

Novel Poly-Bridged-Naphthalene with Blue-Light-Emitting Property via Electropolymerization

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ABSTRACT: Relatively scant work was related to poly-naphthalene (PN) and its derivatives because of the unique nonlinear optical properties which make PN and its derivatives owning potential applications in various domains. According to relevant studies, the pursuit for the synthesis of high quality PN films is a great challenge for the applications of PN. To achieve high quality polymer films, three bridged naphthalene derivatives were designed, and finally two crosslinked PN exhibiting space network were electrosynthesized, respectively, by direct anodic oxidation from 1,6-bis(naphthalen-2-yloxy)hexane and 1,4-bis((naphthalen-2-yloxy)methyl)benzene in mixed electrolyte of dichloromethane containing boron trifluoride diethyl etherate. Furthermore, as-formed conducting films were characterized by cyclic voltammetry, spectroscopic

analysis, thermal analysis, and scanning electron microscopy. And the series of characterizations indicated that films hold high stability and good blue-light-emitting property. Meanwhile, these polymer films were smooth, shiny, and flexible easily being processed into various shapes by conventional mechanical methods. Consequently, these high quality PN films will facilitate their potential applications as blue-light-emitting materials in organic light-emitting diode. Because di(naphthalen-2-yl) terephthalate was difficult to electropolymerize, the effects of bridged spacers to polymerization were also discussed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2706–2714, 2012

Key words: conducting polymers; electropolymerization; naphthalene; crosslinked structure

INTRODUCTION

Electrically conducting polymers (CPs) have been a subject of intensive research in which significant progress has been made during the last 30 years. These materials containing a π -conjugated carbon backbone exhibit the novel property of a dynamically changeable conductivity after synthesis, and in addition, the color, volume, wettability, and optical absorption, among other properties, can be tuned by the applied potential also. In recent years, a great deal of researches covering various aspects of the field have appeared, such as light emitting diodes,¹ batteries,² solar cells,³ enzyme immobilization matri-

ces,^{4,5} sensors,^{6,7} photovoltaics,⁸ ion exchange membrane in fuel cells,⁹ drug release systems,¹⁰ and electrochromic devices,¹¹ etc. However, the complexity of these materials makes the pathway from interesting findings to real applications long, and fundamental research on these materials is still needed.

CPs intensively investigated were basically focused on polypyrrole (PPy), polythiophene (PTh), poly(p-phenylene) (PPP), polyaniline (PANI), and poly(3,4-ethylenedioxythiophene) (PEDOT).^{12–14} And recently, increasing work was related to polynaphthalene (PN) and its derivatives, because of their remarkable inherent properties such as intense fluorescence, nonlinear optical properties, and good chemical stabilities. With these properties, PN owns considerable prospect of application in various domains.^{15–21} However, the pursuit for synthesis of high quality polymer films is a great challenge for the applications of PN. And generally, it is difficult to produce high quality and freestanding polymer films by simple and direct electrochemical polymerization of naphthalene and its derivatives. Hence, design and synthesis of novel PN with improved properties are still quite necessary and essential.

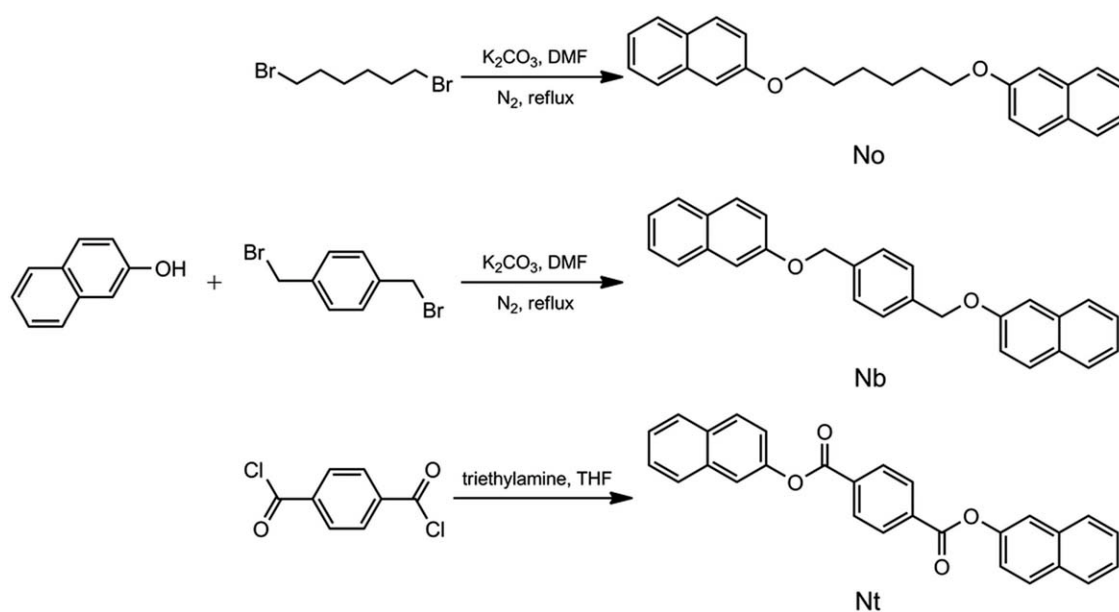
Till date, a series of high quality inherently CPs have been produced by electropolymerization from

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Scheme 1 Synthetic routes of No, Nb, and Nt.

boron trifluoride diethyl etherate (BFEE), which is a middle strong Lewis acid together with high ionic conductivity and good electrocatalytic properties. The complexation of aromatic monomers such as thiophene, benzene, pyrrole, and fused ring aromatic compounds, with BFEE can significantly lower the anodic oxidation potentials of the monomers, which is beneficial to the preparation of high quality CPs.^{22–31} Accordingly, to obtain high quality PN, some tries have been made via electropolymerization in BFEE systems using naphthalene. But unfortunately, the results did not come up to our expectations, which may be attributed to the molecular structures of PN.³²

