doi:10.1246/cl.2012.979
Published on the web September 8, 2012

# Two Synthetic Approaches from 2,5-Di(2-thienyl)pyridine to a $BF_3$-modified Polymer Film

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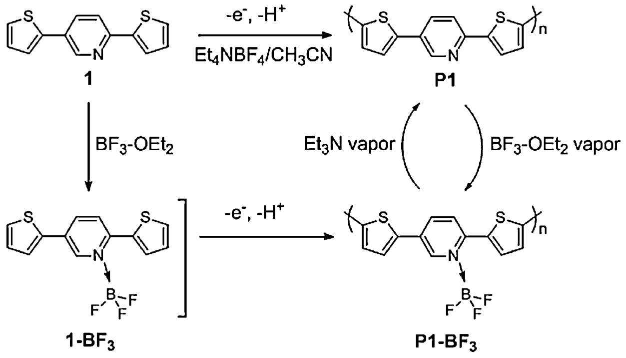
(Received June 15, 2012; CL-120649; E-mail: shayashi@nda.ac.jp)

A $BF_3$-modified poly[2,5-di(2-thienyl)pyridine] film was prepared through two synthetic approaches: electropolymerization of 2,5-di(2-thienyl)pyridine (**1**) followed by film-state post-functionalization using a trifluoroborate diethyl ether complex (BFEE) vapor (method 1), and BFEE electropolymerization of **1** (method 2).

Recently, post-functionalization of $\pi$-conjugated compounds has become attractive from the view point of band gap tuning.[1] When boron Lewis acids bind to a nitrogen in imine (C=N)-based aromatic compounds, electron density on the $\pi$-conjugated system decreases, resulting in a narrowing of the band gap.[1a,1b,2] This functionalization can occur because of the interaction between the lone pair of the nitrogen atom and the vacant p-orbital of the boron atom. Recently, we have successfully demonstrated the $BF_3$-modification of pyridine-based $\pi$-conjugated polymer films.[2] In addition, this approach offers "Lewis acidchromism (also called halochlomism)" and macrogradation optical patterning of conjugated polymer films. More importantly, high-performance solid-state nuclear magnetic resonance measurements contributed to the characterization of the $BF_3$-modified polymer films. Formation of the $BF_3$–pyridine complex unit in the $\pi$-conjugated system induces bathochromic shift in both absorption and fluorescence spectra. This preparative route to the $BF_3$-modified polymer films is multistep as follows: (A) polymerization (polymer synthesis), (B) cast coating on a glass plate (preparation of film), and (C) film-state modification by Lewis acid vapor treatment (polymer reaction).

On the other hand, polymerization of boron-modified monomers for synthesis of boron-based Lewis acid-modified $\pi$-conjugated polymers is a better approach to alleviate the synthetic process. However, the polymerization of the Lewis acid-modified pyridine-based monomers is difficult due to the low stability under conventional polymerization conditions. Therefore, we focused the BFEE (trifluoroborate diethyl ether complex, $BF_3$–$OEt_2$) electropolymerization method[3] of the pyridine-based monomer for direct synthesis of the $BF_3$-modified $\pi$-conjugated polymer film because of the following two advantages: (i) electropolymerization can be carried out using $BF_3$ (Lewis acid)-modified monomer, thus electropolymerization in the presence of BFEE offers one-pot preparation of $BF_3$-modified pyridine-based polymer film; (ii) BFEE is a helpful reagent to electropolymerize aromatic monomers due to lowering their oxidation potentials.[3] In this communication, we wish to report the preparation of a $BF_3$-modified pyridine-based conducting polymer film through two synthetic routes as follows: electropolymerization of a pyridine-based monomer followed by BFEE vapor treatment (method 1), and BFEE electropolymerization of a pyridine-based monomer (method 2).



**Scheme 1.** Two synthetic routes to $BF_3$-modified pyridine-based conjugated polymer film. Lewis halochromism of **P1** film using BFEE and $Et_3N$ vapors.

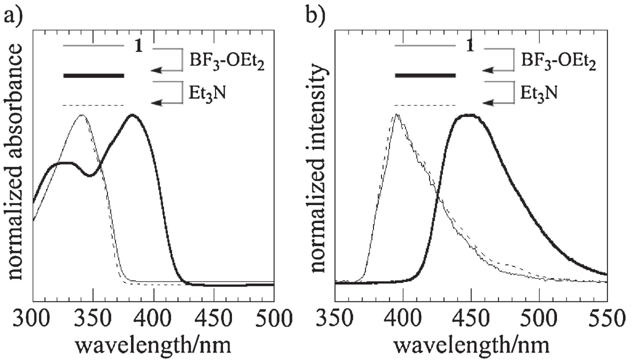


**Figure 1.** UV–vis absoption (a) and photoluminescence (b) spectra of **1** in a dilute THF solution. Reversible change of spectra through treatment with acid (BFEE) and base ($Et_3N$).

