

ELECTROSYNTHESES AND CHARACTERIZATION OF A FLUORESCENT CONDUCTING COPOLYMER OF BENZANTHRONE AND THIOPHENE*

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Abstract Poly(benzanthrone-co-thiophene), a new conducting copolymer, was successfully prepared by direct anodic oxidation of benzantrone and thiophene (Th) in a binary solvent system containing boron trifluoride diethyl etherate (BFEE) and acetonitrile (ACN). The as-formed copolymer film electrodeposited with monomer feed ratio of benzantrone/Th = 1:1 at the applied potential of 1.3 V versus Ag/AgCl exhibited the advantages of both polybenzantrone and polythiophene, such as active electrochemical behavior, excellent thermal stability, relatively high electrical conductivity and mechanical properties. UV-Vis spectroscopy, ¹H-NMR and SEM were used to characterize and investigate the structures and morphologies of the copolymers. Fluorescence spectroscopy studies revealed that the obtained copolymer films show strong emission at about 525 nm. Moreover, the emitting properties of the copolymers could be tuned by changing some parameters during the electropolymerization process, such as monomer feed ratio.

Keywords: Conducting polymers; Electrochemical copolymerization; Benzantrone; Thiophene; Fluorescence property.

INTRODUCTION

Since discovery of the first conducting polymer (*i.e.* polyacetylene) in 1970s^[1], conducting polymers (CPs), also being called as “synthetic metals”, have received considerable attentions because of their unique properties such as highly-conjugated chain structure, a reversible doping/de-doping process, covering whole insulator-semiconductor-metal region of electrical properties and an unusual conducting mechanism^[2]. These unique properties of CPs not only lead to promising applications, but also hold an important position in material science^[3–7]. With excellent fluorescence properties and other outstanding properties, conjugated polymers from fused ring aromatic compounds have also been investigated for years, such as polycarbazole^[7–9], polyfluorene (PF)^[10], polyanthracene (PAn)^[11] and oligopyrene (ONP)^[12, 13]. As one of them, polybenzantrone, a good green-light-emitter with fluorescence quantum yield (ϕ_{overall}) up to 0.52, was successfully electrodeposited by direct anodic oxidation of benzantrone in the binary solvent system of boron trifluoride diethyl etherate (BFEE) and acetonitrile (ACN)^[14]. However, the as-formed polybenzantrone film is brittle and its electrical conductivity is relatively low (1.9 S cm⁻¹), which may limit its applications in some certain practical domains^[1, 15–19]. Therefore, it will be necessary and meaningful to further improve the mechanical properties and electrical conductivity of the resulting polybenzantrone film, and that will make it being more competent for its

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future applications in some specific and sophisticated domains, such as polymer light-emitting diodes (PLEDs)^[18] and electrochromic windows^[20]. According to the literature^[21–24], copolymerization is one feasible and effective method to make the idea described above come true. Furthermore, copolymerization of different monomers no matter through chemical or electrochemical method can effectively modify the structures and properties of CPs, by which one can obtain novel materials with controlled properties without suffering the experimental disadvantages associated to the synthesis of new homopolymers, *e.g.* complex synthetic routes to sophisticated monomers. Thus, it is an easy alternative to prepare copolymers with properties that are usually intermediate between those of individual homopolymers but significantly distinct from those of a composite or a blend^[25].

As one of representative CPs, polythiophene (PTh) has been focused on much attention in recent years. According to the literature, high quality PTh films with a high tensile strength of 60 MPa and a high electrical conductivity of 153 S cm^{-1} ^[26], have been electrochemically prepared in a binary solvent solution containing BFEE (90 vol%) and ACN (10 vol%), which has been considered as the optimal electrosyntheses medium for PTh. In recent years, thiophene was chosen to copolymerize with monomers such as funan^[27, 28], pyrrole^[29], fluorene^[30], thiophene derivatives^[31, 32] and thiophene functionalized polystyrenes^[33], *etc.* The utilization of thiophene units is much attractive, because of the advantages of PTh, such as good environment stability, relatively high electrical conductivity, high mechanical properties and ease of electrochemical deposition of free-standing films. However, the relatively low photoluminescence quantum efficiency of PTh in solid state, typically 1%–3%, has limited its applications in PLEDs. Therefore, it is easy to deduce that the combination of thiophene and benzantrone units may modify the band gap of the copolymer and thus tune its light-emission.

In this paper, benzantrone and Th were copolymerized electrochemically in the binary solvent system containing BFEE (90 vol%) and ACN (10 vol%)^[26]. For the monomers, BFEE can decrease their onset oxidation potentials and ACN can increase the solubility of benzantrone in this medium^[14]. The electrochemical and spectroscopic properties, thermal stability, electrical conductivities and morphologies of the as-formed copolymer films were investigated in detail.