Because the crosslinked structures in polymers have proven to increase the strength, brittleness, rigidity, or even the elasticity of the resultant polymers,^{33–36} new naphthalene derivatives containing bridge structures were designed and synthesized. And PN containing crosslinked structures were prepared, in which three-dimensional and space networks finally formed. In this article, three monomers 1,6-bis(naphthalen-2-yloxy)hexane (No), 1,4-bis((naphthalen-2-yloxy)methyl)benzene (Nb), and di(naphthalen-2-yl) terephthalate (Nt) were synthesized, and two free-standing bridged naphthalene polymer films poly(1,6-bis(naphthalen-2-yloxy)hexane) (PNo) and poly(1,4-bis((naphthalen-2-yloxy)methyl)benzene) (PNb) were easily electrodeposited by direct anodic oxidation of their monomers in mixed electrolyte of CH_2Cl_2 containing BFEE. The electrochemical properties, fluorescent properties, thermal stability, conductivities, and morphologies of bridged PN films were studied in detail.

EXPERIMENTAL

Materials

Beta-naphthol and terephthaloyl dichloride (analytical reagent, Aladdin, Shanghai, China), 1,6-dibromohexane (98%, Acros Organics, New Jersey), 1,4-bis(bromomethyl)benzene (Acros Organics, New Jersey), *N,N*-Dimethylformamide (DMF), tetrahydrofuran (THF) (analytical reagent, Beijing Chemical Reagent Factory, Beijing, China), dichloromethane (CH_2Cl_2 , analytical reagent, Kermel Chemicals Co. Tianjin, China). BFEE ($1.12 \sim 1.14 \times 10^3 \text{ g L}^{-1}$, $\text{BF}_3 = 48.24\%$; Changyang Chemical Plant, Beijing, China) was purified by distillation and stored at 0°C before use. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4 , 95%; Acros Organics, New Jersey) was dried under vacuum at 60°C for 24 h before use.

Monomers synthesis

1,6-bis(naphthalen-2-yloxy)hexane (No), was synthesized via Williamson reaction of beta-naphthol and 1,6-dibromohexane. K_2CO_3 (1.66 g, 12 mmol), 2-naphthol (1.73 g, 12 mmol), and DMF (5 mL) were added to a round-bottom flask and vigorously stirred at room temperature under argon. After 1 h, 1,6-dibromohexane (1.46 g, 6 mmol) as a solution in DMF (10 mL) was added into the mixture slowly. The final mixture was heated to reflux for 24 h. The reaction solution was poured into 500 mL of water, and the precipitated crude product was collected, dried, and recrystallized from CHCl_3/n -hexane (1 : 1) to afford pure compound as colorless crystals (Scheme 1).

Yield: 1.82 g, 82%. $^1\text{H-NMR}$ (400 MHz CDCl_3): δ 7.77–7.70 (d, 6H), 7.44–7.41 (d, 2H), 7.34–7.30 (d, 2H), 7.26–7.23 (t, 2H), 7.15–7.13 (t, 2H), 4.12–4.09 (t, 4H), 1.70–1.68 (m, 4H), and 1.37–1.31 (m, 4H).

1,4-bis((naphthalen-2-yloxy)methyl)benzene (Nb), was also synthesized via Williamson reaction of beta-naphthol and 1,4-bis(bromomethyl)benzene. K_2CO_3 (1.66 g, 12 mmol), beta-naphthol (1.73 g, 12 mmol) and DMF (5 mL) were added to a round-bottom flask and vigorously stirred at room temperature under nitrogen. After 30 min, 1,4-bis(bromomethyl)benzene (1.58 g, 6 mmol) as a solution in DMF (10 mL) was added into the mixture slowly. The final mixture was heated to reflux for 24 h. The reaction solution was poured into 500 mL of water, and the precipitated crude product was collected, dried, and recrystallized from CHCl_3/n -hexane (1 : 1) to afford pure compound as colorless crystals (Scheme 1).

Yield: 1.82 g, 78%. $^1\text{H-NMR}$ (400 MHz CDCl_3): δ 7.77–7.70 (d, 6H), 7.55–7.53 (t, 2H), 7.44–7.42 (t, 2H), 7.38 (s, 2H), 7.25–7.23 (d, 2H), 7.20 (s, 4H), and 5.21 (s, 4H).

Di(naphthalen-2-yl) terephthalate (Nt), was synthesized via alcoholysis reaction of terephthaloyl dichloride. Terephthaloyl chloride (3.0 g, 0.0144 mol), dissolved in 100 mL THF was taken in three-necked reaction flask fitted with a stirrer, a condenser, and dropping funnel. Beta-naphthol (5.18 g, 0.036 mol) and triethylamine (25 mL, 0.180 mol) dissolved in THF (25 mL) was added drop wise to terephthaloyl chloride solution at 0°C . The reaction mixture was stirred for 16 h at room temperature. After completion of reaction, triethylamine hydrochloride was removed by filtration. Sufficient distilled water was added to the stirred filtrate. The separated solid was filtered, washed repeatedly with water, and dissolved in ethyl acetate. Undissolved solid (terephthalic acid) was removed by filtration. The filtrate was washed with 5% sodium carbonate and sodium chloride solution, respectively. The organic layer was dried over anhydrous sodium sulfate, filtered, and solvent was removed under vacuum. Single product spot was confirmed by thin layer chromatography with ethyl acetate and heptane 1 : 1 (by volume) as an eluent. Finally, we obtained pink powder (Scheme 1).

