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Efficient anodic pyridination of poly(3-hexylthiophene) toward post-functionalization of conjugated polymers

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Nucleophilic substitution reaction of poly(3-hexylthiophene) (P3HT) with pyridine derivatives as nucleophile was demonstrated in anodic oxidation process. The key reaction involves efficient nucleophilic attack of the pyridine derivatives toward thiophene rings in partly oxidized polymer, i.e., doped state, in the similar manner in which anodic pyridination of electrochemically generated π-radical cation of a series of oligothiophene takes place in quantitative yield (Y. Li, K. Kamata, T. Kawai, J. Abe and T. Iyoda, *J. Chem. Soc., Perkin Trans. 1*, 2002, 1135–1140). When 1-methyl-4-(4′-pyridyl)pyridinium hexafluorophosphate ($MPP^+PF_6^-$) was used as a functional nucleophile, the anodic pyridination reaction gave viologen-tailored poly(3-hexylthiophene) (P3HT), which was confirmed by electrochemical and spectroelectrochemical methods. The introduced ratio of viologen units was about 60% with respect to the polaron, *i.e.*, one-electron oxidized state localized over five thiophene units.

Introduction

Polythiophene (**PT**) and its derivatives have received considerable attention among electrically conductive heterocyclic polymers for many years.[1,2] Remarkable progress has been made in the syntheses of tailored conducting polymers from well-designed monomers. Moreover, a post-functionalization[3–5] strategy can also provide an effective way of modifying π-conjugated polymer bearing reactive sites. For example, Holdcroft and Vamvounis have prepared poly(3-bromo-4-hexylthiophene) through bromination of poly(3-hexylthiophene).[4a] Poly(3-bromo-4-hexylthiophene) was further applied as a starting substrate to convert the bromo group into aryl, vinyl and alkynyl side chains through Pd-catalytic coupling reactions.[4b,4c] The post-functionalization of the π-conjugated polymers, such as polyacetylene, polyaniline, polypyrrole, and polythiophene, has received a large amount of attention in recent years with respect to widely controlled modification.[3–5]

Recently, we have shown[6] that π-radical cations of oligothiophene can exclusively react with pyridine derivatives to yield 2-pyridiniooligothiophenes similar to the anodic pyridination reaction of aromatic compounds reported before.[7] The reaction is governed by the oxidation potential of the oligothiophenes and nucleophilicity of the pyridine derivatives. This kind of synthetic strategy is based on the high reactivity of the electrochemically generated oligothiophene π-radical cations as intermediates, which have potential to be attacked by nucleophiles.

It is well known that π-radical cations should become more stable and less reactive as the number of repeated thiophene units increases.[1] Can π-radical cations of polythiophene be attacked by a nucleophile, for example, pyridine derivatives? The answer is positive. This reaction may be lead to post-functionalization of conjugated polymers by introducing pyridine derivatives as functional nucleophiles based on anodic nucleophilic substitution reactions.

To extend the application field of anodic pyridination reactions of oligothiophene, we have set out to examine the reaction for polythiophene as the extended π-conjugated system. Our original exploration focuses on poly(3-hexylthiophene) (**P3HT**) based on the following considerations: a) both chemical and electrochemical polymerization are available and b) the solubility and processability of **P3HT** may be lead to the study of solution chemical processes by choosing suitable oxidants and nucleophiles.

In this study, the anodic pyridination of pristine **P3HT** films has been developed. The modification of **P3HT** with photoelectrochemical active pyridinium units was demonstrated by cyclic voltammetry (CV), FT-IR and *in-situ* spectroelectrochemical techniques. The amount of nucleophile introduced was calculated based on an electrochemical analysis method.

Results and discussion

Phenomena

A neutral (insulating state) **P3HT** film on the surface of a Pt electrode looks red. When 1.5 V of potential was applied to the **P3HT** film in acetonitrile containing 0.1 M $TBAPF_6$, the film color changed to blue due to an anodic doping process. The red color reappeared when more cathodic potential than 0 V was applied. The redox process of the film with the color change is reversible. This evidence has been well accepted in polythiophene derivatives as the electrochemical doping–undoping process with electrochromism.[1,2] The doped state is known to be stable in air or in solution. When the doped blue film was immersed in 0.1 M $TBAPF_6$–CH_3CN solution containing 0.1 M pyridine, it changed from blue to red immediately. Nothing changed in 0.1 M $TBAPF_6$–CH_3CN solution without pyridine. Apparently, some reaction with pyridine, followed by the undoping process seemed to take place in the presence of pyridine, which was our motivation to begin this study.

