

# Electrochemical synthesis of a pyridinium-conjugated assembly based on nucleophilic substitution of oligothiophene $\pi$ -radical cation

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A series of pyridinium-conjugated oligothiophenes is synthesized electrochemically by nucleophilic substitution of the oligothiophene  $\pi$ -radical cation. The nucleophilic reaction is designed on the basis of high reactivity of the  $\pi$ -radical cation of oligothiophene with various pyridine derivatives as nucleophiles. While electrochemical oxidation of oligothiophene gave a conducting polythiophene film on an electrode, the addition of pyridine depressed formation of the polythiophene film but the corresponding pyridinium-conjugated oligothiophene was exclusively formed as the product of nucleophilic substitution of the oligothiophene  $\pi$ -radical cation. In prolonged electrolysis at a higher potential, successive (two-step) substitution occurred to yield both mono- and di-(1-pyridinio)oligothiophenes. The nucleophilic substitution reaction was optimized with respect to the electrolytic conditions, and the nucleophilic attack toward the oligothiophene  $\pi$ -radical cation is discussed. The UV-visible absorption spectra and redox activities of the resulting pyridinium-conjugated oligothiophene were measured. Negative solvatochromism due to intramolecular charge transfer (IMCT) and redox behavior resulting from oligothiophene and pyridinium moieties are demonstrated.

## Introduction

$\pi$ -Radical cations of aromatic molecules are often revealed as their one-electron-oxidized species in electrochemistry, organic chemistry and photochemistry.<sup>1</sup> Due to their increased electron-deficient character,  $\pi$ -radical cations have the potential to be attacked by a nucleophile and yield an adduct with the resulting  $sp^3$  carbon, followed by re-aromatization with loss of the hydrogen. The anodic substitution and addition reactions of aromatic compounds *via* their  $\pi$ -radical cations as key intermediate have been of continuing interest to organic electrochemists.<sup>2-5</sup>

Anodic pyridination<sup>3</sup> of aromatic compounds, *e.g.*, anthracene, benzo[*a*]pyrene, perylene, thianthrene and so on, was reported long ago,<sup>4</sup> mainly using pyridine nucleophiles. Apart from the interest in electroorganic synthesis, anodic pyridination has been targeted as a model reaction for mechanistic study, including electron transfer and proton transfer,<sup>2,5</sup> since systematic pyridination was available with widely varied electronic and steric effects. Afterwards, to our knowledge, few studies have been reported to extend this fundamental reaction to other  $\pi$ -conjugated molecules.

Recently, L. Ruhlmann *et al.* reported viologen-linked porphyrin polymers on the basis of repeated anodic pyridination by using multifunctional aromatic substrates and nucleophiles.<sup>6</sup> Their study should be a significant milestone in the application of anodic pyridination to polymer synthetic strategy leading to functional material chemistry. It strongly stimulated us to study the reactivity of  $\pi$ -radical cations of functional  $\pi$ -conjugated systems again, with respect to both interesting synthetic macromolecular chemistry and the following unresolved issue

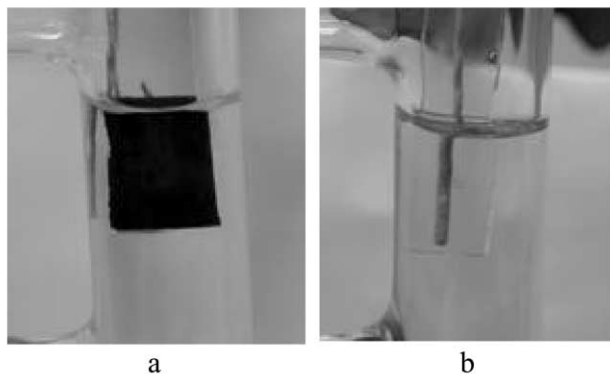
in conducting-polymer chemistry. †<sup>7-10</sup> ‘What about the reactivity of the electrogenerated  $\pi$ -radical cation of both the monomer and the oligomer with nucleophiles, with respect to the increasing  $\pi$ -conjugated system?’ We conducted a significant study of the anodic pyridination on oligothiophene derivatives as the intermediates for polythiophenes with several pyridine derivatives. It should be worthwhile evaluating anodic pyridination of oligothiophenes that has never yet been reported. Here, we report the anodic pyridination of oligothiophenes, which competed with electropolymerization, and briefly report spectroscopic and electrochemical properties of new pyridinio-oligothiophene derivatives obtained in this study.

## Results and discussion

### Electro-oxidation of BT in the presence of pyridine

It is well known that 2,2'-bithiophene (**BT**) is oxidatively polymerized to form a black (doping state) conducting polythiophene film on an electrode surface.<sup>7</sup> As Fig. 1a shows, **BT** was effectively polymerized when the electrode potential was

†  $\pi$ -Radical cations are often encountered in electropolymerization of aromatic molecules such as thiophene and pyrrole toward the conducting polythiophene and polypyrrole, respectively, and even in polaron and bipolaron states. In the former case, electrogenerated  $\pi$ -radical cations of the monomer are coupled through deprotonation to yield a dimer, which is more easily oxidized to the  $\pi$ -radical cations due to the developing  $\pi$ -conjugated system. Further successive oxidative-coupling reactions include many kinds of  $\pi$ -radical cation intermediates and finally give a conducting polymer film on an electrode.