2,5-Di(2-thienyl)pyridine (**1**) was synthesized by Stille cross-coupling reaction between 2-(tri-*n*-butylstannyl)thiophene and 2,5-dibromopyridine with tetrakis(triphenylphosphine)palladium(0) as a catalyst.[2] Two synthetic routes to a Lewis acid ($BF_3$)-modified poly[2,5-di(2-thienyl)pyridine] (**P1-BF$_3$**) are outlined in Scheme 1.

UV–vis absorption spectrum of **1** in THF exhibited a maximum at 340 nm (Figure 1a). Coloration from transparent to yellow was observed by visual inspection on addition of BFEE (2.0 equiv). The spectrum (bold line) revealed the appearance of a red shifted band with a maximum at 387 nm and blue-shifted transition band centered at 318 nm. This red shift (47 nm) results from the intramolecular charge-transfer (CT) interaction[4] between the electron-donor thiophene and the electron-acceptor $BF_3$-modified pyridine unit. Moreover, blue shift (22 nm) evidences the existence of steric hindrance (–$BF_3$). Twisted

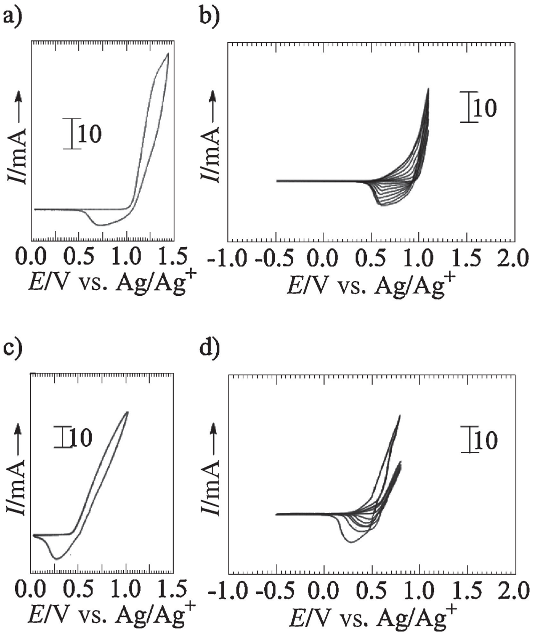


**Figure 2.** (a) CV curve of **1** measured in 0.1 M $Et_4NBF_4$/acetonitrile. (b) Electropolymerization of **1** in 0.1 M $Et_4NBF_4$/acetonitrile. (c) CV curve of **1** in BFEE. (d) BFEE electropolymerization of **1**. ITO working electrode; scan rate, 0.1 V $s^{-1}$.