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Cyclic voltammetry

To investigate what happened in the presence of pyridine, cyclic voltammetry was used to monitor the possible following reaction between electrochemically generated doped **P3HT** with pyridine. As shown in Fig. 1, the dashed lines in both a and b show the typical cyclic voltammograms indicating reversible doping (oxidation) and undoping (reduction) processes of the pristine **P3HT**. This change can be repeated hundreds of times with no obvious difference. When the electrode potential was scanned from 0 V in the anodic direction in the presence of 0.1 M pyridine, a large anodic wave centered at *ca.* 1.30 V appeared but no corresponding cathodic wave was observed even in the first reverse scan, as shown in Fig. 1a. After that the resulting film looked red and gave non-Faradaic response in a potential range up to 2.0 V.

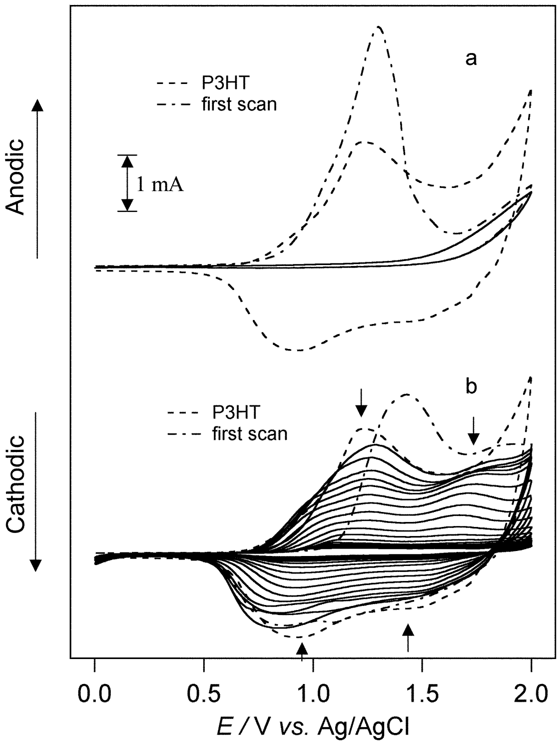
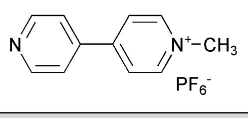


Fig. 1 Cyclic voltammograms of the pristine **P3HT** film in CH_3CN solution containing 0.1 M $TBAPF_6$ in the presence of (a) 0.1 M pyridine and (b) 0.1 M $\mathbf{MPP^+PF_6^-}$. Scan rate: 100 mV s^{-1}. Pt stick electrode: ϕ 1 × 5 mm. The pristine **P3HT** film was prepared by passing 100 mC of electrolysis charge. The doping–undoping processes of pristine **P3HT** are shown as dashed lines (—) in (a) and (b), respectively.

Moreover, as a weaker nucleophile than pyridine and a precursor of the viologen structure, 1-methyl-4-(4′-pyridyl)pyridinium hexafluorophosphate ($\mathbf{MPP^+PF_6^-}$) was used in the CV measurement.[8] Fig. 1b shows the cyclic voltammogram of the film treated with 0.1 M $\mathbf{MPP^+PF_6^-}$. Different from the case of pyridine, the peak current and reversibility decreased gradually during the potential scanning process, which can be attributed to the reaction between the doped **P3HT** and the $\mathbf{MPP^+}$ nucleophile. The first anodic scan shows the larger anodic peak current than that of the fresh film. The peak potential was shifted anodically and located at 1.44 V. From the second scan, the anodic peak went back to 1.30 V and the anodic current decreased gradually with the increasing number of scanning. After 20 cycles of the potential scanning, the film gave non-Faradaic response in this potential range and the red film was swollen on the surface of the Pt stick electrode.