EXPERIMENTAL

Materials

Th (99%, Acros Organics), benzantrone (Alfa Aesar), commercial high-performance liquid chromatography grade ACN (analytically pure, Beijing East Longshun Chemical Plant, China) were used directly without further purification. BFEE (Changyang Chemical Plant, Beijing, China) was purified by distillation before use. Other reagents were all analytical pure and used as received without further retreatment.

Electrochemical Experiments

Electrochemical polymerization and examinations were carried out in a one-compartment three electrodes cell with a Model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. The working and counter electrodes for the cyclic voltammetry (CV) experiments were two platinum wires with diameter of 0.5 mm, respectively, placed 0.5 cm apart. Before each examination, they were carefully polished and cleaned with water and acetone successively. An Ag/AgCl electrode was used as the reference electrode and all the potentials in this paper were versus Ag/AgCl electrode. To obtain a sufficient amount of polymer, two stainless steel sheets with surface area of 10 and 12 cm², were employed as the working and counter electrodes, respectively, which were carefully polished with abrasive paper (1500 mesh) and then washed with water and acetone successively before each examination. The polymers deposited on indium tin oxide (ITO) glasses were used for ultraviolet visible (UV-Vis) and fluorescence spectroscopy measurements and morphology analysis.

Characterization

The electrical conductivities of the polymer and copolymers (PTh and copolymer (1:1) free-standing films: 12 mm × 4 mm × 0.1 mm; polybenzantrone pressed-pellet: 12 mm × 4 mm × 1.2 mm) were determined by the

conventional four-probe technique. UV-Vis spectra were measured with a Perkin-Elmer Lambda 900 UV-visible-near-infrared spectrophotometer. With an F-4500 fluorescence spectrophotometer (Hitachi), fluorescence spectra were determined. A VEGA\LSU TESCAN scanning electron microscope (SEM) was used to analysis the surface morphologies of the as-formed polymer films.

RESULTS AND DISCUSSION

Electrochemical Copolymerization

To ensure the electrochemical copolymerization of benzanthrone and Th and determine the proper conditions for their copolymerization in BFEE + ACN (9:1, vol), the electrochemical experiments were carried out in 4 subordinate groups based on different monomer feed ratios (benzanthrone/Th). It should be noted here that the background electrolyte is electrochemically inert in the whole potential range. The successive cyclic voltammograms (CVs) of Th, benzanthrone, and monomer mixtures with different feed ratios are illustrated in Fig. 1. As the first cycle of CVs exhibited, the onset oxidation potentials of Th and benzanthrone were located at about 1.20 (f) and 1.25 V (a), respectively. The small distinction (0.05 V) between the onset oxidation potentials of the two monomers indicates that the copolymerization of benzanthrone and Th in the binary solvent system is feasible. The monomer mixtures with different feed ratios of benzanthrone/Th could be oxidized initially between 1.20 V and 1.25 V. The small distinctions between the onset oxidation potentials of the monomer mixtures might be partly ascribed to some changes of the electrochemical environment caused by the successive deposition of the two monomers during the anodic polarization or a drift of the potential of the reference electrode, or partly due to the influence of the low electrical conductivity accompanied by the incorporation of benzanthrone units into the copolymer chains^[22].

As the CV continued, the conducting polymer film was formed on the working electrode surface. The increase of the redox wave current densities implied that the amount of the polymer deposited on the working electrode surface was increasing. Moreover, the obvious potential shift of the wave current density maximum provided information about the increase in the electric resistance of the polymer film and over-potential needed to overcome the resistance. In detail, benzanthrone and its oligomers or polymers could be oxidized and reduced at 1.47 and 1.00 V (Fig. 1a). For Th system, its oxidation and reduction peaks located at 0.89 and 0.22 V (Fig. 1f). The CVs of the monomer mixtures with different feed ratios were also recorded to choose a suitable feed ratio for copolymerization. When the CVs were recorded in monomer mixtures with benzanthrone/Th = 1:5 (Fig. 1e), their CV curves were very similar to those of Th system, with redox peaks being located at 0.81 and 0.26 V, indicating the domination of Th units in the copolymer. With an increase in benzanthrone concentration in the solution, obvious changes could be easily observed in corresponding CVs. When the monomer feed ratio (benzanthrone/Th) increased to 5:2 (Fig. 1b), the CVs of the system were quite similar to those of benzanthrone, implying that more benzanthrone units incorporated into the copolymer film. However, for the monomer mixtures with benzanthrone/Th = 1:1 and 1:3, great changes could be observed in their CVs (Figs. 1c, 1d), in which new redox peaks were observed at about 0.40 ($E_{p,c}$), 0.51 ($E_{p,a}$) and 0.92 ($E_{p,c}$) V, compared with those of Th and benzanthrone. The evolution of new redox waves different from those of pure benzanthrone or Th suggests that benzanthrone and Th units were oxidized simultaneously and a new copolymer was obtained during the potentiodynamic polymerization process of benzanthrone and Th.

