 299 (1993).

6 Z. Zhou, T. Maruyama, T. Kanbara, T. Ikeda, K. Ichimura, T. Yamamoto and K. Tokuda, *J. Chem. Soc., Chem. Commun.*, **1991**, 1210; T. Yamamoto, M. Shimura, K. Osakada and K. Kubota, *Chem. Lett.*, **1992**, 1003; T. Kanbara, Y. Miyazaki and T. Yamamoto, *J. Polym. Sci. Part A: Polym. Chem.*, **33**, 999 (1995).

7 M. V. Lakshmikantham, D. Lorcy, C. Scordilis-Kelly, X.-L. Wu, J. P. Parakka, R. M. Metzger, and M. P. Cava., *Adv. Mater.*, **5**, 723 (1993).

8 C. Kitamura, S. Tanaka and Y. Yamashita, *J. Chem. Soc., Chem. Commun.*, **1994**, 1585.

9 S. Tanaka and Y. Yamashita, *Synth. Met.*, **69**, 599 (1995).

10 K. Karikomi, C. Kitamura, S. Tanaka and Y. Yamashita, *J. Am. Chem. Soc.*, **117**, 6791 (1995).

11 G. Brocks, *J. Chem. Phys.*, **102**, 2522 (1995).

12 The MNDO-PM3 calculations suggest that **TDQ** has a significantly lower-lying LUMO level (−2.39 eV) and a slightly higher-lying HOMO level (−9.27 eV) compared with those of **TP** (−1.41 and −9.45 eV, respectively).

13 T. Uno, K. Takagi and M. Tomoeda, *Chem. Pharm. Bull.*, **28**, 1909 (1980).

14 Crystal data for **1c**: $C_{28}H_{32}N_4S_3$, M = 520.77, triclinic, space group $P\bar{1}$, Z = 2, a = 11.717(4), b = 16.005(4), c = 7.552(3) Å, α = 92.04(2), β = 106.46(2), γ = 97.63(2)°, V = 1342.2(8) Å^3, D_c = 1.29 g cm^{-3}, Cu Kα radiation, 3357 reflection used, R = 0.073, R_w = 0.076. Because of some 180°-rotation disorders, the geometrical parameters of the thiophene rings are less reliable. Calculations of the structural analysis were carried out in the Computer Center of Institute for Molecular Science.

15 The polymers were prepared on an electrode by repeated potential scans in dry and deoxygenated PhCN for **1** or MeCN for **2** under argon (**1** or **2**: 10^{-3} mol dm^{-1}, Bu_4NClO_4: 0.1 mol dm^{-1}, scan rate: 100 mVs^{-1}, potential limits: −0.1 to +1.1 V for **1** and −0.1 to +0.8 V for **2**). Dedoping was conducted electrochemically.

16 Conformation analysis by the PM3-calculations suggested the dihedral angles of >60°.