FT-IR measurement

Further evidence for the reaction of the doped **P3HT** with the pyridine derivatives was obtained from infrared spectroscopy. 3-Acetylpyridine was adopted as a nucleophile having a characteristic IR probe such as a carbonyl group. The **P3HT** film was treated with potentiostatic electrolysis at 1.60 V in CH_3CN containing 0.1 M 3-acetylpyridine by controlling the passed charges. The modified film was carefully peeled out of the electrode surface for FT-IR measurement (KBr pellet). Representative spectra as a function of passed charges (*Q*) during the electrolysis are displayed in Fig. 2c–2f, which were normalized as internal standards by the absorption at 2928 cm^{-1} assigned to the alkyl chain of the **P3HT**. The FT-IR spectra of 3-acetylpyridine (a) and neutral pristine **P3HT** (b) were also collected for comparison.

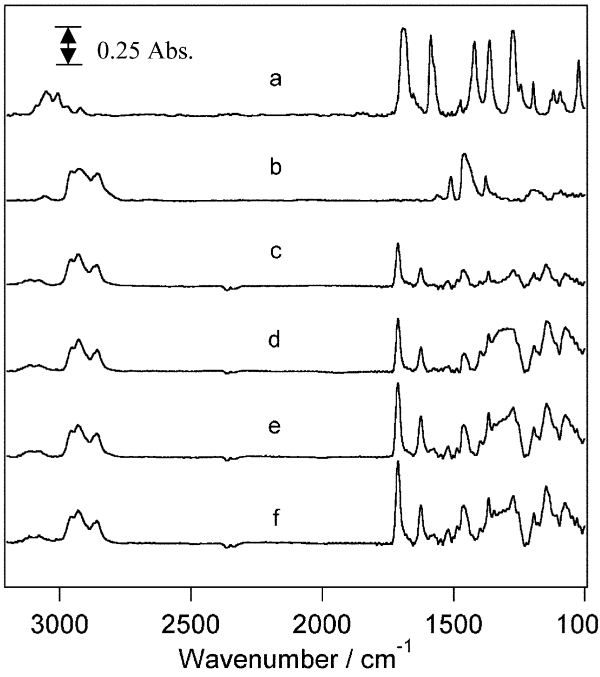


Fig. 2 FT-IR spectra of (a) 3-acetylpyridine and (b) neutral **P3HT** and modified **P3HT** film with 0.1 M 3-acetylpyridine–CH_3CN solution containing 0.1 M $TBAPF_6$ at 1.60 C with respect to different electrolysis charges (1, 2, 4 and 8 mC corresponding to the spectra c, d, e, and f). Pt stick electrode: ϕ 2 × 5 mm, 160 mC electrolysis charges were passed for the preparation of film.

As shown in Fig. 2c–2f, the modified **P3HT** film with 3-acetylpyridine presents two noticeable features at 1711 cm^{-1} (C=O) and 1624 cm^{-1} (C=N) due to the formation of 3-acetylpyridinium[9] attached to the polymer. A shift toward high-wavenumber was revealed in the comparison of the free 3-acetylpyridine at 1690 cm^{-1} (C=O) and 1586 cm^{-1} (C=N) (Fig. 2a). With increasing the passed charges, the peak intensity of both the C=O and C=N groups increased monotonously. The broad peak at 840 cm^{-1} (not shown in Fig. 2) assigned to the counter ions, PF_6^-, was observed, which is further strong evidence to support the formation of 3-acetylpyridinium on the **P3HT** main chain.

Cyclic voltammetry of the modified P3HT film

The red swollen film obtained by potential scanning in the presence of the pyridine derivatives as nucleophiles showed non-Faradaic processes in the range of the doping–undoping that the pristine film shows (Fig. 1). After rinsing carefully with freshly distilled CH_3CN several times, the film on the electrode was immersed into a deaerated CH_3CN solution containing 0.1 M $TBAPF_6$ without nucleophiles. Compared to the pristine film (Fig. 3a) in the range of −1.50 and 0 V, the film modified