Yield: 3.85g, 64%. $^1\text{H-NMR}$ (400 MHz CDCl_3): δ 8.01 (s, 4H), 7.86–7.85 (q, 4H), 7.76–7.75 (d, 2H), 7.57–7.56 (t, 2H), 7.48–7.47 (t, 2H), 7.40 (s, 2H), and 7.17–7.16 (d, 2H).

Electrosynthesis and electrochemical examinations

Electrochemical polymerization and examinations were performed in a one-compartment cell with a model 263A potentiostat/galvanostat (EG&G Princeton Applied Research) under computer control. For

electrochemical examinations, the working and counter electrodes were a Pt wire with diameter of 0.5 mm and a stainless steel wire with diameter of 1 mm, respectively. They were placed 5 mm apart during the experiments. To obtain a sufficient amount of polymer for characterization, stainless steel sheets with surface areas of 4 and 6 cm^2 were used as the working and counter electrodes, respectively. It should be emphasized here that the use of Pt electrodes or stainless steel sheets has little impact on the electrochemical polymerization. The aforementioned electrodes were carefully polished with abrasive paper (1500 mesh), and successively cleaned with water and acetone, and then dried in air oven before every examination. All potentials were referred to Ag/AgCl electrode in the binary solvent systems of $\text{CH}_2\text{Cl}_2 + \text{BFEE}$ and $\text{CH}_2\text{Cl}_2 + \text{Bu}_4\text{NBF}_4$, and all the solutions were deaerated by a dry nitrogen stream and maintained under a slight overpressure through all the experiments. The polymer films were grown potentiostatically and their thickness was controlled by the total charge passed through the cell, which was read directly from the current-time (I - t) curves by computer. After polymerization, the polymer films were washed repeatedly with anhydrous diethyl ether to remove the electrolyte and monomers. For solid spectral analyses, the polymer films were deposited on an indium-tin-oxide (ITO) coated glass.

Characterizations

The electrical conductivity of the obtained polymer films was determined by applying a conventional four-probe technique with free-standing films of the sample. Ultraviolet-visible (UV-vis) spectra were measured with a UV-vis-near-infrared spectrophotometer (Perkin-Elmer Lambda 900). Fluorescence spectra were determined with a fluorescence spectrophotometer (Hitachi F-4500). Thermogravimetric analysis was performed with a TG/DTA thermal analyzer (Perkin-Elmer Pyris Diamond) under a nitrogen stream at a heating rate of 10 K min^{-1} . Scanning electron microscopy (SEM) measurements were made with a Cold Field Emission Scanning Electron Microscope (Tescan VEGA\LSU).

RESULTS AND DISCUSSION

Synthesis and electropolymerization of monomers

Monomers No, Nb, and Nt were synthesized as described in the literatures,^{37–39} and synthetic procedures for monomers are shown in Scheme 1.

The No has low solubility in many organic solvents except CH_2Cl_2 . Moreover, our previous studies demonstrated that the addition of a certain amount

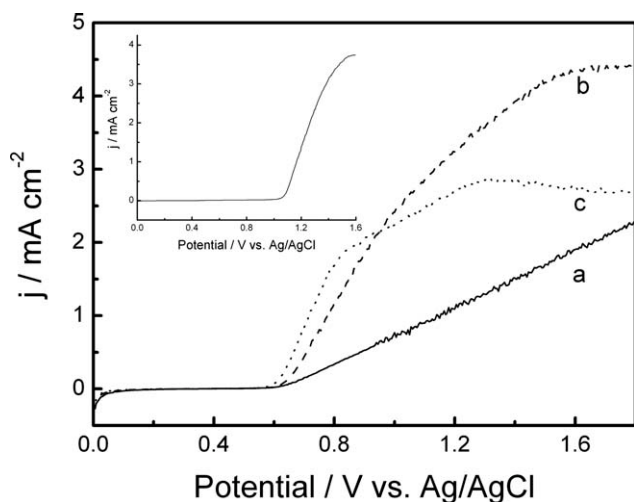


Figure 1 Anodic polarization curves of No in mixed electrolytes of CH_2Cl_2 containing 10% (a), 30% (b), and 50% (c) BFEE (by volume) and CH_2Cl_2 containing 0.1 mol L^{-1} Bu_4NBF_4 (inset). Potential scanning rate: 50 mV s^{-1} ; j is the current density.

of BFEE into CH_2Cl_2 as a mixed electrolyte could further improve the ionic conductivity of the electrolyte to obtain high quality polymer.⁴⁰ So, we chose CH_2Cl_2 as the solvent for the 0.005 mol L^{-1} No and added a series of different volume percentages (i.e., 10%, 30%, and 50%) of BFEE as supporting electrolyte. Figure 1 shows the anodic polarization curves of No tested, respectively, in the mixed electrolyte of $\text{CH}_2\text{Cl}_2 + \text{BFEE}$ and $\text{CH}_2\text{Cl}_2 + 0.1 \text{ mol L}^{-1} \text{Bu}_4\text{NBF}_4$.

The onset oxidation potentials of No in $\text{CH}_2\text{Cl}_2 + \text{BFEE}$ were initiated much lower than that in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ mol L}^{-1} \text{Bu}_4\text{NBF}_4$ ($1.10 \text{ V vs. Ag/AgCl}$), as shown in the inset of Figure 1. The addition of 10, 30, and 50% BFEE (by volume) into CH_2Cl_2 further decreased the oxidation potential of the monomer significantly to about 0.66, 0.63, and 0.60 V [Fig. 1(a–c)], respectively. This phenomenon is attributed to the interactions of BFEE with the aromatic ring of the monomer, which reduce its resonance stability through the formation of π -complex between the monomer and BFEE, thus making electron loss from it much easier.