**Fig. 1** Photographs around the ITO working electrode during electrolysis of **BT** in acetonitrile containing 0.1 M TBAP in the (a) absence and (b) presence of 0.1 M pyridine. While a black polythiophene film formed on the electrode in the absence of pyridine, no such film did in the presence of pyridine.

set to 1.16 V vs SCE in acetonitrile containing 0.01 M **BT** and 0.1 M tetrabutylammonium perchlorate (TBAP). On the other hand, no film formed in the presence of 0.1 M pyridine and the solution color changed from colorless to yellow, as Fig. 1b shows. This contrasting behavior has been experienced long before when various electrolytic solvents were examined for effective electropolymerization, but here stimulated us to reassess this reaction with pyridine. After a stoichiometric amount of charge was passed in the electrolysis, 5-(1-pyridinio)-2,2'-bithiophene perchlorate (**2c**) was isolated as the main product in the resulting electrolytic solution. The addition of pyridine completely depressed the formation of a polythiophene film. The resulting  $\pi$ -radical cations reacted with pyridine as a competition reaction to their coupling to afford electropolymerization products.

A similar observation was found in the case of 2,2':5',2''-terthiophene (**TT**). The solution was red-orange in color and no polythiophene film formed on electrolysis of **TT** at 1.00 V in the presence of 0.1 M pyridine. 5-(1-Pyridinio)-2,2':5',2''-terthiophene perchlorate (**3**) as the main product was isolated from the resulting electrolytic solution. In the case of thiophene (**Th**), however, a brown film formed on an electrode even when a higher potential (1.80 V) was applied. Even in neat pyridine as the electrolytic solvent, the film still formed and little color change was visible. FT-IR analysis indicated that the deposited film has the pyridinium structure is not a pure polythiophene film. ‡ The  $^1\text{H-NMR}$  spectrum of the electrolytic solution indicated the formation of 2-(1-pyridinio)thiophene perchlorate (**1**) although the yield was low (<10%).

Let us summarize the above interesting phenomena here so as to examine those reactions applicable to the electrochemical construction of  $\pi$ -conjugated molecular assemblies. (1) These pyridinium products were detected when the  $\pi$ -radical cations were formed electrochemically. (2) The addition of pyridine depressed the formation of the conducting polythiophene. The key to these findings is considered to be the reactivity of the resulting  $\pi$ -radical cations of oligothiophene toward a nucleophile such as pyridine. This reaction competes with their repeated coupling reaction, followed by deprotonation crucial for electropolymerization, as Scheme 1 shows. In the former, either dehydrogenation or deprotonation with oxidation of the resulting intermediate after nucleophilic attack should form the pyridinium-conjugated products. The following parameters were examined to help us understand this reaction: concentration of oligothiophene and pyridine, basicity of pyridine

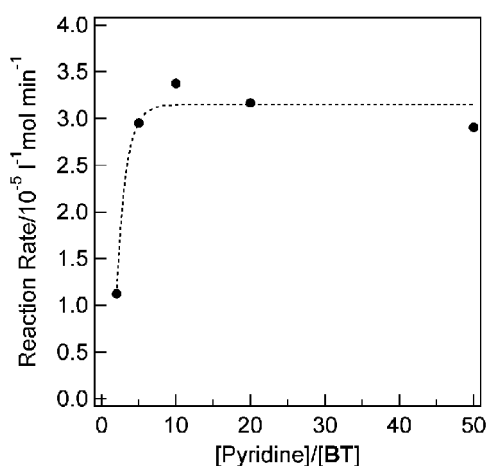
‡ The obtained polymer on the electrode surface was easily removed as a brown amorphous powder which contained polythiophene, pyridinium-modified polythiophene, and pyridinium-terminated oligothiophene structures. This was supported by FT-IR. This result will be elucidated in our following paper published elsewhere.

derivatives, electrode potential, and electrolyte, some of which will be reported in this study.

### Nucleophilic substitution of $\pi$ -radical cation

Quantitative  $^1\text{H-NMR}$  analysis with ethanol as the internal standard was used to determine the yield of the product. An analytical sample was prepared by the following isolation procedure: the solvent and volatile reactants such as pyridine were evaporated from the electrolytic solution after electrolysis under designated electrode potential and electrolytic charge. The residue was washed with water to remove both the supporting electrolyte,  $\text{NaClO}_4$ , and protonated pyridine (pyridinium perchlorate), which resulted from deprotonation of the intermediate (Scheme 1). The remaining solid was dissolved in the minimum amount of acetonitrile, followed by reprecipitation with diethyl ether.

Apparent reaction rate ( $\text{M min}^{-1}$ ) was defined as the yield of the product determined in the initial 10% of stoichiometric electrolysis. § The reaction rate increases steeply as a function of molar ratio ( $R$ ) of pyridine to **BT** (Fig. 2). Even at  $R = 2.0$ , no