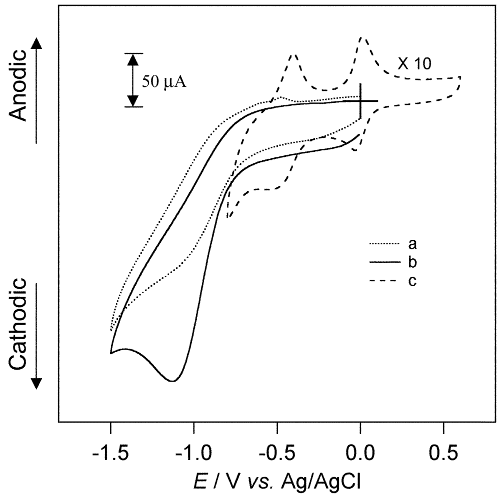


Fig. 3 Cyclic voltammograms of (a) the pristine **P3HT** film, (b) the film modified with pyridine, and (c) film modified with **MPP$^+$PF$_6$$^-$** in CH_3CN solution containing 0.1 M $TBAPF_6$. Pt stick electrode: ϕ 1 × 5 mm; scan rate: 100 mV s^{-1}. The characteristic redox responses corresponding to pyridinium (b) and viologen (c) units were observed in the modified films.

with pyridine shows a cathodic reduction peak (Fig. 3b) at −1.12 V, characteristic of a redox process of a pyridinium compound.[10]

To our interest, the film modified by **MPP$^+$PF$_6$$^-$** shows two sets of reversible redox peaks at −0.01 and −0.45 V (Fig. 3c) when scanned between −0.8 V and 0.6 V, which was attributed to the formation of electrochemically active viologen units through the reaction of doped **P3HT** with **MPP$^+$PF$_6$$^-$** nucleophile. In this case, the redox potential of the formed viologen units shifted rather anodically than those of methylviologen (−0.42 and −0.84 V in 0.1 M $TBAPF_6$–CH_3CN solution). This anodic shift may be due to strong interaction among the viologen units, conjugated to each other through **P3HT** main chain. A similar anodic shift was observed in the viologen linked to the *meso*-position of the porphyrin[11] (0.02 and −0.58 V *vs.* SCE).

In-situ potential scanning anodic pyridination

The anodic pyridination of **P3HT** in the presence of the **MPP$^+$** nucleophile was performed with continuous potential scanning in the range of −0.7 to 1.8 V to monitor the total reaction process. The CV of the **MPP$^+$** nucleophile revealed a reversible one-electron reduction peak at $E_{1/2}$ = −0.79 V (100 mV s^{-1}), as shown in Fig. 4a. The pristine **P3HT** film was in a neutral (insulating) state between −0.7 and 0.5 V. A reversible doping–undoping process was found between 0.5 and 1.8 V (Fig. 4b). Once the film was scanned in **MPP$^+$** solution, two sets of reversible reduction peaks ($E_{1/2}$ = −0.01 and −0.50 V) corresponding to the viologen unit were observed even in the first cycle. The peak current increased with increasing number of potential scans and then became saturated. The change in the cyclic voltammogram between 0.5 and 1.8 V looks complicated, and is under investigation (Fig. 4c). Compared to a, b and c, the viologen unit should come from the nucleophilic substitution reaction of the doped **P3HT** with **MPP$^+$**.

Both the electrochemical and FT-IR measurements demonstrate that the doped **P3HT** can react with pyridine derivatives to give a polymer modified with pyridinium units, which is a similar reaction as in the case of the anodic pyridination of oligothiophene. A plausible reaction mechanism is shown in Scheme 1.[12,13]

Introduced amount of viologen units

The pristine **P3HT** film[14] was treated by potentiostatic electrolysis at 1.60 V. A cyclic voltammetry measurement was

