Preparation and Properties of Poly-4-(1,3-dithiol-2-ylidene)-4*H*-cyclopenta[2,1-*b*; 3,4-*b*′]dithiophene and its Derivatives

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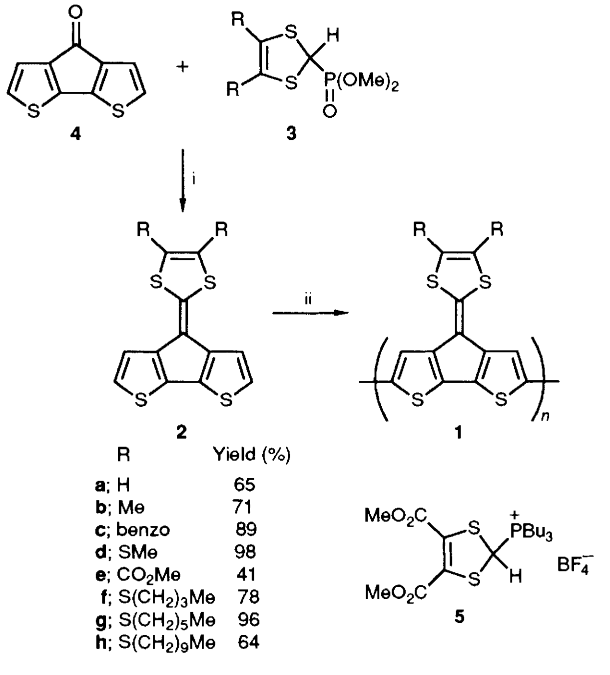
The title polymers, prepared by an electrochemical oxidation of the corresponding 1,3-dithiole derivatives with low oxidation potentials, exhibit high conductivities by doping.

Recently much attention has been focused on the development of new conducting polymers.[1–3] The following two points have been proposed to improve conducting properties: (*i*) the introduction of interchain interactions, which are useful for the enhancement of the charge transport between adjacent chains as well as for the control of structural order,[2] (*ii*) the reduction of bandgap to assist in intramolecular electron movement.[3] In addition stabilization of the doping state is important for the preservation of the conductivity. Therefore, poly-4-(1,3-dithiol-2-ylidene)-4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophenes **1** are interesting for the following reasons. They may have intermolecular interactions between the chalcogen atoms as observed in tetrathiafulvalene (TTF) series[4] leading to interchain interactions. The extended π-conjugation and polarization by the introduction of the 1,3-dithiole rings may lead to smaller bandgaps. The p-doping, conducting states may be stabilized by aromatic 1,3-dithiolium ions formed by the oxidation. Moreover they have the advantage that substituents are easily introduced to modify the polymers. We report here their preparation and properties.

1,3-Dithiole compounds **2a–d** were prepard in 65–98% yields by a Wittig–Horner reaction of the corresponding phosphonate esters **3** with ketone **4**[5] (Scheme 1). Dimethoxycarbonyl derivative **2e** was prepared by a Wittig reaction of phosphonium compound **5** with **4** in 41% yield. Compounds **2** are air-stable orange solids whose absorption maxima are shown in Table 1. The fact that absorption maxima are observed at longer wavelengths in derivatives containing electron donating groups suggests that some polarization takes place in **2**. The X-ray structural analysis of the benzo derivative **2c** revealed that the molecule is planar.† Cyclic voltammograms of **2** showed irreversible oxidation waves; their peak oxidation potentials (E_{pa}) are summarized in Table 1. The values are significantly lower than those for bithiophene [1.32 V *vs.* standard calomel electrode (SCE)][6] and dithieno[3,2-*b*; 2′,3′-*d*]thiophene (DTT) (1.31 V *vs.* SCE).[7] This fact is attributed to the electon donating property of the 1,3-dithiole rings.

Polymers **1** were prepared by the electrolytic oxidation of the corresponding monomers **2**. The oxidation potentials of **1** summarized in Table 1 are relatively low compared with those of polythiophene (0.96 V *vs.* SCE)[6] and polyDTT (0.98 V *vs.* SCE).[7] Cyclic voltammograms of **1a** measured at various scan rates are shown in Fig. 1. The peak current is proportional to the scan rate in the potential range −0.7 to 1.0 V *vs.* SCE, indicating that the electrode reactions of the films are phenomenologically equivalent to that of a surface-attached redox species.[8] Similar properties were observed in polymers **1b–e**.