The oxidative electrochemical polymerization of No was performed via potentiodynamic technique. The successive cyclic voltammograms (CVs) of No (0.005 mol L^{-1}) in the different mixed electrolytes are illustrated in Figure 2. The CVs of No in $\text{CH}_2\text{Cl}_2 + \text{BFEE}$ [Fig. 2(b–d)] show distinct reduction waves of the polymer, while the corresponding oxidation waves are overlapped with the oxidation waves of the monomer and cannot be observed clearly. The potential shifts of the reduction wave current maximum provides information about the increase of the electrical resistance in the polymer film and the over-potential needed to overcome the resistance.⁴¹ Meanwhile, the color of the solutions close to the working electrode all changed slightly from colorless to red, indicating that part of the monomer was oxidized. As the CV scan continues, red film formed on the surface of working electrode. However, the

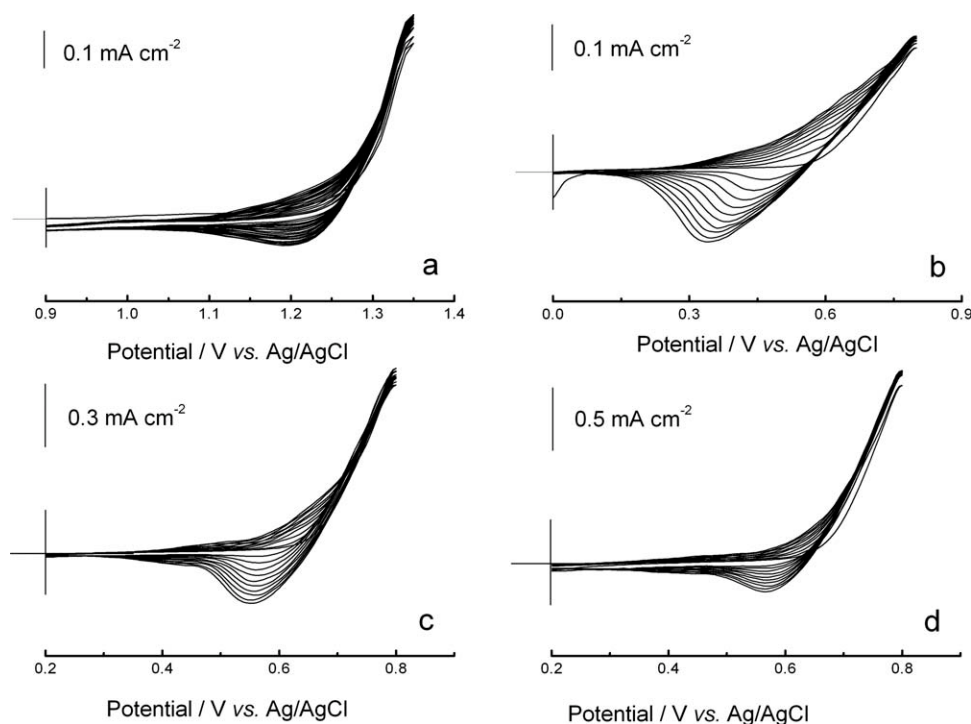


Figure 2 CVs of 0.005 mol L^{-1} No in CH_2Cl_2 containing $0.1 \text{ mol L}^{-1} \text{Bu}_4\text{NBF}_4$ (a), and mixed electrolytes of CH_2Cl_2 containing 10% (b), 30% (c), and 50% (d) BFEE (by volume). The potential scanning rates was 100 mV s^{-1} .