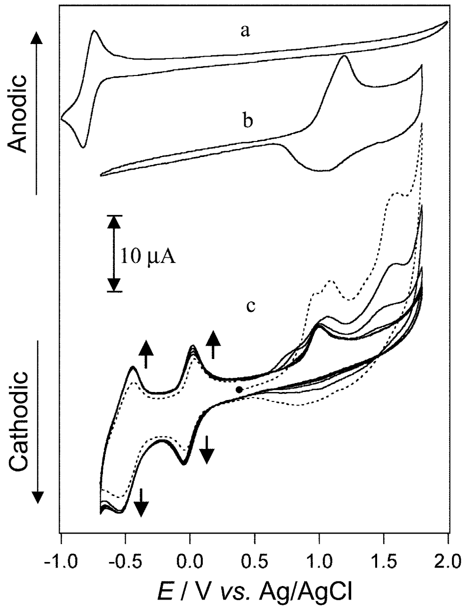
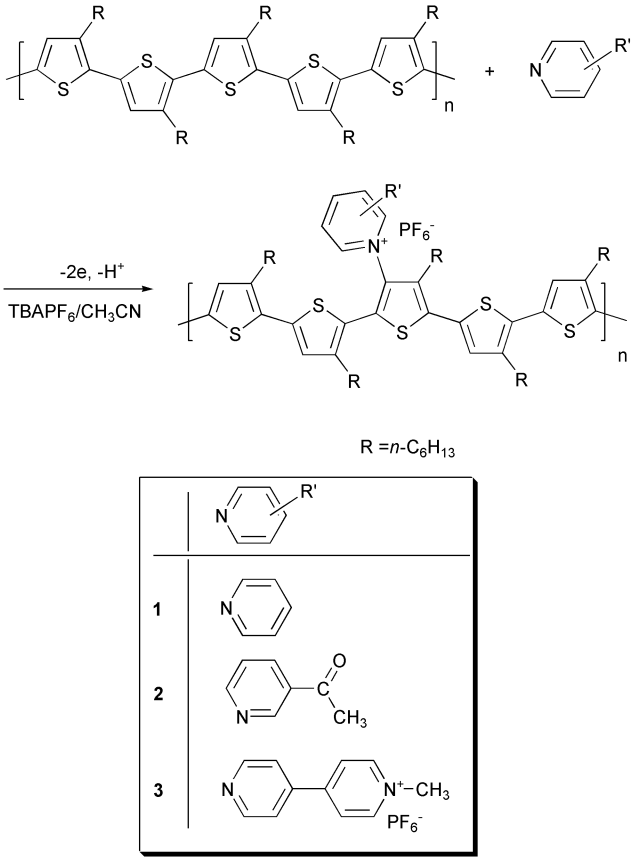


Fig. 4 Cyclic voltammogram of (a) 1 mM **MPP$^+$** nucleophile and (b) the thin **P3HT** film described in ref. 14 in CH_3CN solution containing 0.1 M $TBAPF_6$. *In-situ* anodic pyridination of the thin **P3HT** film was monitored by cyclic voltammetry between −0.7 and 1.8 V in the presence of 0.1 M **MPP$^+$** nucleophile (c). Scan rate: 100 mV s^{-1}. Pt plate electrode: ϕ 1 mm.



Scheme 1 Anodic nucleophilic substitution of polythiophene derivatives in the presence of pyridine derivatives as nucleophiles.

carried out to detect the formed viologen unit[15,16] in the modified polymer. As shown in Fig. 5, the amount of viologen units introduced increased as a function of passed charges in the potentiostatic electrolysis. After 150 μC of charge was passed, the amount of viologen introduced reaches saturation. The oxidation potential of the modified polymer should be shifted anodically due to the strong electron-withdrawing property of

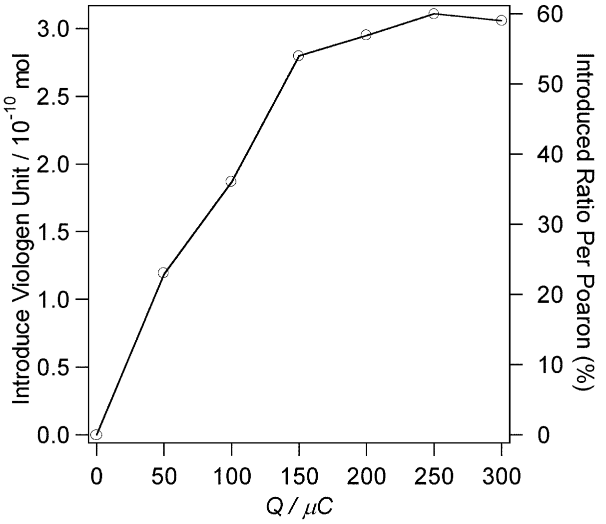


Fig. 5 The amount of viologen units introduced and the introduction ratio per polaron as a function of the passed charges during anodic pyridination with the **MPP**$^+$ nucleophile under 1.60 V. The pristine film contains a 5.2×10^{-10} mol polaron described in ref. 14.

the viologen units. The anodic pyridination gave a maximum of 3.0×10^{-10} mol of viologen units and about 60% of introduced ratio with respect to the polaron, *i.e.*, one-electron oxidized state, which is localized over five thiophene units.