Furthermore, the redox wave current densities in the CVs of benzanthrone (Fig. 1a) increased continuously as the cyclic voltammetry continued. However, for the CVs of Th (Fig. 1f) recorded in the same medium, the redox wave current densities increased gradually at first as the number of the CVs increased, but they remained almost unchanged when the cyclic scanning number reached a certain value, which was in accordance with the literature. This phenomenon described above could also be observed easily in the CVs of the monomer mixtures with feed ratio of benzanthrone/Th = 1:5 (Fig. 1e). While, as the concentration of benzanthrone increased in the monomer mixtures, this characteristic phenomenon of the CVs of Th disappeared, indicating that there were benzanthrone units incorporated into PTh chains. Based on the comparisons of the CVs recorded in different

monomer mixtures, it is reasonable to imply that benzanthrone and Th have been electrochemically copolymerized to greater extent in the monomer mixtures with feed ratio of benzanthrone/Th = 1:1, compared with the other monomer mixtures. All the above-described indicate the occurrence of the copolymerization between benzanthrone and Th units in BFEE + ACN (9:1, vol). Considering the better quality of the copolymer film, an appropriate feed ratio of benzanthrone/Th = 1:1 was chosen for their copolymerization and property analysis in the following study.

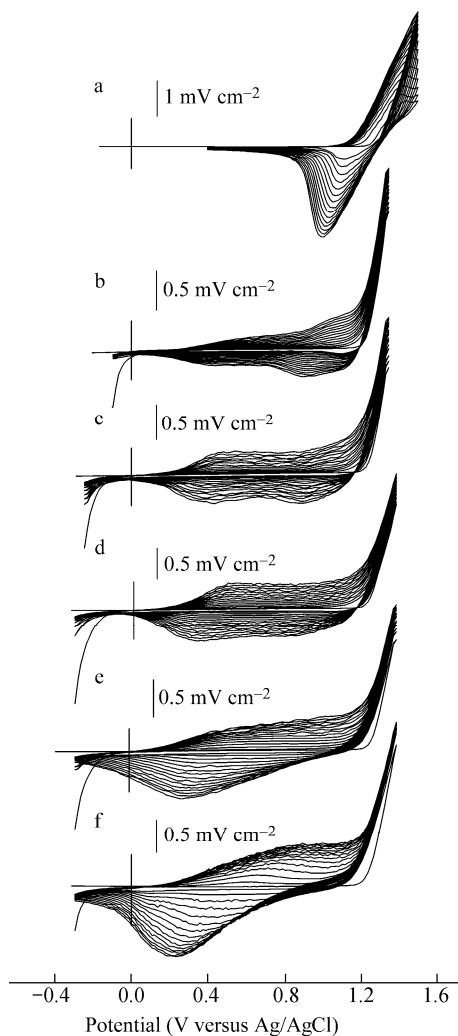


Fig. 1 CVs of benzanthrone (a), Th (f) and the monomer mixtures with benzanthrone/Th = 5:2 (b), 1:1 (c), 1:3 (d), and 1:5 (e), respectively, in BFEE + ACN (9:1, vol) solutions
Potential scan rate: 100 mV s^{-1}

Electrochemistry of the Copolymer Films

To further improve the occurrence of the copolymerization of benzanthrone and Th and study the electrochemical properties of the copolymers, the CVs of PTh, polybenzanthrone, and their copolymer films deposited in BFEE + ACN (9:1, vol) were recorded in the monomer-free BFEE + ACN (9:1, vol) (Fig. 2), BFEE, and concentrated sulfuric acid, respectively, under different potential scanning rates. For brevity, the CVs recorded in BFEE and concentrated sulfuric acid were not shown here. All the films mentioned above could be cycled repeatedly between their conducting and insulating states without serious decomposition, and the peak current densities were proportional to the scanning rates (insets of Figs. 2a, 2b, 2c), indicating the

reversible redox behavior of the polymers or copolymers. As shown in Fig. 2, the performance of the CVs of polybenzanthrone (Fig. 2a) was not satisfactory enough and the film could be oxidized and reduced from 1.40 V to 1.04 V, in which the oxidation peaks of the foremost several cycles were unclear. For PTh (Fig. 2c), much lower potentials were needed to oxidize and reduce the film (from 0.78 V to 0.2 V). In comparison, a new pair anodic and cathodic peaks located at 0.60 and 0.38 V appeared in the CVs of the copolymer film (Fig. 2b), indicating that the two monomers were oxidized together and the polymer chain was composed of benzanthrone and Th units. Similar results could also be observed in the CVs recorded in BFEE and concentrated sulfuric acid.