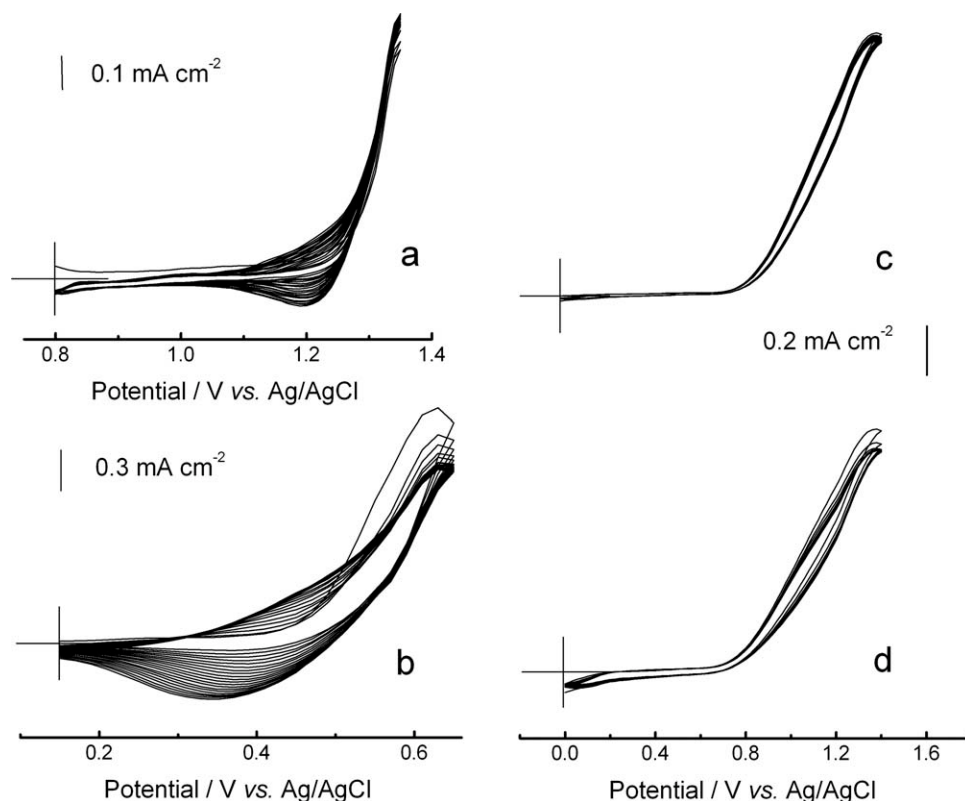


Figure 3 CVs of 0.005 mol L^{-1} Nb in CH_2Cl_2 containing 0.1 mol L^{-1} Bu_4NBF_4 (a), and mixed electrolytes of CH_2Cl_2 containing 30% BFEE (by volume) (b). CVs of 0.005 mol L^{-1} Nt in CH_2Cl_2 containing 0.1 mol L^{-1} Bu_4NBF_4 (c), and mixed electrolytes of CH_2Cl_2 containing 30% BFEE (d). The potential scanning rates was 100 mV s^{-1} .

successive CVs of No in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ mol L}^{-1}$ Bu_4NBF_4 [Fig. 2(a)] were not very successful, and only small amount of deformed polymer was observed on the electrode surface after repeated potential scanning. Thus, the CH_2Cl_2 containing BFEE system was a better medium.

For Nb and Nt, as solubility was similar to No, their electrochemical examinations were also performed in the $\text{CH}_2\text{Cl}_2 + \text{Bu}_4\text{NBF}_4$ and $\text{CH}_2\text{Cl}_2 + \text{BFEE}$, respectively. Figure 3(b) shows CVs of Nb in $\text{CH}_2\text{Cl}_2 + 30\%$ BFEE (by volume). In the first cycle, Nb oxidation occurred at 0.45 V (vs. Ag/AgCl), and in the subsequent cycles, the current increased due to the deposition of the polymer. In some medium, the oxidation potential of Nb was lower than that of No at 0.63 V , which could be attributed to the grant electron effect of benzyl. Following the oxidation of monomer, a polymer film quickly grew on Pt electrode surface. The CVs also showed an irreversible oxidation at 0.55 V , which refers to the further oxidation of the monomer. The CVs of Nb were also tested in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ mol L}^{-1}$ Bu_4NBF_4 [Fig. 3(a)], but only trace amount of the polymer was observed on the electrode surface.

However, there have been no polymer films of Nt electrodeposited on the electrode surface via electropolymerization in two mediums. It can be seen that

the CVs of Nt in $\text{CH}_2\text{Cl}_2 + \text{Bu}_4\text{NBF}_4$ and $\text{CH}_2\text{Cl}_2 + 30\%$ BFEE show no apparent redox waves [Fig. 3(c,d)]. By comparing the molecular structure of Nb and Nt, it could reasonably be speculated that the carbon-oxygen double bonds ($\text{C}=\text{O}$) of ester as electron-withdrawing group made electron loss from aromatic ring difficult, thus hindering the occurrence of electropolymerization. Therefore, the subsequent characterizations were mainly focused on PNo and PNb. Considering the quality of obtained polymer films, the binary solvent system consisting of CH_2Cl_2 and 30% BFEE was selected for their electropolymerization.

Electrochemistry of PNo and PNb

Cyclic voltammetry is a valuable and convenient tool for monitoring the electroactivity of the polymer film coated on the electrode, because the electron transfer between the solution species and the electrode must occur by tunneling either through the film or through the defects in the film. Hence, the electrochemical behaviors of two PN films were studied in monomer-free $\text{CH}_2\text{Cl}_2 + 30\%$ BFEE [Fig. 4(A,B)]. It is evident that all the steady-state CVs display broad anodic and cathodic peaks, and the peak current densities are proportional to the potential scan rates [insets of Fig. 4(A,B)], indicating that a reversible

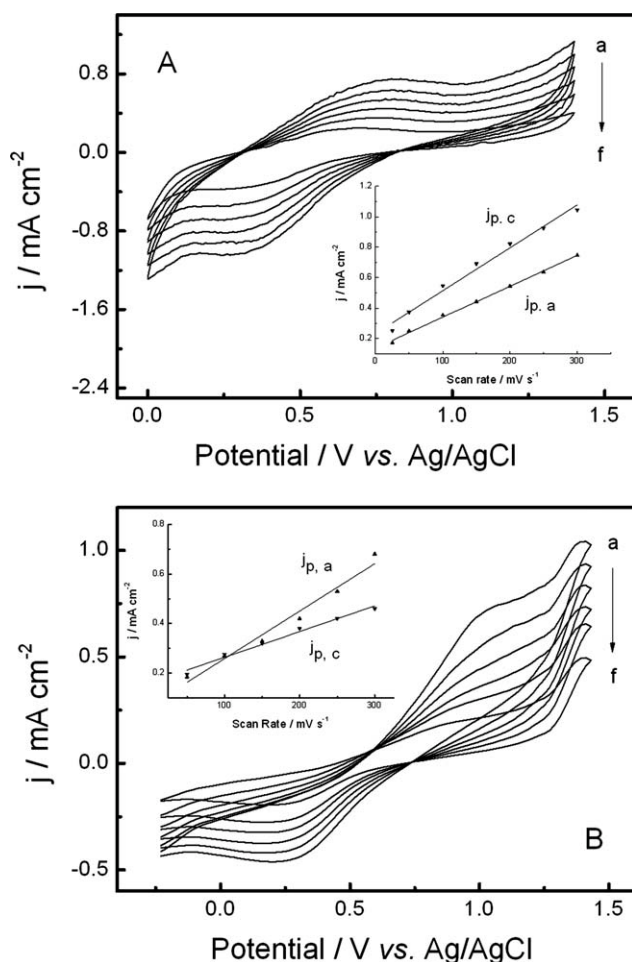


Figure 4 CVs of PNo (A) and PNB (B) films in monomer-free CH_2Cl_2 containing 30% BFEE, at potential scanning rates of 300, 250, 200, 150, 100, and 50 mV s^{-1} (from a to f). The PNo and PNB films were synthesized electrochemically in $\text{CH}_2\text{Cl}_2 + 30\%$ BFEE at constant applied potential of 0.91 and 0.88 V vs. Ag/AgCl, respectively. j , j_p , $j_{p,a}$, $j_{p,c}$ are defined as the current densities, the peak current densities, the anodic peak current densities, and the cathodic peak current densities, respectively.