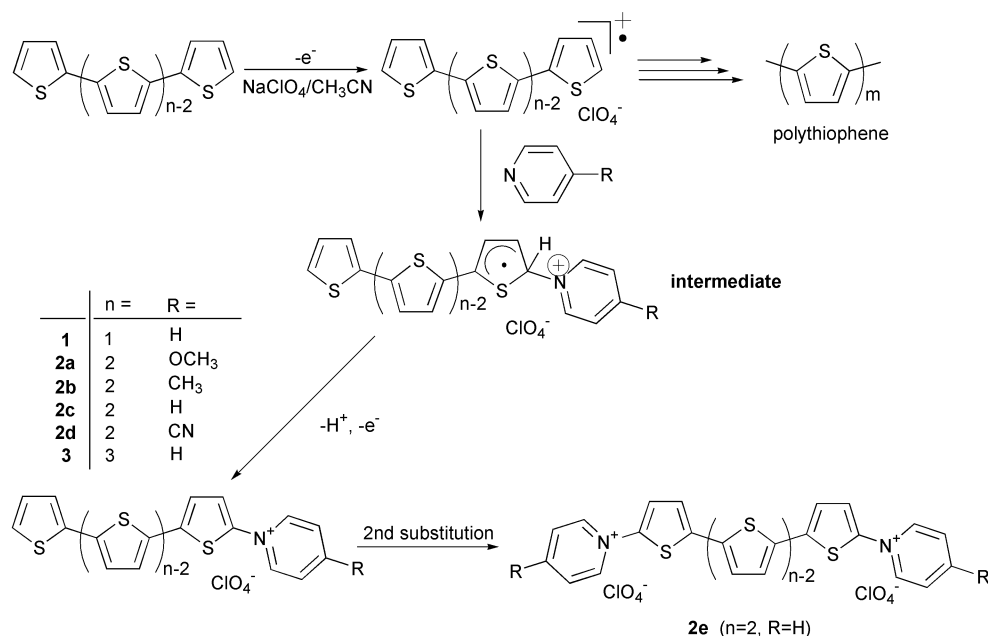


**Fig. 2** The dependence of the apparent reaction rate on the molar ratio of pyridine to **BT**, of which concentration was set to 5 mM. The rate is defined as the yield of **2c** when 10% of equivalent charge ( $0.2 \text{ F mol}^{-1}$  of **BT**) is passed under potentiostatic electrolysis at 1.16 V, assuming a two-electron oxidation process in the concerned reaction.

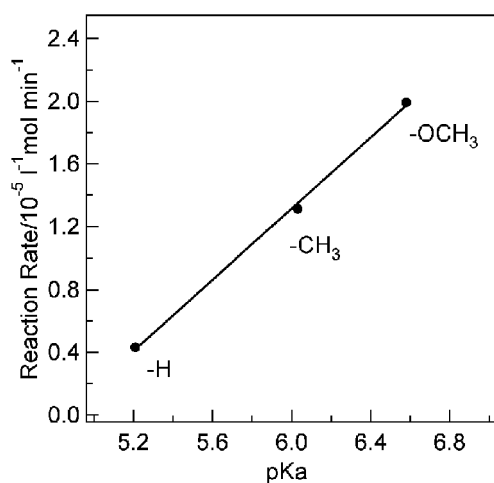
conducting film was observed. At  $R > 5$ , the rate of the substitution reached a saturation and **2c** was exclusively obtained, based on an analysis of  $^1\text{H-NMR}$  results.

The reactivity of the pyridine nucleophile toward the  $\pi$ -radical cations of **BT** was examined by using 4-substituted pyridine derivatives in the initial 20% of stoichiometric electrolysis. A plot of the apparent reaction rate against  $\text{p}K_{\text{a}}$ -value of the pyridine derivatives (as an evaluation of their nucleophilicity) shows good linearity with a positive slope (Fig. 3). In the case of 4-cyanopyridine with  $\text{p}K_{\text{a}} = 1.86$ , the corresponding product (**2d**) could not be detected by  $^1\text{H-NMR}$  and the electrode surface was covered with a considerable amount of a black film (polythiophene with cyanopyridinium moieties) under the same conditions. When an excess amount ( $R = 20$ ) of 4-cyanopyridine was added, a satisfactory yield (40%) of **2d** was obtained. These observations can be easily explained by nucleophilic reaction of oligothiophene  $\pi$ -radical cations with pyridine derivatives, which compete with the electropolymerization.

§ One substitution process of an  $\alpha$ -proton of an oligothiophene by the pyridinium moiety involves two-electron oxidation and one deprotonation. The first one-electron oxidation results in a  $\pi$ -cation radical of the oligothiophene, and the second one-electron oxidation with deprotonation takes place in the intermediate bearing the  $N$ -pyridinio moiety and hydrogen. Another description might be dehydrogenation in the latter process.



**Scheme 1** Two reaction routes of  $\pi$ -radical cations of oligothiophene. One is nucleophilic substitution to give pyridinium-conjugated oligothiophene derivatives as in this study, and the other is electropolymerization through  $\alpha$ ,  $\alpha$ -coupling to give polythiophenes.

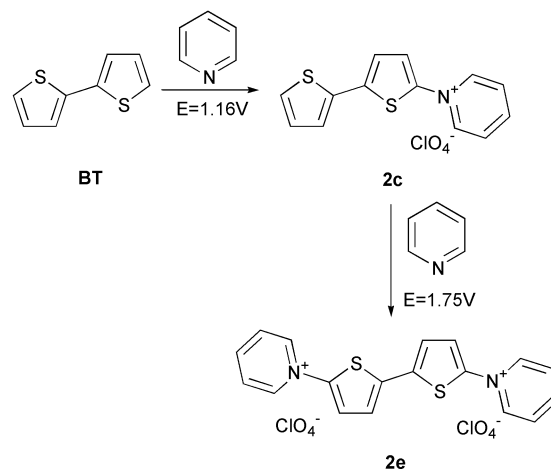


**Fig. 3** The dependence of the apparent reaction rate on the basicity of 4-substituted pyridine derivatives, as their  $pK_a$ -values. Electrolysis at 1.16 V was carried out under the conditions of  $[BT] = 5$  mM and  $[pyridine] = 10$  mM. The rate is defined as the yield of **2c** when 20% of equivalent charge ( $0.4 F mol^{-1}$  of **BT**) is passed.