Spectroelectrochemical measurement

A **P3HT** film modified by the **MPP**$^+$ nucleophile was measured by spectroelectrochemical techniques in order to detect the viologen units as describe in the literature.[17] Fig. 6 shows the differential UV-vis spectra of the modified film on an ITO transparent electrode under potentiostatic conditions from 0.0 to −0.7 V at every 100 mV interval. All the spectra at ⩽0.0 V are given by subtraction of the spectrum at 0.1 V. In the potential range from 0.1 to −0.2 V, a broad absorption band appeared over the 500–700 nm region and an intense absorption band around 400 nm was assigned to the viologen cation radical.[17] The first inflection point in the absorbance titration curves at 400 nm and 600 nm (inset) is observed around −0.05 V, close to the first reduction potential obtained in the cyclic voltammogram in Fig. 3c and Fig. 4. In a more negative potential region (−0.2 to −0.7 V), the broad band in the visible region vanished gradually, while the 400 nm intense band remained. The 600 nm titration curve shows a second inflection point around −0.48 V, in good agreement with the second reduction potential of −0.45 V (Fig. 3c) and −0.50 V (Fig. 4). During the two-step reduction process, the film on the ITO electrode looked light brown, blue, and brown successively. Multi-electrochromism including the introduced viologen and the doping–undoping of **P3HT** main chain can be demonstrated. Especially, the multi-electrochromic features such as color change and redox potentials should be designed by controlling the amount of the introduced viologen.

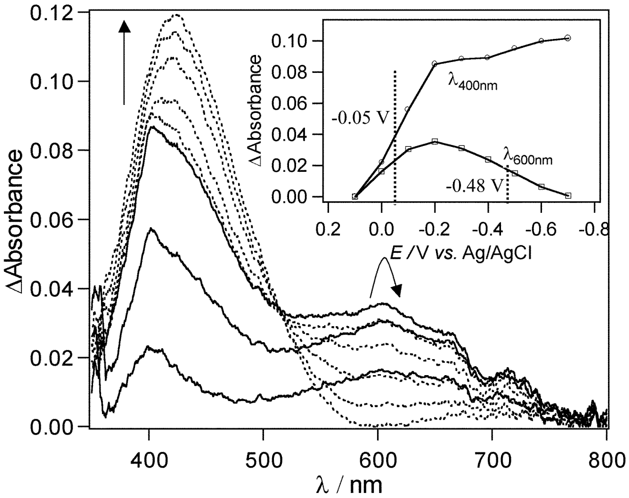


Fig. 6 UV-vis spectra of the **P3HT** film modified by **MPP**$^+$ on an ITO transparent electrode under potentiostatic conditions. All the spectra were subtracted by the spectrum at +0.1 V. The solid lines are the spectra taken at 100 mV intervals from +0.1 to −0.2 V and the dashed line are those from −0.3 to −0.7 V with arrows indicating the absorbance changes. Insert figure: the absorbance at 400 nm (○) and 600 nm (□) as a function of the applied potential. The pristine **P3HT** film resulting from chemical preparation was deposited on the ITO surface by the spin-coating method from 0.2 wt% $CHCl_3$ solution.

While the reduction potentials of the viologen introduced in **P3HT** were independent of its amount, the doping–undoping potentials were strongly influenced by the amount of the introduced viologen. Fig. 7 shows the absorbance titration curves at 750 nm characteristic of the doped polythiophene derivatives[18] by which the doping–undoping process of **P3HT** modified with **MPP**$^+$ could be monitored spectrophotometrically as a function of electrode potential. In the case of the pristine film, the absorbance steeply increased from 0.5 V to a maximum at 1.3 V and then decreased. A 0.9 V of the potential giving half of the maximal absorbance in the first oxidation process is regarded as the doping–undoping potential, $E(\Delta A_{1/2})$.[19] A similar spectrophotometrical measurement was carried out on two kinds of **P3HT** film modified with **MPP**$^+$ in which the undoped **P3HT** film on the electrode was treated with one and five scans in the same electrolytic solution as the case of Fig. 4. Judging from the passed charge of the introduced viologen, these two **P3HT** films are modified with **MPP**$^+$ in 36% and 45% of the introduction ratio per polaron, respectively. The former, lightly modified **P3HT**, shows 1.3 V of the doping–undoping potential, and the latter, heavily modified **P3HT**, shows 1.5 V. This large anodic shift results from the strong electron withdrawing property of the introduced viologen. This observation leads one to tune the electronic band structure, especially the top of the valence band by electrochemical control of the amount of the introduced viologen. The electronic band structure has been controlled so far by molecular design of aromatic compounds as the monomer or repeated unit, in which the band gap energy is determined by the aromatic compound and the band edge potentials can be shifted by the induction effect of the substituent[16,20] Here, the present study provides a new powerful method of continuously controlling the band structure of **P3HT**, and