redox couple were fixed on the electrode and the redox processes were not controlled by diffusion limited.⁴¹ Furthermore, these polymer films could be repeatedly cycled between the conducting (oxidized) and insulating (neutral) states without significant decomposition, indicating the high redox stability. According to Figure 4, PNo could be oxidized and reduced from 0.83 V (anodic peak potential, E_a) to 0.28 V (cathodic peak potential, E_c) and from 1.01 V (E_a) to 0.23 V (E_c) was needed for PNB. The differences between E_a and E_c related to the kinetics of doping-dedoping reaction are equal to 0.55 V and 0.78 V in $\text{CH}_2\text{Cl}_2 + 30\%$ BFEE. From these results, we could reasonably conclude that the doping-dedoping reaction of PNo was faster than PNB in the monomer-free solution, i.e., $[(\text{C}_2\text{H}_5)_3\text{O}]^+\text{BF}_4^-$ as doping anions in BFEE solution moved into and out of the PNo

more easily than PNB, which may be attributed to different steric hindrance of polymer chains.

Spectra characterizations

PNo and PNB films were deposited electrochemically from CH_2Cl_2 containing 30% BFEE (by volume), and constant applied potential were 0.91 and 0.88 V vs. Ag/AgCl, respectively. During the potentiostatic process, the colors of solutions progressively darkened. This indicated that there were soluble oligomers formed during anodic oxidation. With the propagation of polymerization, a few of the soluble oligomers became insoluble and were deposited on the working electrode with elongation of the polymer main chain. However, there were still some oligomers diffused away from the electrode, making the color of the solution dark. The PNB was similar to PNo which owned poor solubility in common polar solvents, such as ethanol, chloroform, and tetrahydrofuran, and could be partly dissolved in DMSO. But the dissolved parts were deemed to be oligomers which doped into the polymer backbones during the electropolymerization of monomers. They owned the higher molecular weight than the monomers which diffused into electrolyte solution and were denoted herein by ONo and ONb, respectively. These oligomers could be demonstrated by the following UV-vis and fluorescence spectra. The dissolved parts of PNo and PNB in DMSO were, respectively, red and dark red in color and both could turn to intense bluish violet fluorescence under the UV light. The undissolved parts still held free-standing films as the polymer with high degree of polymerization.

UV-vis spectra

The UV-vis spectra of monomers and polymers are shown in Figure 5. Two monomers of No and Nb showed the strong absorptions at 300–350 nm (A-a and B-a), which were typically absorptions of naphthalene owned narrow peaks with fine structures. In the same region, the spectra of the dissolved parts of PNo and PNB in DMSO also showed strong absorptions (A-b and B-b), which could be assigned to the unpolymerized naphthalene at one end of bridged naphthalene in crosslinked structures. In addition, other broader absorptions could be found from 350 to 400 nm, which indicated a wider molar mass distribution of the polymer during the electrosynthesis. Generally, a longer wavelength in spectra usually indicates longer polymer sequences.⁴² The red shifts of UV-vis spectra in comparison with the monomer means higher conjugate backbones,⁴³ but the fairly small values indicated that the polymer sequences of the oxidation product were not very long and it

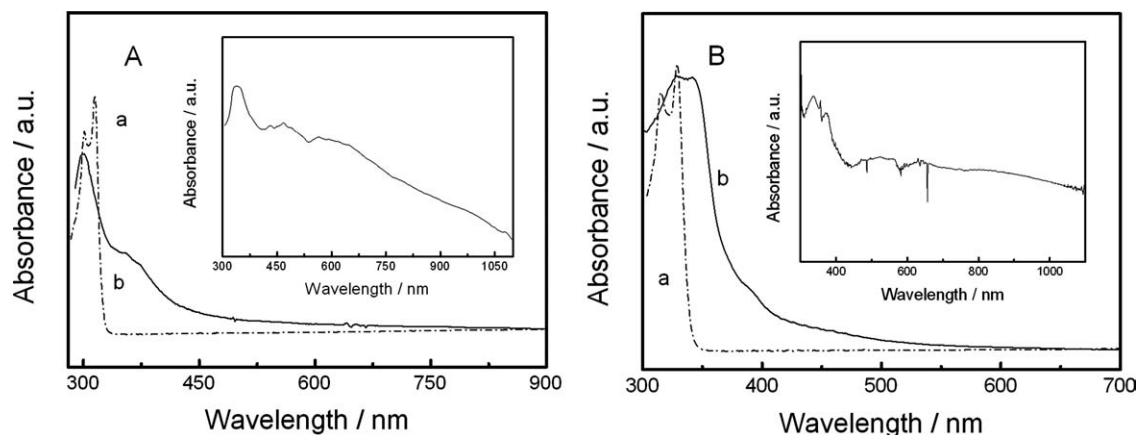


Figure 5 UV-vis spectra of No (A-a), Nb (B-a), ONo (A-b) and ONb (B-b) dissolved in DMSO. Insert: UV-vis spectra of the PNo and PNb films in solid-state on ITO electrode, respectively.

could only be called oligomer. While the UV-vis spectra of PNo and PNb as solid films coated on ITO transparent electrode showed broad characteristic absorptions from 400 to 500 nm, which were ascribed to high conjugate backbones forming highly crosslinked polymer films. These absorption peaks were due to the valence band-conduction band (π - π^*) transition of polymer, while the broad absorptions tailed off to 600 nm and longer were the characteristics of conductive species such as the existence of polarons or bipolarons. These spectral results confirmed the formation of conjugated polymers with broad molar mass distribution.

