

# A new phthalocyanine derivative having peripheral 2-thienyl substituents

Tsuyoshi Muto, Tetsuji Temma, Mutsumi Kimura, Kenji Hanabusa and Hirofusa Shirai\*

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan. E-mail: hshirai@giptc.shinshu-u.ac.jp

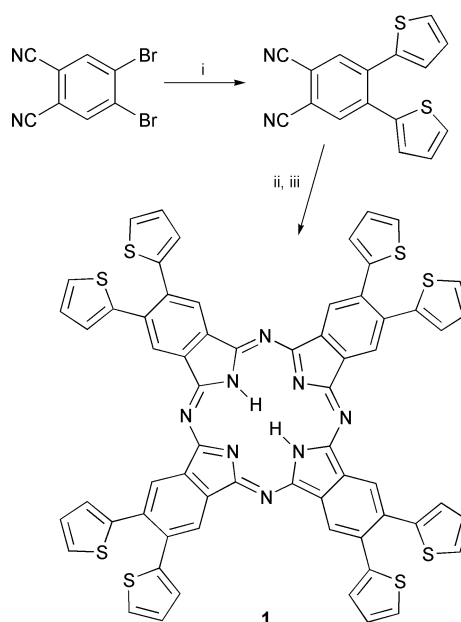
Received (in Cambridge, UK) 9th June 2000, Accepted 24th July 2000

A phthalocyanine derivative having eight 2-thienyl substituents at the  $\beta$ -position was synthesized and electrochemical oxidation of the phthalocyanine gave an insoluble polymer film on the electrode surface.

$\pi$ -Conjugated polymers such as polythiophenes or polyphenylenes have been the subject of intensive studies.<sup>1</sup> Due to the high stability of the polymers, they are readily characterized by chemical or physical methods, making them good candidates for electronic or photonic devices. Polythiophenes are the type most frequently investigated because they are easily obtained from chemical reactions<sup>2</sup> or electrochemical couplings of thiophene derivatives,<sup>3</sup> and the monomers or precursors are readily derived by conventional synthetic methods from thiophene.<sup>4</sup> Recently, several groups reported the design of novel conducting polymer architectures which alternatively contain functional moieties and  $\alpha\alpha'$ -coupled oligothiophene moieties.<sup>5</sup> The wide range of these studies contributed towards the application of the polymers as organic semiconductors, sensory materials or electrocatalysts.<sup>6</sup> Our current interest in this class of materials is motivated by the property of the attractive characteristics, endowed by functional molecules embedded in the polymer backbone, for the development of electronic devices. Phthalocyanines or phthalocyanine metal complexes are known to have a diversity of functions such as electrocatalysts or organic electronic devices.<sup>7</sup> Therefore, introduction of phthalocyanine moieties to the new polymer architectures imparts a variety of functions to the polymers. In this communication we demonstrate the synthesis, photo- and electrochemical properties of a new phthalocyanine (pc) derivative which has thiophene moieties as substituents, and the electrochemical construction of a pc-based polymer film deposited on the electrode surface.

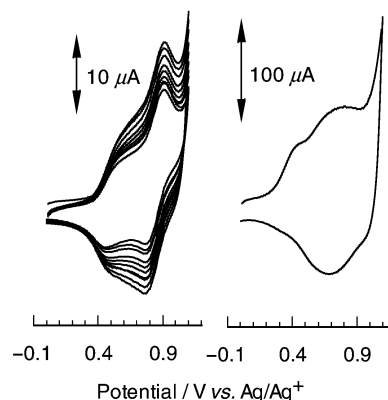
The synthetic route to **1** used 4,5-dibromophthalonitrile<sup>8</sup> as starting material which was converted into 4,5-di-2-thienylphthalonitrile with thiophene-2-boronic acid<sup>9</sup> in the presence of Pd(0)(PPh<sub>3</sub>)<sub>4</sub> under basic conditions (Scheme 1). Refluxing of 4,5-di-2-thienylphthalonitrile with NaOMe in MeOH gave 5,6-di-2-thienyl-2,3-dihydro-1,3-diiminoisoindole, and the reaction of this compound in *N,N*-dimethylaminoethanol at 140 °C gave **1** as a dark-green solid. Analytically pure **1** was obtained by column chromatography of the crude product on silica gel by eluting with CH<sub>2</sub>Cl<sub>2</sub>-*n*-hexane (2/1 v/v). This new pc derivative **1** was characterized by <sup>1</sup>H NMR and MALDI-TOF mass spectrometry.†

The pc derivative **1** was soluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, THF and DMF but not in hexane, toluene or acetonitrile. The shape of absorption and emission spectra of **1** in CHCl<sub>3</sub> were similar to that of tetrakis(*tert*-butyl)phthalocyanine (*t*Bupc) except for a broad absorption around 430 nm and a weak, structureless emission peak centered around 500 nm. The position of both absorption and emission bands of **1** were red-shifted about 20 nm from that of the corresponding *t*Bupc. These results obtained from the photophysical measurements are consistent with the presence of electronic interaction between the pc ring and 2-thienyl substituents in a molecule of **1** at their ground and excited states.