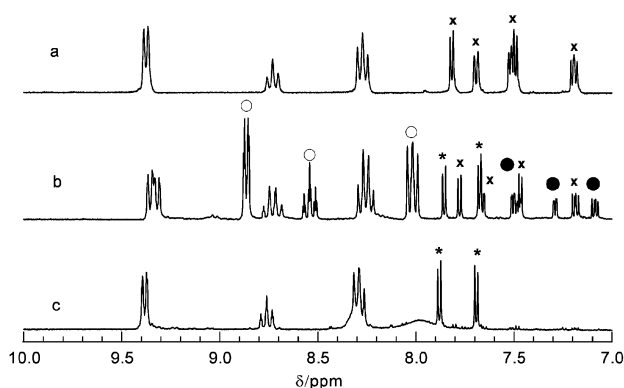
### Successive nucleophilic substitution

**BT** has two major reactive sites, the 2- and 5'-position, for possible substitution, so that the second substitution was examined (Scheme 2). The oxidation potential of **2c** should shift to about 1.50 V due to the strong electron-withdrawing property of the substituted pyridinium moiety. Under controlled-potential electrolysis at 1.16 V, therefore, the second substitution of **2c** was unlikely to take place. Exhaustive oxidation of **2c** as the reactant at 1.75 V was attempted in the presence of an excess amount of pyridine ( $R = 50$ ). After sufficient electrolysis [1.1 equivalent charges ( $2.2 F mol^{-1}$  of **2c**)]<sup>¶</sup> the product was identified as **2e** by <sup>1</sup>H-NMR (Fig. 4c). Since the proton peaks of **BT** become simple and symmetrical, the di-substituted product **2e** was confirmed as occurring in more than 90% yield, in addition to a trace amount of unchanged **2c**. Successive substitution was also examined with **BT** as the reactant in the presence of 10 equiv. of pyridine at 1.75 V. Mono-

<sup>¶</sup> In this paper, F is used for a Faraday ( $\equiv 1$  mole of electrons).



**Scheme 2** Potential-controlled successive pyridinations of **BT**. Mono-substituted product **2c** was exclusively obtained at 1.16 V, not enough to oxidize the product. Di-substituted product **2e** was obtained by electrolysis of **2c** at 1.75 V. Both **2c** and **2e** were obtained by electrolysis of **BT** at 1.75 V.



**Fig. 4** <sup>1</sup>H-NMR spectra of (a) isolated **2c**, (b) the reaction mixture after electrolysis of **BT** at 1.75 V, and (c) isolated **2e** from the electrolysis of **2c** at 1.75 V vs SCE. In spectrum (b) are also found signals from unchanged **BT** (●), and from the protonated pyridine (○), which results from deprotonation of the intermediate in substitution. **2c** (x, **BT** unit) and **2e** (\*, **BT** unit) were found in the electrolytic solution. All of the peaks in spectrum (b) undergo some shift due to the high concentration of  $NaClO_4$  as supporting electrolyte.

**Table 1** Electrochemical data of the pyridinium-conjugated oligothiophenes

	$E_c^{CV}/V$	$E_c^{DPV}/V$	$E_a^{CV}/V$	$E_a^{DPV}/V$
<b>BT</b>			1.13	1.16
<b>TT</b>			0.92	1.00
<b>2a</b>	-1.09	-1.13	1.42	1.54
<b>2b</b>	-0.83	-0.99	1.48	1.55
<b>2c</b>	-0.65	-0.86	1.51	1.57
<b>2d</b>	-0.38	-0.33	1.61	1.65
<b>2e</b>		-0.39, -0.81		2.19
<b>3</b>	-0.68	-0.84	1.13	1.20

$E^{CV}$  and  $E^{DPV}$  are the onset potentials (V vs SCE) in a cyclic voltammogram and the peak potentials in differential pulse voltammogram, respectively.  $E_c$  and  $E_a$  are the reduction and the oxidation potentials, respectively, which were determined in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP) with respect to the ferrocene/ferrocenium couple (0.392 V vs SCE) as internal standard.

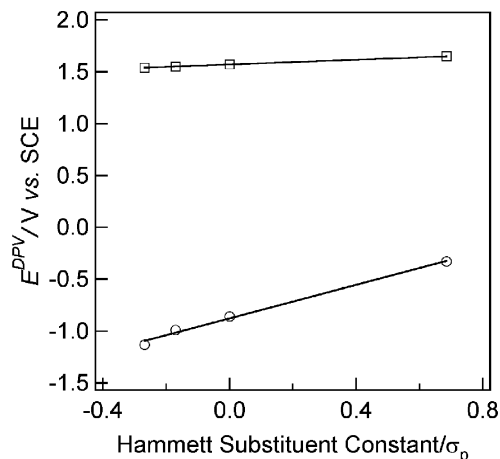
and di-substituted pyridinium products, **2c** and **2e**, in the ratio  $\approx 55 : 45$ , were obtained with unchanged **BT** and protonated pyridine after passage of  $2 \text{ F mol}^{-1}$  of **BT** (Fig. 4b). The protonated pyridine is the product formed by capture of the leaving proton from **BT** after the substitution. Unfortunately, successive electrolysis of **BT** was time-consuming due to passivation of the Pt electrode surface. In other words, **2c** can be exclusively obtained by electrolysis at 1.16 V and the fraction of **2e** in the products would increase as a function of electrode potential in the oxidative electrolysis. Under the conditions of controlled-current bulk electrolysis at  $<0.5 \text{ mA cm}^{-2}$ , a relatively high yield ( $>50\%$ , not optimized) of **2e** was also obtained from **BT**.