Conductivities of **1a**, **c** and **d** measured by a four-probe method were 4.1×10^{-1}, 4.4×10^{-1} and 1.4 S cm^{-1} in the doping state, respectively.‡ These values are slightly lower than that of polyisothianaphthene (50 S cm^{-1})[9] but higher than those of heterocycle-fused polythiophenes such as polyDDT (0.4 S cm^{-1})[10] and poly-5,6-dioxymethylenisothianaphthene (3×10^{-2} S cm^{-1}).[11] Furthermore doping states of **1** are stable and conductivities did not change after storage under air for a month. The stability may be attributed to the 1,3-dithiole ring.



R	Yield (%)
a; H	65
b; Me	71
c; benzo	89
d; SMe	98
e; CO_2Me	41
f; $S(CH_2)_3Me$	78
g; $S(CH_2)_5Me$	96
h; $S(CH_2)_9Me$	64

Scheme 1 *Reagents and conditions*: i, Bu^nLi–THF; ii, electrolytic polymerisation

Table 1 Oxidation potentials of monomers **2** and polymers **1** and absorption maxima **2**

Monomer	E_{pa}[a]	λ_{max}/nm[b]	Polymer	E_{pa}[a]
2a	0.83	411	**1a**	0.74
2b	0.75	419	**1b**	0.63
2c	0.78	400	**1c**	0.66
2d	0.82	411	**1d**	0.70
2e	0.92	389	**1e**	0.72
2f	0.94	412	**1f**	0.78
2g	0.96	412	**1g**	0.77
2h	0.82	412	**1h**	0.81
Thiophene	2.06	232	Polythiophene	0.96

[a] 0.1 mol dm^{-3} $Bu^n_4NClO_4$ in MeCN, Pt electrode, scan rate 100 mV s^{-1}, V *vs.* SCE. [b] In EtOH.

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† *Crystal data* for **2c**: $C_{16}H_8S_4$, M = 328.48, orthorhombic, space group *Pbca*, $Z = 8$, $a = 18.854(9)$, $b = 6.098(1)$, $c = 24.183(6)$ Å, $V = 2780(2)$ Å^3, D_c = 1.57 g cm^{-3}. The final R value is 8.31% for 1611 reflections with $|F_o| > 3\sigma|F_o|$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ For the measurement of conductivity films of **1a**, **c** and **d** were grown on an ITO electrode by using a potentiostatic technique at 0.70, 0.75 and 0.70 V *vs.* SCE, respectively, in a benzonitrile solution containing 0.1 mol dm^{-3} $Bu^n_4NClO_4$ and 0.01 mol dm^{-3} monomer under an argon atmosphere. The thickness of film was measured by scanning electron microscopy.

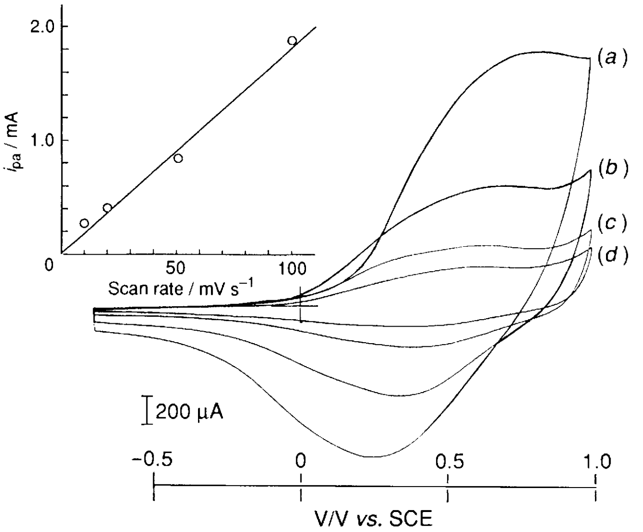

Fig. 1 Cyclic voltammogram of **1a** measured in a monomer-free MeCN–0.1 mol dm^{-3} Bu$^n_4$NClO$_4$ electrolyte at various scan rates under an argon atmosphere: (*a*) 100, (*b*) 50, (*c*) 20 and (*d*) 10 mV s^{-1}. Indium-tin oxide (ITO) electrode, platinum wire and SCE were used as the working, counter and reference electrodes, respectively. The insert shows the dependence of anodic peak current (i_{pa}) on scan rate.