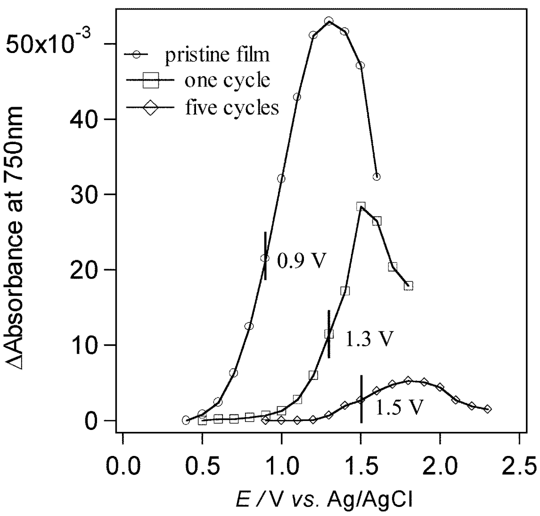


Fig. 7 The absorbance at 750 nm in the difference UV-vis spectra of pristine **P3HT** film (a) modified by MPP$^+$ (b and c) with respect to the applied potential. The pristine **P3HT** film used here is same as the one described in Fig. 6.

possibly any kind of π-conjugated polymer, through the anodic pyridination as post-functionalization. Another feature of the doping–undoping process is a drastic decrease of the maximal absorbance, *i.e.*, 60% for lightly modified **P3HT** and 10% for heavily modified **P3HT**, which indicate the decrease of the doping ratio and will be reported elsewhere.

Conclusion

The anodic nucleophilic substituted reaction of poly(3-hexylthiophene) (**P3HT**) in the presence of pyridine derivatives gives pyridinium-tailored polymers, which was demonstrated by cyclic voltammetry, FT-IR and spectroelectrochemical measurement. This kind of reaction indicated that doped polythiophene has the potential to react with nucleophiles with respect to the π-radical cations of oligothiophene as an extended π-conjugated system. The amount of viologen units introduced by use of 1-methyl-4-(4′-pyridyl)pyridinium hexafluorophosphate (**MPP**$^{+}$**PF**$_6^{-}$) as the nucleophile can be controlled by passed charges with potentiostatic electrolysis. The maximum of the introduced ratio is 60% with respect to the polaron. Post-functionalization of π-conjugated polymers based on anodic pyridination will open a wide road to tuning their electronic band structures and constructing functional electrodes by use of appropriate functional nucleophiles. The present result also encourages us to extend this study to bulk chemical reactions of soluble polythiophene derivatives by selecting suitable oxidants and functional nucleophiles, which is in progress.

Experimental

General remarks

3-Hexylthiophene (Tokyo Kasei), tetrabutylammonium hexafluorophosphate (TBAPF$_6$) and nitrobenzene were used as received. Acetonitrile was refluxed with CaH$_2$ and then distilled. Reagent grade pyridine was distilled from NaOH under a nitrogen atmosphere. 1-Methyl-4-(4′-pyridyl)pyridinium hexafluorophosphate (**MPP**$^{+}$**PF**$_6^{-}$) was synthesized and characterized according to the published literature[21] and followed by ion exchange with NH$_4$PF$_6$. Poly(3-hexylthiophene) was prepared using FeCl$_3$ oxidant as previously described.[22] The head to tail fraction was estimated to be 70% by ^{1}H-NMR. Mw/Mn = 2.61; Mn = 38000 (polystyrene standard).