#### Redox properties of pyridinio-oligothiophene

The resulting pyridinio-oligothiophenes, **2a–e** and **3**, in which an oxidation of the oligothiophene moiety gives  $\pi$ -radical cations similar to the one-capped oligothiophene<sup>10</sup> and a reduction of the pyridinium moiety gives neutral pyridyl radical.<sup>11</sup> The first reduction and the first oxidation potentials of these pyridinio-oligothiophenes were measured by cyclic voltammetry (CV). In the oxidation process, anodic waves were observed without the corresponding cathodic waves, because of successive reaction of the resulting  $\pi$ -radical cations, e.g., dimerization at the 2-position of the oligothiophene moiety.<sup>10</sup> In the reduction process, cathodic waves were clearly observed but the corresponding anodic waves were so distorted as to preclude elucidation of their peaks. Possible explanations for the unclear cathodic waves may be (i) deposition of the neutral pyridyl radical or (ii) formation of their dihydropyridine dimers.<sup>11</sup> On the other hand, differential pulse voltammetry (DPV) gave distinct redox peaks, which are listed as the half-wave potentials in Table 1.

Both onset potentials of the oxidation and the reduction waves in cyclic voltammograms and peak potentials of differential pulse voltammograms depend on both the oligothiophene moieties and the 4-substituents on the pyridinium. Based on DPV measurements, both the oxidation and the reduction potentials of **2a** (Hammett substituent constants  $\sigma_p$ ,  $-0.268$ ), **2b** ( $-0.17$ ), **2c** ( $0.0$ ), and **2d** ( $0.685$ ) show linear relationships against the  $\sigma_p$  values (Fig. 5). Comparing **2c** and **3**, the first oxidation peak shifts to the negative direction upon increasing conjugated length of the oligothiophene moiety, while the reduction peak of the pyridinium moiety does not (Table 1). The pyridino-oligothiophene products show high oxidation potential with respect to the corresponding oligothiophene sub-

|| A terminal-capped **BT** such as 5-methylbithiophene can undergo anodic pyridination to give the corresponding pyridinium salt. A quasi-reversible redox wave was observed as the first oxidation at  $0^\circ \text{C}$  and  $500 \text{ mV s}^{-1}$ .

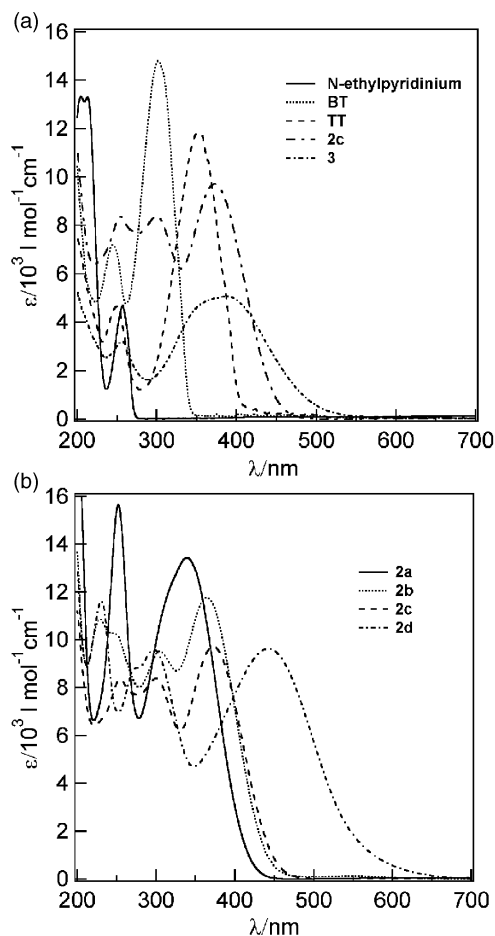


**Fig. 5** The dependence of DPV data of **2a**, **2b**, **2c** and **2d** with respect to Hammett substituent constant ( $\sigma_p$ ).

strates, due to the strong electron-withdrawing effect of pyridinium units. Disubstituted product **2e** showed two-step reduction peaks ( $-0.39 \text{ V}$ ,  $-0.81 \text{ V vs SCE}$ ) assigned to both pyridinium moieties linked through the bithienylene linker. The peak separation in DPV was  $420 \text{ mV}$ , as large as that ( $416 \text{ mV}$ ) of viologen in which two pyridinium rings are directly linked at their 4-positions.

#### Spectroscopic property of pyridinio-oligothiophene

Fig. 6a shows the UV-visible absorption spectra of a typical



**Fig. 6** UV-visible absorption spectra of pyridinium-conjugated oligothiophene derivatives; (a) **2c** and **3** with the corresponding oligothiophenes, **BT**, and **TT**; and (b) **2a**, **2b**, **2c** and **2d**, in  $\text{CH}_3\text{CN}$ .

pyridinio-oligothiophene in CH<sub>3</sub>CN. The absorption maxima are red-shifted in the order **2c** < **3**, consistent with the increasing conjugated length. This intense absorption band can be assigned to a  $\pi$ - $\pi^*$  transition, in which the HOMO is localized on the oligothiophene part and the LUMO is localized on the pyridinium moiety. That is to say, this transition is an intramolecular charge-transfer (IMCT) band from the oligothiophene part to the pyridinium one. The absorption maxima are red-shifted due to the increasing strength of the electron-withdrawing substituents (Fig. 6b).