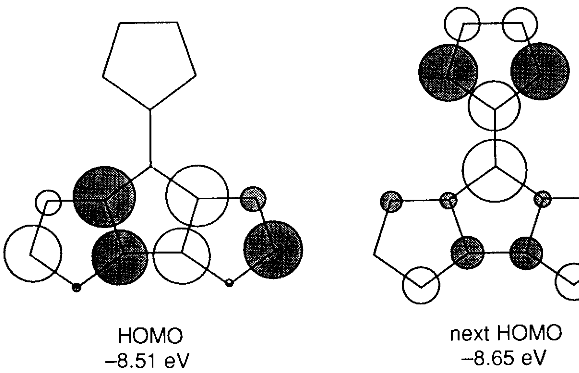

Fig. 2 HOMO and next HOMO energy levels of **2a**

MNDO calculations[12] of **2a** show that the HOMO and next HOMO are close in energy (−8.51 and −8.65 eV, respectively; see Fig. 2). Carbon atoms at the α-positions have large atomic orbital (AO) coefficients in the HOMO, suggesting that the polymerization selectively occurs at these positions. On the other hand, atoms of the 1,3-dithiole ring have large AO coefficients in the next HOMO, supporting the fact that compounds **2** have low oxidation potentials due to the easy oxidation of the rings.

It is important to introduce long alkyl chains in polymers to increase solubility as well as for structural control.[13] For this purpose compounds **2f–h** containing long alkyl chains were synthesized in 64–96% yields by using a similar method as described above. Electrochemical polymerizations gave the corresponding polymers **1f–h**. Studies on their properties are now in progress.

We thank Professor Noboru Oyama of Tokyo University of Agriculture and Technology for valuable discussions. This work was supported by a Grant-in Aid of Scientific Research No. 03804039 from the Ministry of Education, Science and Culture, Japan.

Received, 21st April 1992; Com. 2/02029G

References

1 A. O. Patil, A. J. Heegar and F. Wudl, *Chem. Rev.*, 1988, **88**, 183.
2 C. Taliani, G. Ruani, R. Zamboni, A. Bolongnesi, M. Catellani, S. Destri, W. Porzio and P. Ostoja, *Synth. Met.*, 1989, **28**, C507.
3 J. Kërti, P. R. Surjàn and M. Kertesz, *J. Am. Chem. Soc.*, 1991, **113**, 9865; J. P. Ferraris and T. L. Lambert, *J. Chem. Soc., Chem. Commun.*, 1991, 1268.
4 Y. Yamashita, S. Tanaka, K. Imaeda and H. Inokuchi, *Chem. Lett.*, 1991, 1213; M. R. Bryce, G. Cooke, A. S. Dhindsa, D. J. Ando and M. B. Hursthouse, *Tetrahedron Lett.*, 1992, **33**, 1783.
5 P. Jordens, G. Rawson and H. Wynberg, *J. Chem. Soc.* (*C*), 1970, 273.
6 R. J. Waltman, J. Bargon and A. F. Diaz, *J. Phys. Chem.*, 1983, **87**, 1459.
7 T. R. Jow, K. Y. Jen, R. L. Elsenbaumer, L. W. Shacklette, M. Angelopoulos and M. P. Cava, *Synth. Met.*, 1986, **14**, 53.
8 N. Oyama, T. Ohsaka and H. Miyamoto, *Synth. Met.*, 1989, **28**, C193.
9 M. Kobayashi, N. Colaneri, M. Boysel, F. Wudl and A. J. Heegar, *J. Chem. Phys.*, 1985, **82**, 5717.
10 R. Lazzaroini, C. Tailian, R. Zamboni, R. Danzeli, P. Ostoja, I. Lamel, W. Pprzio and J. L. Brëdas, *Synth. Met.*, 1989, **28**, C515.
11 Y. Ikenoue, F. Wudl and A. J. Heeger, *Synth. Met.*, 1991, **40**, 1.
12 MNDO calculations (MOPAC program; J. J. P. Stewart, *QCPE Bull.*, 1983, **3**, 43) were performed by using the MNDO optimized geometry. These calculations were carried out in the Computer Centre of Institute for Molecular Science.
13 R. D. McCullough and R. D. Lowe, *J. Chem. Soc., Chem. Commun.*, 1992, 70.