FT-IR spectra were recorded on a Bio-Rad FTS 3000 in a transmission geometry using the KBr pellet technique. Electrochemical experiments including cyclic voltammetry (CV) were recorded with an HZ-3000 automatic polarization system (Hokuto Denko, Japan). An optical transparent ITO (geometric area: 5 × 20 mm) working electrode on which the **P3HT** was spin-coated, bare ITO counter electrode, Ag/AgCl wire quasi-reference electrode and a 5 mm thick Teflon spacer were assembled into a sandwich-type electrolytic cell for UV-vis–near-IR spectroelectrochemical measurement. The electrode potential was set at intervals of 100 mV. Every spectrum was taken 1 min after the electrode potential was applied. UV-vis–near-IR spectra were carried out in the spectral range of 300–1100 nm on a UV-3100 spectrophotometer (Shimadzu, Japan).

General method for polymer modification

All electrochemical experiments were carried out in conventional H-type cell three-electrode systems under a nitrogen atmosphere at room temperature. The working electrode was a platinum stick (ϕ 1 × 5 mm, and ϕ 2 × 5 mm) or a platinum plate electrode (ϕ 1 mm) sealed in a Teflon tube for electropolymerization and an *in-situ* anodic pyridination reaction. Potentials cited in this study are referenced to the Ag/AgCl wire acting as the quasi-reference electrode.

Polymer films were prepared by electropolymerization under a constant current mode (0.4 mA) from a 0.1 M solution of 3-hexylthiophene monomer in nitrobenzene containing 0.02 M TBAPF$_6$ on a Pt stick electrode.[23] The obtained film on the electrode was rinsed with freshly distilled CH$_3$CN and transferred in another three-electrode cell containing 0.1 M TBAPF$_6$ in CH$_3$CN. A −600 mV of the potential was applied for 20 min to complete the undoping process.

Anodic pyridination reactions were generally carried out in CH$_3$CN solution containing 0.1 M pyridine derivatives by controlled potential electrolysis at 1.60 V or by potential scanning electrolysis. After the reaction, the potential was set to 400 mV for 5 min to reduce the remaining doped state.

Acknowledgements

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8 **MPP**$^{+}$**PF**$_6^{-}$ was a suitable nucleophile for anodic pyridination. The reaction gives a viologen structure. Both the electrochemical and spectroscopic methods are available to confirm the viologen formation. Yi Li *et al.*, unpublished results.

9 1-Methyl-3-acetylpyridinium hexafluorophosphate, as a model compound for FT-IR characterization, was synthesized. FT-IR (KBr): ν_{max}/cm^{-1} 1711 (C=O), 1640 (C=N) and 838 (PF$_6^{-}$, broad).

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12 The reaction scheme described here is based on the following consideration: a) the maximum doping level of polythiophene is about 20%,[1a] that is, one-electron oxidized state localized over five

thiophene rings, and b) the reactive position is mainly the β-position[13] of the polymer backbone. Basically, the electron population of HOMO responsible for the present nucleophilic substitution is higher at the α-position than that at the β-position. Since the reactive sites of the β-position are much more than those of the α-position at both ends of the polymers, the substitution at the β-position is shown in Scheme 1.

13 We have confirmed the reactivity of the β-positions by using 5,5′-dimethyl-2,2′-bithiophene as a reactant for the anodic pyridination. Both 3- and 4-(*N*-pyridinio)-5,5′-dimethyl-2,2′-bithiophene perchlorate were identified as products by means of ^{1}H-NMR and FAB-MS. The β-position is also available for the anodic pyridination.

14 A thin **P3HT** film was used as a substrate to ignore the influence of film thickness, which was electrochemically deposited on a platinum plate electrode (1 mm ϕ) by CV scanning between 0 and 2.0 V from 0.1 M hexylthiophene–CH_3CN solution containing 0.1 M $TBAPF_6$ (one cycle scanning at 100 mV s^{-1}) and then kept at 0 V to complete the undoping process. The polymer contains 5.2×10^{-10} mol of polaron (50 μC calculated from the reversible doping–undoping peak area by assumption of 20% doping level[1a]). The theoretical passed charge should be 100 μC with respect to the polaron because of two electron oxidation processes (Scheme 1). The amount of viologen units introduced was calculated from the area of first reduction peak.

15 Strictly speaking, the number of electrochemically active viologen units can be evaluated by cyclic voltammetry. A part of the introduced viologen might be inert due to the sterically restricted mobility of the counteranion, which has been realized in our study on highly cross-linked polyviologen film and its photoelectrochemical anion recognition.[16] In this case, even the electrochemically determined amount of the viologen should be underestimated here.

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