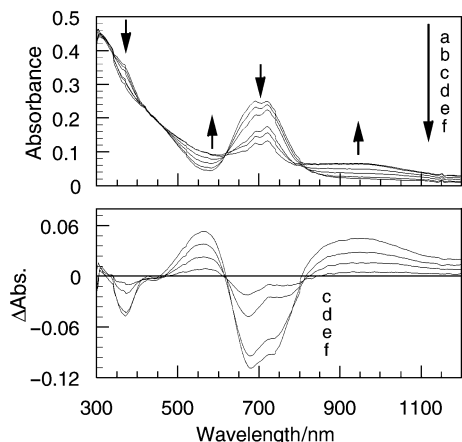


**Scheme 1** (i) Thiophene-2-boronic acid, Pd(0)(PPh)<sub>4</sub>, toluene, THF, EtOH, 2 M Na<sub>2</sub>CO<sub>3</sub> aq., reflux under N<sub>2</sub>, 18 h, 62%; (ii) NaOMe, MeOH, reflux under NH<sub>3</sub> gas, 5 h, 95%; (iii) *N,N*-dimethylaminoethanol, reflux under N<sub>2</sub>, 36 h, 32%.

The pc derivative **1** was oxidatively polymerized when the potential of the electrode was swept between 0.0 and +1.1 V vs. Ag/Ag<sup>+</sup> at a scan rate of 100 mV s<sup>-1</sup>. [Working electrode, indium/tin oxide coated glass (ITO) electrode; Counter electrode, Pt wire; Reference electrode, Ag/Ag<sup>+</sup>; Solvent, 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub>). An anodic polymerization trace of **1** is shown in Fig. 1. The first oxidative scan is characterized by monomer



**Fig. 1** Trace of oxidative scan of **1** ([**1**] =  $2 \times 10^{-4}$  M) in 0.1 M TBAPF<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub> with ITO glass electrode (left) and cyclic voltammogram of poly(**1**) film deposited on ITO glass electrode in 0.1 M TBAPF<sub>6</sub>-CH<sub>3</sub>CN (right). Conditions: 0.1 V s<sup>-1</sup>, Pt wire counter electrode; Ag/Ag<sup>+</sup> reference electrode.



**Fig. 2** *In situ* UV-Vis-NIR absorption spectra of poly(**1**) on ITO electrode upon applied potential (top): (a) 0.0 V vs. Ag/Ag<sup>+</sup>; (b) +0.3 V; (c) +0.5 V; (d) +0.6 V; (e) +0.7 V; (f) +0.8 V. Difference spectra obtained from the data of the *in situ* spectra (bottom). The neutral-point spectrum (V = 0.0 V) was used as the reference.

oxidation at +0.60 and +0.90 V followed by associated reduction at +0.45 and +0.75 V in the return process. The first oxidation wave observed in the oxidative trace of **1** is attributed to the oxidation of free-base pc<sup>10</sup> and the second could be attributed to the oxidation of 2-thienyl substituents at the  $\beta$ -position. In subsequent potential sweeps, an oxidation wave grows in around +0.70 V. Applied potential cycling results in further increased electroactivity of the electrode, indicative of insoluble polymer deposition on the electrode surface.<sup>5</sup> The cyclic voltammogram (CV) of the electrochemical deposited polymer (poly(**1**)) in monomer-free 0.1 M TBAPF<sub>6</sub>-CH<sub>3</sub>CN is shown in Fig. 1. The CV is characterized by the appearance of an oxidation wave at +0.4 V and a redox couple at +0.70 V. The observed difference between the redox potentials of monomer **1** and poly(**1**) is in agreement with the difference in  $\pi$ -conjugation length elongated in the polymerization and oxidation processes.

The *in situ* electronic absorption measurement of poly(**1**) film deposited on the ITO electrode recorded at various doping levels shows that the transition around 360 nm and pc Q-band absorption ( $\lambda_{\text{max}} = 634, 662, 692, 724$  nm) decreases continuously as doping proceeds while two new absorption bands appear around 560 and 950 nm (Fig. 2). In the absorption of poly(**1**) film at high doping levels, the new lower energy  $\pi$ - $\pi^*$  transition<sup>11</sup> around 950 nm was promoted and grew as shown in Fig. 2. The optoelectrochemical behavior observed in our system is assigned to formation of oxidized states of poly(**1**) and the effective conjugation paths include a pc ring system and  $\alpha\alpha'$ -bithienyl bridges have been formed. The position of the lower energy  $\pi$ - $\pi^*$  absorption maximum is close to that reported for cation radicals of oligothiophenes, but the shape of the band is broader than that of oligothiophene cation radicals.<sup>12</sup>

From these observations, we assume that poly(**1**) in the oxidized state has intermediary effective conjugation length of oxidized oligothiophenes and oxidized polythiophenes.