Fluorescence spectra

The fluorescence spectra of No, Nb, the dissolved parts of PNo and PNb in DMSO, and solid films of polymer coated on ITO were recorded, as shown in Figure 6. From Figure 6(A), an emission peak at 350 nm illustrated the emission spectrum of No, and strong emission peaks of ONo could be found at 388 nm when excited at 300 nm. The fairly small red

shift of spectrum indicated a low degree of polymerization for ONo, and it owned near UV fluorescence emission. Similarly, for ONb in Figure 6(B), when excited at 310 nm, one near UV emission peak at 381 nm would emerge, which exhibited small red shift compared with the emission of monomer at 355 nm. These fluorescence emissions at 388 and 381 nm showed remarkable blue-shift compared with the emission of electropolymerized PN (417 nm),^{44,45} which further proved the formation of oligomers. Additionally, the fluorescence of PNo solid film showed a broad emission band with two intensive peaks at 385 and 414 nm, which could obviously be related to the ONo and PNo, respectively. For the film of PNb, two intensive peaks also appeared and were located at 380 and 411 nm, respectively. It should be noted here that PNo and PNb showed slight blue-shift compared with the emission of electropolymerized PN, probably because the introduction of bridged groups decreased the effectively conjugated configuration of as-formed polymer based on the following two reasons: (1) increasing steric hindrance; (2) stabilizing the radical cations due to

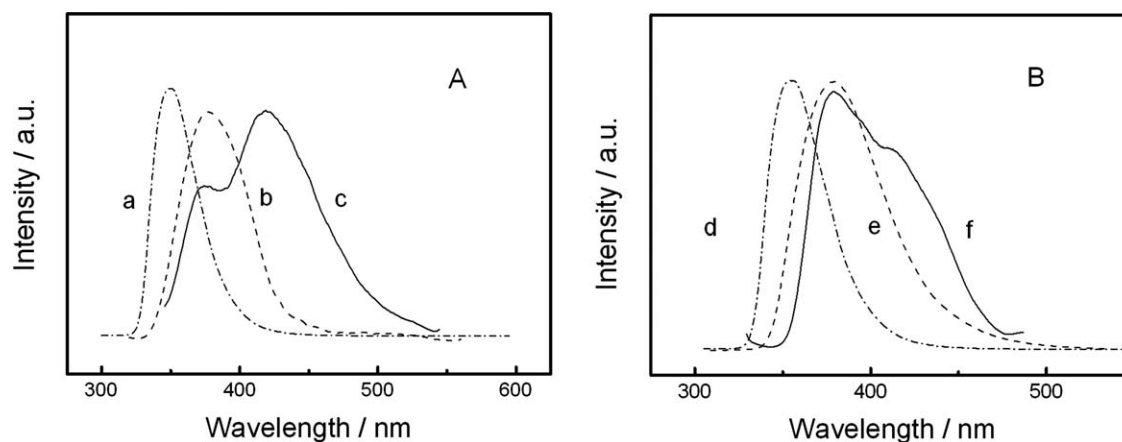


Figure 6 Emission spectra of No (a), Nb (d), ONo (b), and ONb (e) in DMSO, PNo (c) and PNb (f) on the ITO glass.

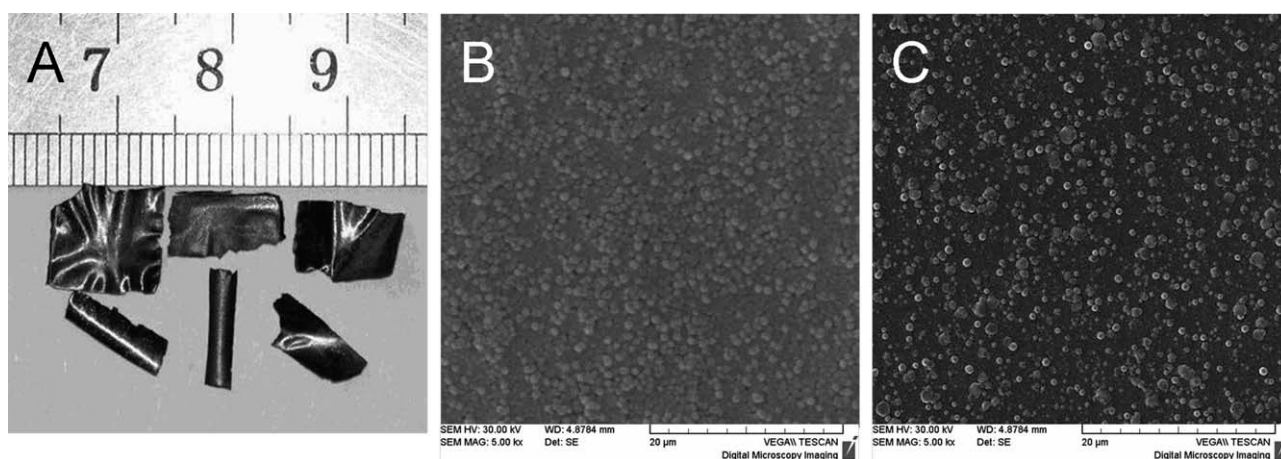


Figure 7 Photograph of PNb films peeled from stainless steel sheet (A) and SEM micrographs of PNo (B) and PNb (C) films deposited on the ITO glass electrode surface.

its electron-donating nature.⁴⁶ All these spectral results confirmed the occurrence of electrochemical polymerization and the formation of conjugated systems owned different emissions, such as near UV and blue fluorescent light, due to various conjugated chain lengths. Therefore, these oligomers and polymers will facilitate their potential applications in organic light emitting diode.