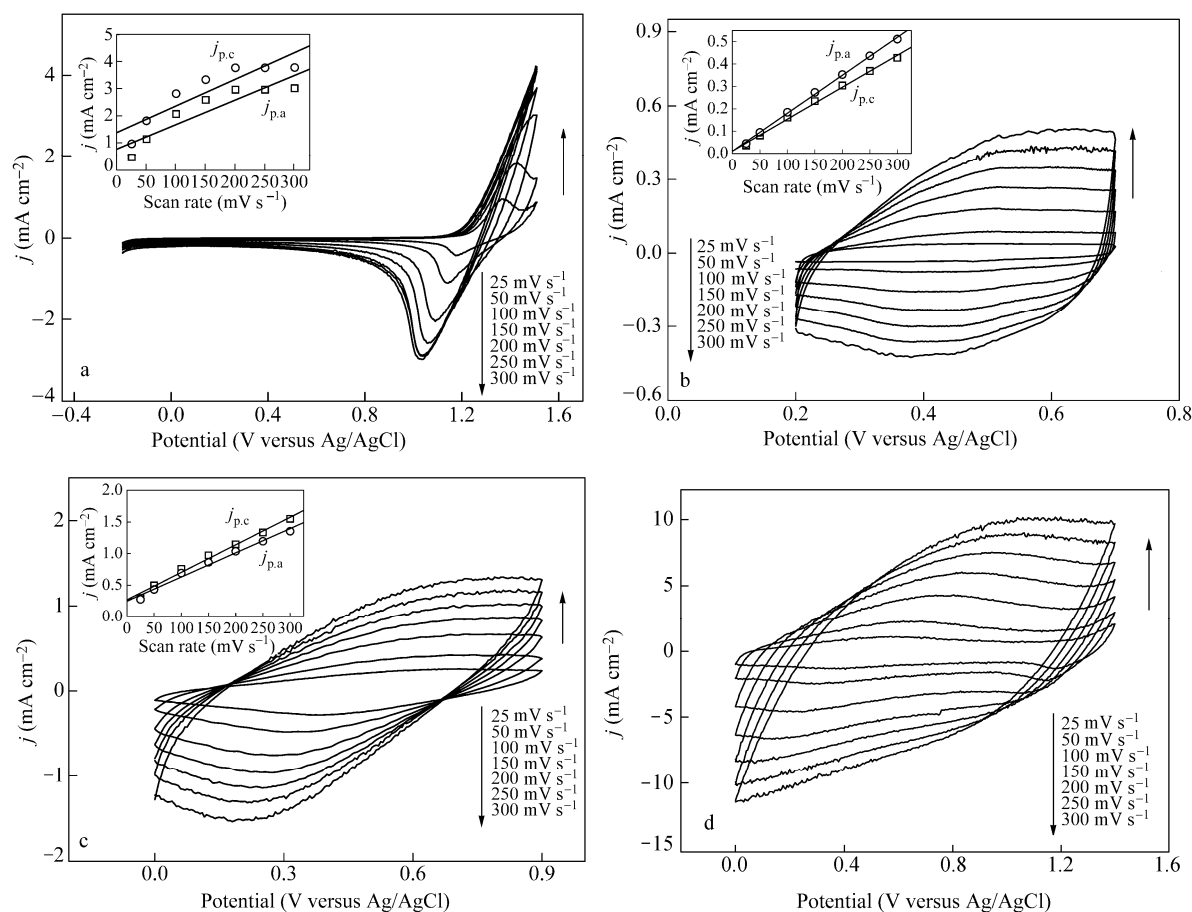


Fig. 2 CVs of (a) polybenzanthrone, (b) copolymer (1:1), (c) PTh, and (d) mixed bilayer films (polybenzanthrone/PTh) recorded in monomer-free BFEE+ACN (9:1, vol) at different potential scan rates
 Insets: redox peak current density versus potential scan rates