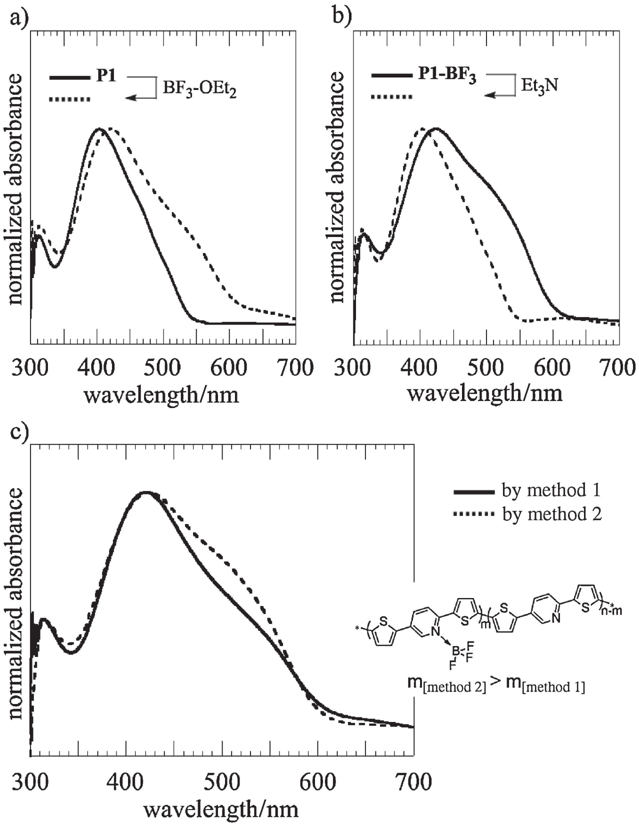


**Figure 3.** (a) UV–vis absoption spectra of **P1** before and after BFEE vapor treatment. (b) UV–vis absoption spectra of **P1-BF₃** before and after $Et_3N$ vapor treatment. (c) UV–vis absoption spectra of **P1-BF₃** by both method 1 and method 2.

configurations of **1-BF₃** reduce the mean conjugated length. The spectrum of **1-BF₃**/THF added with triethylamine ($Et_3N$) blue-shifted and completely corresponded to the absorption spectrum of **1** (dotted line). Photoluminescence (PL) spectrum of **1** in THF exhibited a maximum at 395 nm (Figure 1b). After addition of BFEE (2.0 equiv), the spectrum (bold line) revealed the appearance of a red-shifted band with a maximum at 446 nm. This red shift (51 nm) is derived from the intramolecular CT emmision.[4] The spectrum of **1-BF₃**/THF added with $Et_3N$ blue-shifted and completely corresponded to the PL spectrum of **1** (dotted line).

A cyclic voltammogram (CV) of **1** is displayed in Figure 2a. A three electrode system equipped with an indium tin oxide (ITO)-coated glass substrate (working electrode), platinum counter electrode, and Ag as a reference electrode was used in an electrolytic solution of acetonitrile containing 0.1 M tetraethylammonium tetrafluoroborate ($Et_4NBF_4$). The onset oxidation potential ($E_{onset,ox}$) of 0.05 M **1** was evident at 1.07 V (vs. Ag/$Ag^+$). Electropolymerization of di(2-thienyl) compound **1**[5] (potential sweep between −0.5 and 1.1 V (vs. Ag/$Ag^+$)) in 0.1 M tetraethylammonium tetrafluoroborate ($Et_4NBF_4$)/acetonitrile) successfully proceeded to deposit a pale yellow-colored thin film on the ITO working electrode (Figure 2b). The obtained polymer **P1** was washed with acetonitrile, then chloroform and dried under reduced pressure, and showed relatively high stability under normal conditions. Next, **P1** film was exposed to BFEE vapor by mounting the sample face down in a clamp stand 1 cm above the surface of a BFEE bath at 20 °C (1 min). The color of the polymer film changed from pale yellow to deep orange.

CV of **1** in BFEE (neat) is shown in Figure 2c. The oxidation potential of **1** in BFEE (**1-BF₃**) was lower than that in $Et_4NBF_4$/acetonitrile (vs. Ag/$Ag^+$) because of lowering of the aromatic resonance energy and promoting the abstraction of an electron from the most electron-rich position in the aromatic ring.[3] The onset oxidation potential of **1** was 0.44 eV (vs. Ag/$Ag^+$). BFEE electropolymerization of **1** (potential sweep between −0.5 and 0.8 V (vs. Ag/$Ag^+$)) in BFEE (neat) successfully proceeded to deposit an orange-colored thin film on the ITO working electrode (Figure 2d). The obtained polymer, **P1-BF₃**[6] was washed with acetonitrile, then chloroform and dried at room temperature. Next, **P1-BF₃** film was exposed to $Et_3N$ vapor by mounting the sample face down in a clamp stand 1 cm above the surface of a $Et_3N$ bath at 20 °C (1 min). The color of the polymer film changed from deep orange to pale yellow.

UV–vis absorption spectra of the polymer films are shown in Figure 3. In Figure 3a, **P1** exhibited a single absorption maximum at 405 nm. After BFEE vapor treatment by mounting the sample face down in a clamp stand 1 cm above the surface of a BFEE bath at 20 °C (5 min), a red-shifted absorption band centered at 425 nm was observed. In addition, the absorption edge was red-shifted by 72 nm. This red shift was derived from the inter- or intramolecular CT interaction between electron-donor thiophene moiety and electron-acceptor $BF_3$-modified pyridine unit.[2] The spectrum of **P1-BF₃** film prepared through BFEE electropolymerization (method 2) showed a broadened absorption band centered at 425 nm (Figure 3b). This band arising from inter- or intramolecular CT interaction indicates the successful preparation of the $BF_3$-modified polymer film. After $Et_3N$ vapor treatment by mounting the sample face down in a clamp stand 1 cm above the surface of a $Et_3N$ bath at 20 °C (5 min), the spectrum exhibited a narrow absorption band maximized at 405 nm. Moreover, the absorption edge was blue-shifted by 72 nm. This blue-shifted band corresponded with the absorption spectra of **P1** film. These results strongly support the successful preparation of the $BF_3$-modified polymer film via two synthetic approaches and the efficient halochromism using Lewis acid and base vapor treatment. In addition, the halochromism of the polymer films was achieved by repitition of acid–base treatment (Figure S1[7]).