In conclusion, we have synthesized a new pc derivative **1** and constructed a  $\pi$ -conjugated polymer film by electrochemical oxidation of **1**. The  $\pi$ -conjugation length of the polymer was switched between pc-like and oligothiophene-like by application of the appropriate voltage. Since this switching is accompanied by a color change at the applied potential between 0 and +0.8 V vs. Ag/Ag<sup>+</sup>, the polymer has potential electrochromic material applications.<sup>11</sup>

This work was supported by a Grant-in-Aid for COE Research 'Advanced Fiber/Textile Science and Technology' (No. 10CE2003) and Scientific Research (No. 11450366) from the Ministry of Education, Science, Sports, Culture of Japan.

## Notes and references

† Selected data for **1**: (400 MHz, CDCl<sub>3</sub>, 298 K, TMS):  $\delta_{\text{H}} = 6.96$  (br, 8H), 7.04 (br, 8H), 7.36 (br, 8H), 8.12 (br, 8H); MALDI-TOF spectrum  $m/z$  calcd. for (C<sub>64</sub>H<sub>34</sub>N<sub>8</sub>S<sub>8</sub>) 1171.5, found 1172.6. UV/Vis (in CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 724 (5.018), 692 (5.033), 662 (4.782), 634 (4.585), 364 (4.865).

- (a) *Handbook of Conducting Polymers*, 2nd edn., ed. T. A. Skotheim, R. L. Elsenbaumer and J. R. Reynolds, Marcel Dekker, New York, 1998; (b) M. E. Lyons, in *Electroactive Polymer Electrochemistry*, ed. M. E. Lyons, Plenum, New York, 1994 vol. 1.
- R. D. McCullough, *Adv. Mater.*, 1998, **10**, 93.
- J. Roncali, *Chem. Rev.*, 1992, **92**, 711.
- P. Bäuerle, in *Electronic Materials: The Oligomer Approach*, ed. K. Müllen and G. Wegner, Wiley-VCH, Weinheim, 1998.
- (a) S. S. Zhu, P. J. Carroll and T. M. Swager, *J. Am. Chem. Soc.*, 1996, **118**, 8713; (b) R. P. Kingsborough and T. M. Swager, *Adv. Mater.*, 1998, **10**, 1100; (c) R. P. Kingsborough and T. M. Swager, *J. Am. Chem. Soc.*, 1999, **121**, 8825; (d) H. Segawa, F.-P. Wu, N. Nakayama, H. Maruyama, S. Sagisaka, N. Higuchi, M. Fujitsuka and T. Shimidzu, *Synth. Met.*, 1995, **71**, 2151; (e) J. L. Reddinger and J. R. Reynolds, *Macromolecules*, 1997, **20**, 673; (f) M. O. Wolf and M. S. Wrighton, *Adv. Mater.*, 1994, **6**, 1526.
- R. P. Kingsborough and T. M. Swager, *Prog. Inorg. Chem.*, 1999, **48**, 123.
- N. B. McKeown, *Phthalocyanine Materials: Synthesis, Structure and Function*, Cambridge University Press, Cambridge, 1998.
- C. C. Leznoff, Z. Li, H. Isago, A. M. D'ascanio and D. S. Terekhov, *J. Porphyrins Phthalocyanines*, 1999, **3**, 406.
- S. Gronowitz and D. Peters, *Heterocycles*, 1990, **30**, 645.
- E. Ough, T. Nyokong, K. A. M. Creber and M. J. Stillman, *Inorg. Chem.*, 1988, **27**, 2724.
- (a) T.-C. Chung, J. H. Kaufman, A. J. Heeger and F. Wudl, *Phys. Rev. B*, 1984, **30**, 702; (b) A. O. Patil, A. J. Heeger and F. Wudl, *Chem. Rev.*, 1988, **88**, 183.
- (a) M. G. Hill, J. F. Penneau, B. Zinger, K. R. Mann and L. L. Miller, *Chem. Mater.*, 1992, **4**, 1106; (b) P. Bäuerle, U. Segelbacher, A. Maier and M. Mehring, *J. Am. Chem. Soc.*, 1993, **115**, 10 217; (c) D. D. Graf, R. G. Duan, J. P. Campbell, L. L. Miller and K. M. Mann, *J. Am. Chem. Soc.*, 1997, **119**, 5888.