By comparison, the CVs of the mixed bilayer films (polybenzanthrone/PTh) recorded in the monomer-free BFEE + ACN (9:1, vol), BFEE and concentrated sulfuric acid were also studied. The blend films were electrodeposited in the solutions of benzanthrone and Th at constant applied potential of 1.3 V for 100 s, respectively. As shown in Fig. 2(d), the CVs of the mixed bilayer films were different from those of PTh, polybenzanthrone, and the copolymers. In BFEE + ACN (9:1, vol), the redox peaks of the CVs of mixed films were located at 0.90 and 0.30 V (Fig. 2d), while for that of the copolymer film, its redox peaks were at about 0.55 and 0.40 V (Fig. 2b). In monomer-free BFEE, the mixed films could be oxidized and reduced from 0.60 V to 0 V different from that of the copolymer film (from 0.45 V to 0.10 V). This might suggest that the copolymer was different from the blend films indicating the occurrence of the copolymerization of benzanthrone and Th in

the binary solvent system. While, for the CVs of the bilayer films recorded in concentrated sulfuric acid, broader redox peaks appeared at 0.55 and 0.48 V, which might be ascribed to the tiny differences between the locations of the redox peaks of polybenzanthrone and PTh. As a result, the redox peaks of polybenzanthrone and PTh films were overlapped and much broader than those of the copolymer film. As the above described, it was reasonable to conclude that Th and benzanthrone were copolymerized together electrochemically during the potentiostatic process in the binary solvent system.

Structural Characterization

It is known that, PTh exhibits electrochromic property, and it can be repeatedly driven from insulating to conducting states with high contrast in color, which can not be observed for polybenzanthrone. In detail, PTh prepared in BFEE + ACN (9:1, vol) changed its color from dark blue in doped state to red in de-doped state. For polybenzanthrone, it kept in yellow both in doped and de-doped states. As for the copolymers of Th and benzanthrone, their color changed from dark green in doped state to light red in de-doped state, which indicated that Th units were inserted into the copolymer chains. On the other hand, as the literature recorded^[14], the solubility of polybenzanthrone is so good that it can dissolve in common organic solvents, such as methanol, ethanol, acetone, dimethyl sulphoxide (DMSO), ACN, ethyl ether, etc. By contrast, PTh prepared electrochemically, hardly dissolves in any common organic solvents. While, for the copolymer of Th and benzanthrone, it could partly dissolve in some common organic solvents such as DMSO, which implied that benzanthrone units were incorporated in the copolymer chain.

The UV-Vis spectra of the copolymer films in doped and de-doped states, electrodeposited on ITO glasses at different applied potentials with feed ratio of benzanthrone/Th = 1:1, were shown in Fig. 3. For comparison, the spectra of PTh, polybenzanthrone, and the mixed bilayer films (polybenzanthrone/PTh) were also included. In doped state, polybenzanthrone showed characteristic absorptions at 428 and 321 nm Fig. 3(A-a), which were derived from a valence band/conducting band (π - π^*) transition. PTh showed a broad absorption at 400–1000 nm, with two maximum absorption peaks at 480 and 720 nm, as shown in Fig. 3(A-b). On the other hand, the spectra of the copolymer films electrodeposited at different applied potentials with the fixed feed ratio of benzanthrone/Th = 1:1 showed the characteristic absorptions of both polybenzanthrone and PTh at 312, 415, and 450–1000 nm, which were a little blue-shift compared with those of polybenzanthrone and PTh. After de-doped, the characteristic absorptions of polybenzanthrone still could be observed in the same region Fig. 3(B-a). For PTh, the spectrum showed a maximum absorption at about 494 nm, as shown in Fig. 3(B-b). The copolymer prepared at constant applied potential of 1.3 V exhibited a broader absorption at 400–600 nm Fig. 3(B-c). While, with an increase in the polymerization potentials, the absorption at 312 nm as the characteristic absorption of polybenzanthrone became more obvious, and the absorption at 350–630 nm was much stronger and broader compared with the others Fig. 3(B-d–f). This phenomenon might indicate that with an increase in the applied potentials, the number of benzanthrone units incorporated in the copolymer chains increased correspondingly, which was ascribed to the higher oxidation potential of benzanthrone compared with that of Th in the electrolytes.

The UV-Vis spectra of the mixed bilayer films (polybenzanthrone/PTh), prepared in the solutions of benzanthrone and Th, successively, were measured to compare them with those of the copolymers, as shown in Fig. 3(g). The absorptions of the mixed bilayer films (Fig. 3g) were so similar to those of polybenzanthrone and PTh that were more like the overlap of the absorptions of polybenzanthrone and PTh, but were different from those of the copolymers, providing information that the copolymerization of benzanthrone and Th in BFEE + ACN (9:1, vol) has happened.