Morphology

As-formed films were very flexible, shiny and could easily be peeled from the working electrode, i.e., stainless steel sheet, as free-standing films so that they could be easily processed into various shapes by conventional mechanical methods [Fig. 7(A) for PNb]. The surface morphology of the resulting polymer films deposited on the ITO electrodes was observed by SEM, as shown in Figure 7. The SEM pictures demonstrated that two bridged PN both displayed sphere-type growth processes on ITO electrode. A number of regular nanospheres with different sizes assembled to a compact layer, then based on the two-dimensional plane, the polymer film continued to grow layer by layer forming to the three-dimensional multilayered structure. The smooth and homogeneous structures of compact films were extremely beneficial to improve their electrical conductivity and electron transfer capability and also make them good candidates for potential applications, such as ion-selective electrodes, ion-sieving films, and matrices for hosting catalyst particles, etc.

Thermal analysis and electrical conductivity

The thermal stability of CPs is very important for their potential application. To investigate the thermal stability of as-formed PN films, the thermal analyses were performed under a nitrogen stream from 288

to 1083 K at a heating rate of 10 K min⁻¹. As can be seen from the thermogravimetric curves (Fig. 8), two bridged PN both presented three-step loss of weight. The first loss of PNo was from 288 to 505 K up to 27.5%, resulting from the evaporation of water or other moisture trapped in PNo.⁴⁷ The second one occurred from 505 to 740 K, up to 31.5%, which may be due to the degradation of the skeletal PNo backbone chain structure. The last one was about 15.6%

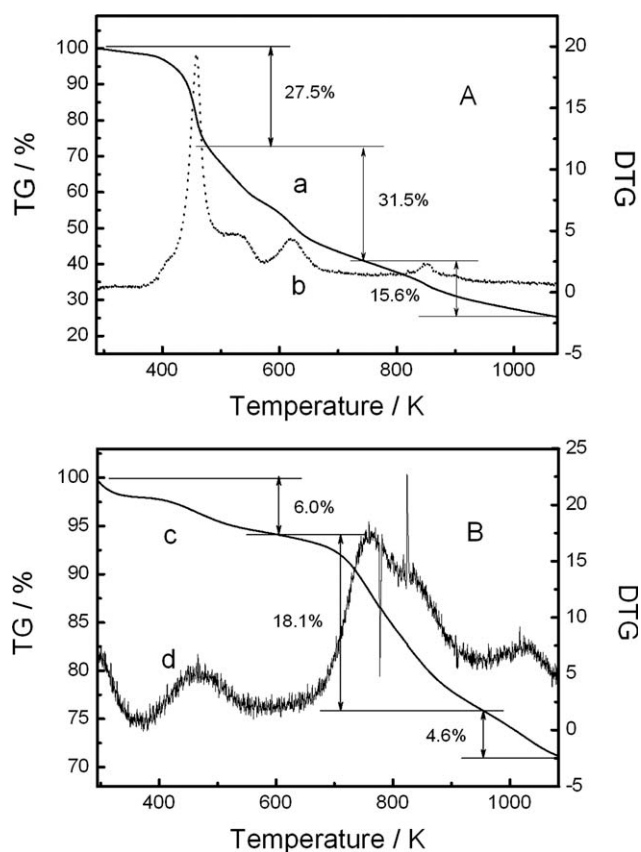


Figure 8 Thermogravimetric analyses of doped PNo (A) and PNb (B) films.

from 740 to 1083 K, probably owing to the overflow of some oligomers decomposing from PNo with the increase of the temperature. Similarly, the weight of PNb [Fig. 8(B)] lessened according to three-step: the first loss occurred from 288 to 600 K up to 6.0%, the second one occurred from 600 to 954 K, up to 18.1%, the last one was about 4.6% from 954 to 1083 K. From the differential thermogravimetric curves [Fig. 8(b,d)], it can be seen that the most rapid weight change rates of PNo and PNb occurred at 620 K and 765 K, respectively. All these results indicated that PNo and PNb had good thermal stability. Moreover, the electrical conductivity of PNo and PNb were measured to be $3.3 \times 10^{-2} \text{ S cm}^{-1}$ and $1.2 \times 10^{-3} \text{ S cm}^{-1}$ as free-standing films at 25°C, respectively. For PNb, the introduction of benzene ring as rigid structure changed the arrangement and compactness of polynaphthalene chains relative to PNo, which caused the high degree of crosslinking but uneasily stretched chains leading to the better stability and lower conductivity.

CONCLUSIONS

In summary, homogeneous free-standing films were successfully electrochemically synthesized from two bridged naphthalene monomers No and Nb in $\text{CH}_2\text{Cl}_2 + 30\% \text{ BFEE}$. These polymer films were very shiny, flexible and had fairly good thermal stability due to the crosslinked structures in polymer. Fluorescence spectral study revealed that as-formed polymer films were good blue-light-emitters. Therefore, these high quality PN films will facilitate their potential applications as blue-light-emitting materials in organic light emitting diode. However, PNT was unobtainable by electropolymerization of Nt in the same system, it further illustrated that the introduction of bridged spacers into the naphthalene units was a conceivable effect factor to the formation of PN via electropolymerization.

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