Non-emitting properties of both the obtained polymer films were observed by visual inspection on excitation at 365 nm. Moreover, PL spectra were not observed by measurement of these films excited at this absorption maximum wavelength.

Figure 3c exhibited UV–vis absorption spectra of **P1-BF$_3$** prepared by both method 1 and method 2. The spectrum of **P1-BF$_3$** prepared by method 2 showed increasing CT band intensity at around 500 nm (vs. $\pi$–$\pi^*$ transition band at around 420 nm) compared with the spectrum of **P1-BF$_3$** prepared by method 1. It is because the film by polymerization of **1-BF$_3$** has higher $BF_3$–pyridine complex ratio ($m$) than that by post-functionalization of **P1**.

In summary, we have successfully demonstrated the preparation of a $BF_3$-modified poly[2,5-di(2-thienyl)pyridine] (**P1-BF$_3$**) film thorough two approaches: electropolymerization of 2,5-di(2-thienyl)-2,5-pyridine (**1**) followed by film-state post-functionalization using BFEE vapor (method 1), and BFEE electropolymerization of 2,5-di(2-thienyl)pyridine (method 2). The advantages of method 2 are not only a short synthetic route but also efficient polymerization due to lowering the oxidation potential of **1**. **P1-BF$_3$** film by method 2 showed higher CT absorption efficiency than that by method 1. The optical property of these polymer films is switchable by using Lewis acid and base vapor.

The authors of this paper would like to thank Grant-in-Aid for Young Scientists (B) (No. 24750116) for financial support of this research.

## References and Notes

1 a) G. C. Welch, R. Coffin, J. Peet, G. C. Bazan, *J. Am. Chem. Soc.* **2009**, *131*, 10802. b) G. C. Welch, G. C. Bazan, *J. Am. Chem. Soc.* **2011**, *133*, 4632.

2 S. Hayashi, A. Asano, T. Koizumi, *Polym. Chem.* **2011**, *2*, 2764.

3 The role of the BFEE in doping during electropolymerization has been proposed. It facilitates electropolymerization by lowering the aromatic resonance energy and promoting the abstraction of an electron from the most electron-rich position in the aromatic ring. And trifluoroborate exists in diethyl ether as a polar adduct and that results in the formation of $Et^+[BF_3OEt]^-$. This complex salt acts as a supporting electrolyte in this media: a) S. Inagi, T. Yamaguchi, S. Hayashi, K. Koseki, T. Fuchigami, *Electrochem. Commun.* **2010**, *12*, 661. b) S. Alkan, C. A. Cutler, J. R. Reynolds, *Adv. Funct. Mater.* **2003**, *13*, 331. c) Q. Hao, W. Lei, X. Xie, M. Xia, F. Wang, X. Yang, *Polym. Chem.* **2011**, *2*, 1085. d) G. Shi, S. Jin, G. Xue, C. Li, *Science* **1995**, *267*, 994. e) W. Chen, G. Xue, *Prog. Polym. Sci.* **2005**, *30*, 783.

4 a) S. Hayashi, T. Koizumi, *Polym. Chem.* **2012**, *3*, 613. b) Y. Zhu, R. D. Champion, S. A. Jenekhe, *Macromolecules* **2006**, *39*, 8712. c) S. A. Jenekhe, L. Lu, M. M. Alam, *Macromolecules* **2001**, *34*, 7315. d) Q. Peng, K. Park, T. Lin, M. Durstock, L. Dai, *J. Phys. Chem. B* **2008**, *112*, 2801.

5 S. Tanaka, M.-A. Sato, K. Kaeriyama, *J. Macromol. Sci., Part A: Pure Appl. Chem.* **1987**, *24*, 749.

6 Obtained polymer showed relatively good stability under inert conditions such as the atmosphere without base.

7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.