To further investigate the structure of the soluble part of the copolymer, the ¹H-NMR spectra of (A) polybenzanthrone and (B) the dissolved part of the copolymer are shown in Fig. 4. Most of the peaks of the soluble copolymer were similar to those of polybenzanthrone. In detail, as Fig. 4(A) shows, the proton chemical shifts of δ = 8.82, 8.64, 8.58, 8.47, 7.87, 7.83, 7.79, and 7.64 can be assigned to the protons at positions of C₆, C₈, C₁, C₄, C₅, C₁₀, C₂, and C₉ of benzanthrone unit, respectively. However, in the spectra of the soluble copolymer Fig. 4(B), besides the peaks belonging to polybenzanthrone, some new peaks appeared. Peaks at

$\delta = 7.52$ could be assigned to the protons at C_3 and C_3' positions of Th units. Multiplets at $\delta = 7.64$ and 8.52 might belong to the protons at C_{10} and C_2 positions of benzanthrone units at the ends of each polybenzanthrone main chain. All the results revealed that the main composition of the soluble part of the copolymer was polybenzanthrone or oligobenzanthrone.

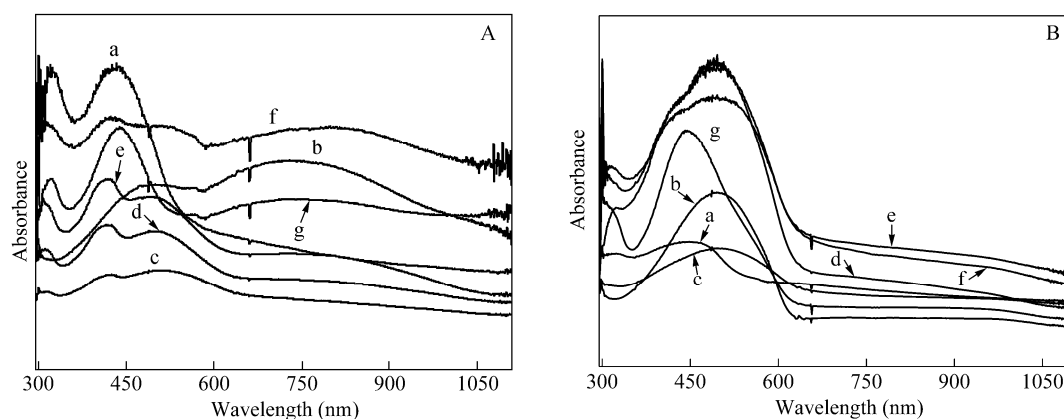


Fig. 3 UV-Vis spectra of (a) polybenzanthrone, (b) PTh, (c–f) poly (benzanthrone-*co*-Th) (1:1) synthesized at (c) 1.3 V, (d) 1.4 V, (e) 1.5 V, and (f) 1.6 V, (g) the mixed bilayer films coated on ITO glasses in (A) doped and (B) de-doped states

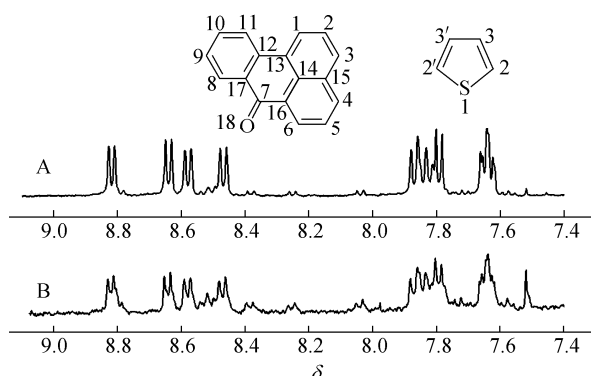


Fig. 4 ^1H -NMR spectra of (A) polybenzanthrone and (B) the soluble part of poly(benzanthrone-*co*-Th) (1:1) electrodeposited in BFEE + ACN (9:1, vol) solutions
Solvent: CDCl_3

Fluorescence Properties

Polybenzanthrone is a good green or yellow green-light emitter. While, PTh has the advantage of easy forming of free-standing film with high electrical conductivity. Therefore, if the novel copolymer of Th and benzanthrone with the properties intermediate between those of polybenzanthrone and PTh is obtained successfully, it may be hopeful to meet the application in PLEDs as the light-emitting thin film. The fluorescence spectra of polybenzanthrone and the copolymers electrodeposited on ITO glasses in doped state are shown in Fig. 5(A). All the polymer films were deposited at a constant applied potential of 1.3 V. Similar with polybenzanthrone, the copolymers deposited with benzanthrone/Th = 5:2 and 1:1 both showed strong emissions at about 525 nm, as shown in Figs. 5(A-a, A-c, A-d). When the feed ratios of benzanthrone/Th changed to 1:3 and 1:5, the emission intensities of the obtained copolymer films at the same range decreased seriously Fig. 5(A-e, A-f), which might be attributed to that more Th units incorporated into the copolymer chains compared with polybenzanthrone and the other copolymers, indicating that the intrachain energy transfers in the copolymer chain or the interchain reaction between the copolymer chains in solid state was less efficient and caused the fluorescence quenching of the copolymers. For comparison, the emission curves of PTh and the

mixed bilayer films (polybenzanthrone/PTh) were also included, although their emission intensities were very weak or no emissions at all, as shown in Figs. 5(A-b, A-g). These emitting curves indicated that the emission intensities of the copolymer films decreased as the feed ratios of benzanthrone/Th decreased, the copolymer films were different from the mixed bilayer films of polybenzanthrone and PTh films, and the fluorescence properties of the copolymers could be easily controlled by changing the monomer feed ratios or some other electropolymerization conditions.