The electron-withdrawing character would stabilize the energy level of the HOMO on the oligothiophene moiety more than that of the LUMO on the pyridinium moiety. Other consistent evidence was obtained as a negative solvatochromism of pyridinio-oligothiophenes **2a-d** and **3** (Fig. 7). In the IMCT

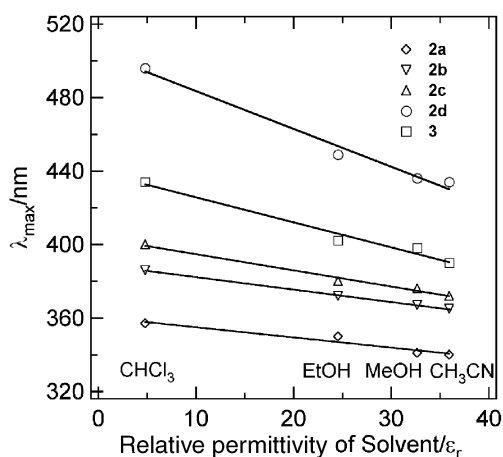


Fig. 7 The dependence of  $\lambda_{max}$  in UV-visible absorption spectra on the relative permittivity of solvent ( $\epsilon_r$ ) for the pyridinium-conjugated oligothiophene derivatives.

transition a positive charge moves from the pyridinium moiety in the ground state to the oligothiophene moiety in the excited state, so that the latter should be more stabilized in polar solvent than the former. As the solvent polarity increases, the ground state would be stabilized more by solvation than would the excited state. Fig. 7 shows the intramolecular charge transfer with respect to the substituent and solvent polarity. A relatively strong negative solvatochromism was found in the case of **2d** compared with others, due to CN electron-withdrawing ability. Comparing **2c** and **3**, the conjugated stabilization effect to the excited state can explain the relatively strong negative solvatochromism of the latter.

## Conclusions

Quantitative anodic pyridination of oligothiophene was achieved as the competition reaction with electropolymerization. An appropriate amount of pyridine nucleophile completely depressed the electropolymerization of oligothiophene to form a conducting polythiophene film on the electrode, but gave the corresponding pyridinio-oligothiophene products in quantitative yield. Nucleophilicity of pyridine derivatives was one of significant factors on reactivity of the anodic pyridination, which was confirmed by the linear relationship between apparent reaction rate and  $pK_a$  of the pyridine derivatives. Two-step substitution of bithiophene with pyridine was also demonstrated at a highly positive potential. The resulting pyridinio-oligothiophene, as a pyridinium-conjugated assembly, shows weak negative solvatochromism due to intramolecular charge transfer and redox active property in both anodic and cathodic processes. The present result encourages us to examine the anodic pyridination of the conducting polymer film as the ultimately developed  $\pi$ -radical cation, which is under investigation.

## Experimental

### General remarks

All solvents and chemicals were of reagent-grade quality, purchased commercially, and used without further purification except as noted below. Acetonitrile for the exhaustive electrolysis was distilled over CaH<sub>2</sub>. Reagent-grade pyridine was distilled over NaOH pellets under nitrogen atmosphere. 2,2'-Bithiophene (**BT**, Tokyo Casei) was purified by chromatography on a silica gel column with CHCl<sub>3</sub>-hexane (1 : 10), followed by recrystallization from hexane.

FT-IR spectra were measured with a Bio-Rad FTS 3000. <sup>1</sup>H-NMR spectra were recorded in DMSO-d<sub>6</sub> on a JEOL FX-270 (270 MHz) spectrometer and referenced to TMS. Fast-atom bombardment mass spectra (FAB-MS) were obtained in a 3-nitrobenzyl alcohol (NBA) matrix on a liquid chromatography mass spectrometer (JMS-LX1000). UV-visible spectra were recorded with a Shimadzu UV-3100 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN Elemental Analyzer.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out in freshly distilled CH<sub>3</sub>CN containing 1 mM compound to be measured and 0.1 M TBAP at room temperature under N<sub>2</sub> atmosphere. Voltammograms were recorded with an HZ-3000 automatic polarization system (Hokudo Denko). A Pt rod electrode ( $\phi$ : 1 mm) sealed with a Teflon tube, platinum wire, Ag/AgCl wire were used as working electrode, counter-electrode and quasi-reference electrode, respectively. Potentials cited in this study are referenced to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>, 0.392 V vs SCE) couple as internal standard.

### Bulk electrolysis

Controlled-potential bulk electrolysis was performed with an HAF501 potentiostat (Hokuto Denko, Japan). An electrochemical H-type cell with two compartments separated by a fritted glass barrier was employed as the reaction vessel. A Pt plate working electrode (2.1 cm<sup>2</sup>), a homemade Ag/Ag<sup>+</sup> (0.01 M, 0.24 V vs SCE, saturated NaClO<sub>4</sub> acetonitrile solution) reference electrode, and a Pt counter-electrode (4.2 cm<sup>2</sup>) were typically used for bulk electrolysis. In a typical electrolysis, 50 ml of dry CH<sub>3</sub>CN solution containing 50 mM of **BT**, 0.5 M of pyridine, and 0.5 M NaClO<sub>4</sub> was loaded into the H-type cell. The electrolytic charge was limited to 0.4 F mol<sup>-1</sup> (20% of theoretical charge) of **BT**, assuming a two-electron oxidation process. A constant potential, 1.16 V or 1.00 V, was applied for the electrolysis of **BT** or **TT**, respectively, which was determined by CV and DPV.