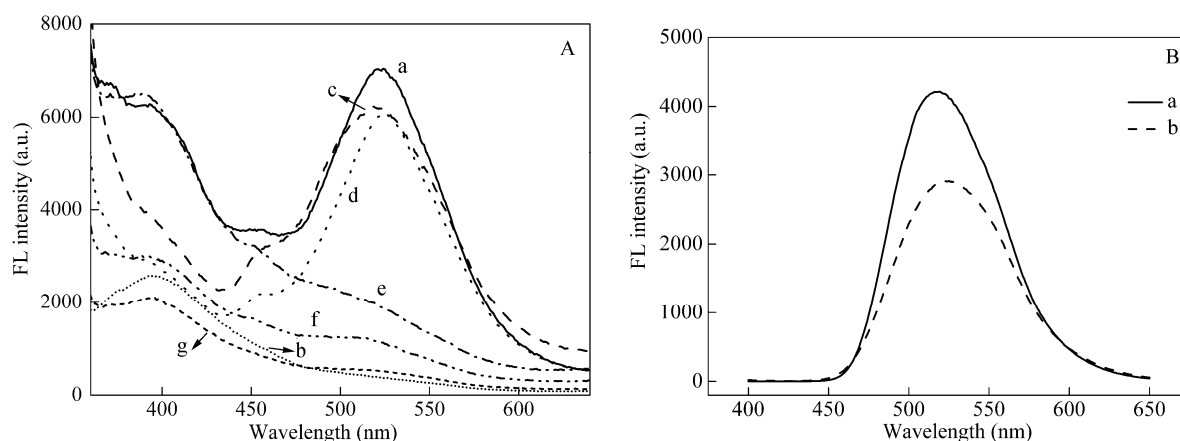


Fig. 5 Fluorescence spectra of (A-a) polybenzanthrone, (A-b) PTh, (A-c–f) poly(benzanthrone-co-Th) synthesized with benzanthrone/Th = (A-c) 5:2, (A-d) 1:1, (A-e) 1:3, and (A-f) 1:5, (A-g) the mixed bilayer films (polybenzanthrone/PTh) deposited on ITO glasses, and of (B-a) polybenzanthrone and (B-b) poly(benzanthrone-co-Th) (1:1) dissolved in DMSO

The fluorescence spectra of dissolved polybenzanthrone and poly(benzanthrone-co-Th) (1:1) in DMSO were shown in Fig. 5(B). Both of them exhibited strong emissions at 470–600 nm with maximum values at 518 nm (B-a) and 523 nm (B-b). The small difference between the fluorescence spectra of the dissolved polybenzanthrone and copolymer suggested that the composition of the dissolved copolymer was similar with that of polybenzanthrone and the obtained soluble polybenzanthrone might be with short conjugated main chains, because of the complicated conjugated molecule structure of benzanthrone.

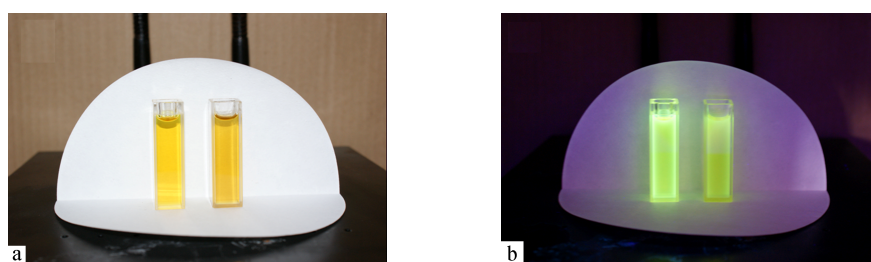


Fig. 6 Photoluminescence of (a, b-left) polybenzanthrone and (a, b-right) poly(benzanthrone-co-Th) (benzanthrone/Th = 1:1) in doped state under (a) nature daylight and (b) UV light irradiation of 365 nm

Figure 6 shows the photoluminescence properties of soluble polybenzanthrone (b-left) and the partly soluble copolymer (b-right) in doped state. As reported previously, polybenzanthrone exhibited bright yellow-green light-emitting property when exposed to 365 nm UV light (b-left). While for the partly soluble copolymer, it showed slight weak emission light, mainly because of the defective solubility of the copolymer or the Th units in the soluble oligomer or polymer causing the fluorescence quenching among the oligomer or polymer matrix.