Prior to the electrolysis the corresponding mixture was stirred and deaerated by bubbling nitrogen through the solution for 10 min. During anodic oxidation, the electrolyzed solution was continuously stirred.

### 5-(4-Methoxy-1-pyridinio)-2,2'-bithiophene perchlorate (2a)

Yield 83%, yellow powder; FT-IR (KBr)  $\nu$  3052 (aromatic C-H stretching), 2955 (CH<sub>3</sub>), 1637 (C=N stretching), 1316 (C-O-C), 1085 [ $\nu$ (ClO<sub>4</sub><sup>-</sup>)], 838 (C-H out-of-plane bend) cm<sup>-1</sup>; <sup>1</sup>H-NMR (270 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si)  $\delta$  9.16 (d, 2H,  $J$  = 7.29 Hz,  $\alpha$ H of pyridinium), 7.76 (d, 2H,  $J$  = 7.29 Hz,  $\beta$ H of pyridinium), 7.65-7.67 (m, 2H), 7.48 (dd, 1H,  $J$  = 3.78, 0.81 Hz), 7.43 (d, 1H,  $J$  = 3.78 Hz), 7.18 (dd, 1H,  $J$  = 4.86, 3.78 Hz), 4.20 (s, 3H, OCH<sub>3</sub>); FAB-MS (NBA)  $m/z$  274 (M<sup>+</sup>, C<sub>14</sub>H<sub>12</sub>NOS<sub>2</sub><sup>+</sup>); UV-vis (acetonitrile)  $\lambda_{max}$ /nm (log  $\epsilon$ ) 252 (4.19), 315 (sh) (4.06), 339.5 (4.13) (Calc. for C<sub>14</sub>H<sub>12</sub>NOS<sub>2</sub><sup>+</sup> ClO<sub>4</sub><sup>-</sup>: C, 44.98; H, 3.24; N, 3.75. Found: C, 44.91; H, 3.30; N, 3.71%).

### 5-(4-Methyl-1-pyridinio)-2,2'-bithiophene perchlorate (2b)

Yield 80%, brown powder; FT-IR (KBr)  $\nu$  3036 (aromatic C-H stretching), 2960 (CH<sub>3</sub>), 1635 (C=N stretching), 1466 (aromatic

ring stretching), 1086 [ $\nu(\text{ClO}_4^-)$ ], 838 (C–H out-of-plane bend)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (270 MHz; DMSO- $d_6$ ; Me $_4$ Si)  $\delta$  9.22 (d, 2H,  $J = 6.48$  Hz,  $\alpha\text{H}$  of pyridinium), 8.12 (d, 2H,  $J = 6.48$  Hz,  $\beta\text{H}$  of pyridinium), 7.77 (d, 1H,  $J = 4.05$  Hz), 7.68 (dd, 1H,  $J = 5.13$ , 1.08 Hz), 7.50 (dd, 1H,  $J = 3.78$ , 1.08 Hz), 7.47 (d, 1H,  $J = 4.05$  Hz), 7.19 (dd, 1H,  $J = 5.13$ , 3.78 Hz), 2.71 (s, 3H, CH $_3$ ); FAB-MS (NBA)  $m/z = 258$  ( $\text{M}^+$ , C $_{14}\text{H}_{12}\text{NS}_2^+$ ); UV-vis (acetonitrile)  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ) 228.5 (4.04), 250 (4.01), 305 (3.98), 365 (4.07) (Calc. for C $_{14}\text{H}_{12}\text{NS}_2^+$  ClO $_4^-$ : C, 46.99; H, 3.38; N, 3.91. Found: C, 47.13; H, 3.32; N, 3.81%).

#### 5-(1-Pyridinio)-2,2'-bithiophene perchlorate (2c)

Yield 90%, yellow–brown powder; FT-IR (KBr)  $\nu$  3060 (aromatic C–H stretching), 1624 (C=N stretching), 1475 (aromatic ring stretching), 1094 [ $\nu(\text{ClO}_4^-)$ ], 837 (C–H out-of-plane bend)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (270 MHz; DMSO- $d_6$ ; Me $_4$ Si)  $\delta$  9.38 (d, 2H,  $J = 5.67$  Hz,  $\alpha\text{H}$  of pyridinium), 8.73 (t, 1H,  $J = 7.83$  Hz,  $\gamma\text{H}$  of pyridinium), 8.27 (t, 2H,  $J = 7.16$  Hz,  $\beta\text{H}$  of pyridinium), 7.82 (d, 1H,  $J = 4.05$  Hz), 7.69 (dd, 1H,  $J = 5.13$ , 0.81 Hz), 7.52 (dd, 1H,  $J = 3.78$ , 0.81 Hz), 7.49 (d, 1H,  $J = 4.05$  Hz), 7.19 (dd, 1H,  $J = 5.13$ , 3.78 Hz); FAB-MS (NBA)  $m/z = 244$  ( $\text{M}^+$ , C $_{13}\text{H}_{10}\text{NS}_2^+$ ); UV-vis (acetonitrile)  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ) 254.5 (3.92), 300 (3.92), 373 (3.99) (Calc. for C $_{13}\text{H}_{10}\text{NS}_2^+$  ClO $_4^-$ : C, 45.41; H, 2.93; N, 4.07. Found: C, 45.40; H, 2.93; N, 4.08%).

#### 5-(4-Cyano-1-pyridinio)-2,2'-bithiophene perchlorate (2d)

Yield 40%, deep-red powder; FT-IR (KBr)  $\nu$  3071 (aromatic C–H stretching), 2240 [ $\nu(\text{CN})$ ], 1630 (C=N stretching), 1450 (aromatic ring stretching), 1085 [ $\nu(\text{ClO}_4^-)$ ], 838 (C–H out-of-plane-bend)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (270 MHz; DMSO- $d_6$ ; Me $_4$ Si)  $\delta$  9.67 (d, 2H,  $J = 7.02$  Hz,  $\alpha\text{H}$  of pyridinium), 8.82 (d, 2H,  $J = 7.02$  Hz,  $\beta\text{H}$  of pyridinium), 7.92 (d, 1H,  $J = 4.05$  Hz), 7.72 (dd, 1H,  $J = 5.13$ , 1.08 Hz), 7.57–7.54 (m, 2H), 7.21 (dd, 1H,  $J = 5.13$ , 3.78 Hz); FAB-MS (NBA)  $m/z = 269$  ( $\text{M}^+$ , C $_{14}\text{H}_9\text{N}_2\text{S}_2^+$ ); UV-vis (acetonitrile)  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ) 230.5 (4.06), 274 (3.95), 297.5 (3.98), 442.5 (3.98) (Calc. for C $_{14}\text{H}_9\text{N}_2\text{S}_2^+$  ClO $_4^-$ : C, 45.59; H, 2.46; N, 7.60. Found: C, 45.29; H, 2.40; N, 7.46%).

#### 5,5'-Di(1-pyridinio)-2,2'-bithiophene diperchlorate (2e)

The title compound **2e** was isolated by Al $_2$ O $_3$  preparative thick-layer chromatography (Merck 150F $_{254}$ ) with CH $_3$ OH–CH $_2$ Cl $_2$  (15 : 85) as eluent. Yield 50%, yellow powder; FT-IR (KBr)  $\nu$  3090 (aromatic C–H stretching), 1617 (C=N stretching), 1440 (aromatic ring stretching), 1085 [ $\nu(\text{ClO}_4^-)$ ], 775 (C–H out-of-plane bend)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (270 MHz; DMSO- $d_6$ ; Me $_4$ Si)  $\delta$  9.38 (d, 4H,  $J = 5.67$  Hz,  $\alpha\text{H}$  of pyridinium), 8.76 (t, 2H,  $J = 7.83$  Hz,  $\gamma\text{H}$  of pyridinium), 8.30 (t, 4H,  $J = 6.48$  Hz,  $\beta\text{H}$  of pyridinium), 7.88 (d, 2H,  $J = 4.32$  Hz), 7.69 (d, 2H,  $J = 4.32$  Hz); FAB-MS (NBA)  $m/z = 422$  [ $\text{M}^{2+} + \text{ClO}_4^-$ , C $_{18}\text{H}_{14}\text{N}_2\text{S}_2(\text{ClO}_4)^+$ ], 161 ( $\text{M}^{2+}$ , C $_{18}\text{H}_{14}\text{N}_2\text{S}_2^{2+}$ ); UV-vis (acetonitrile)  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ) 366 (3.94), 253.5 nm (4.18) (Calc. for C $_{18}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_8\text{S}_2$ : C, 41.47; H, 2.71; N, 5.37. Found: C, 41.18; H, 2.79; N, 5.20%).

#### 5-(1-Pyridinio)-2,2':5',2''-terthiophene perchlorate (3)

Yield 85%, red powder; FT-IR (KBr)  $\nu$  3068 (aromatic C–H stretching), 1624 (C=N stretching), 1475 (aromatic ring stretch-

ing), 1091 [ $\nu(\text{ClO}_4^-)$ ], 833 (C–H out-of-plane bend)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (270 MHz; DMSO- $d_6$ ; Me $_4$ Si)  $\delta$  9.38 (d, 2H,  $J = 5.4$  Hz,  $\alpha\text{H}$  of pyridinium), 8.74 (t, 1H,  $J = 7.83$  Hz,  $\gamma\text{H}$  of pyridinium), 8.28 (t, 2H,  $J = 7.29$  Hz,  $\beta\text{H}$  of pyridinium), 7.83 (d, 1H,  $J = 4.05$  Hz), 7.60 (dd, 1H,  $J = 5.13$ , 1.08 Hz), 7.53 (d, 1H,  $J = 4.05$  Hz), 7.50 (d, 1H,  $J = 3.78$  Hz), 7.43 (dd, 1H,  $J = 3.78$ , 1.08 Hz), 7.38 (d, 1H,  $J = 3.78$  Hz), 7.14 (dd, 1H,  $J = 3.78$ , 5.13 Hz); FAB-MS (NBA)  $m/z = 326$  ( $\text{M}^+$ , C $_{17}\text{H}_{12}\text{NS}_3^+$ ); UV-vis (acetonitrile)  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ) 257.5 (3.51), 360 (sh) (3.68), 390 (3.71) (Calc. for C $_{17}\text{H}_{12}\text{NS}_3^+$  ClO $_4^-$ : C, 47.94; H, 2.84; N, 3.29. Found: C, 47.58; H, 2.79; N, 3.39%).

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