Electrical Conductivity and Morphology

The electrical conductivities of PTh, polybenzanthrone and the copolymers electrodeposited with benzanthrone/Th = 1:1 at different applied potentials were measured. In accordance with the literature^[26], PTh film showed high electrical conductivity up to 50.1 S cm^{-1} . For polybenzanthrone, its electrical conductivity was measured to be 1.9 S cm^{-1} . The electrical conductivities of the obtained copolymers were varied as the applied potential changed. When the applied potential was 1.3 V, the electrical conductivity of the copolymer was measured to be 9.3 S cm^{-1} , and a higher value 10.1 S cm^{-1} was obtained for 1.4 V. As the applied potential continuously increased, the electrical conductivities of the copolymer films took a negative change, which might be attributed to the bad regularity of the copolymer films caused by the overoxidation of the monomers or oligomers during the potentiostatic process.

Figure 7 shows the SEM images of PTh, poly(benzanthrone-*co*-Th) (benzanthrone/Th = 1:1), and polybenzanthrone films deposited on ITO glasses in doped and de-doped states. Microscopically, even at high magnifications, the surfaces of PTh films were smooth, homogeneous and continuous as shown in Figs. 7(a, b). On the contrary, the surfaces of polybenzanthrone films both in doped Fig. 7(e) and de-doped Fig. 7(f) states were rough or discontinuous. However, the surface morphologies of the copolymer films were intermediate between those of PTh and polybenzanthrone films as shown in Fig. 7(c, d).

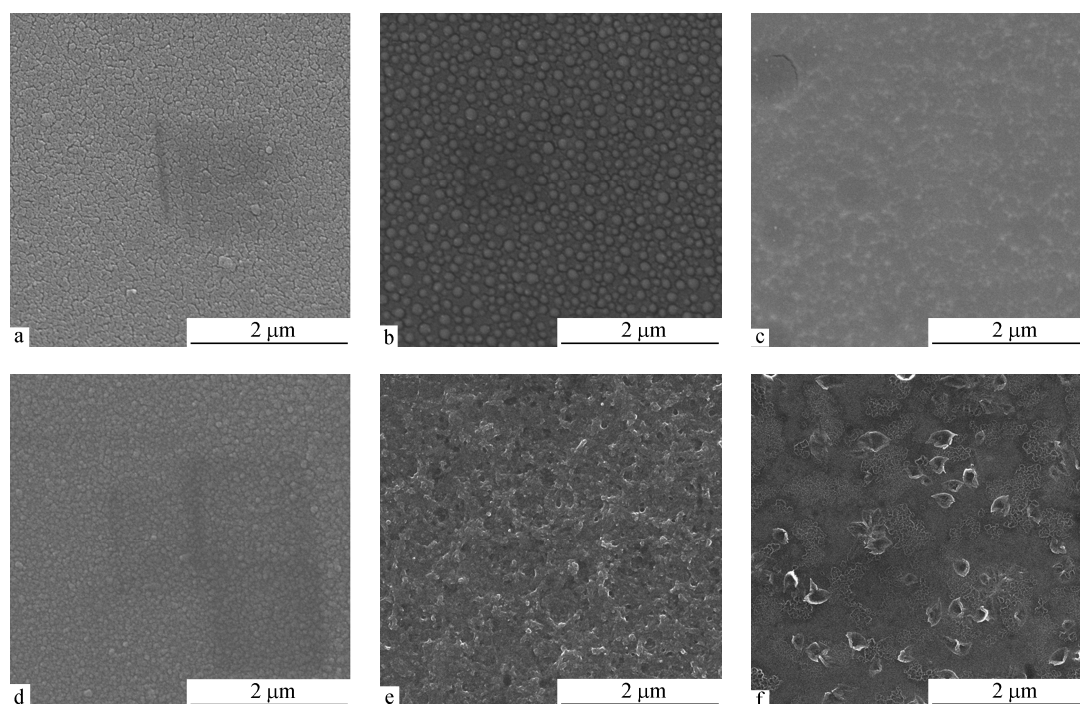


Fig. 7 SEM images of (a, b) PTh, (c, d) poly(benzanthrone-*co*-Th) (benzanthrone/Th = 1:1) and (e, f) polybenzanthrone films in doped state (a, c, e) and de-doped state (b, d, f), deposited on ITO glasses in BFEE + ACN (9:1, vol) at a constant applied potential of 1.3 V

As the literature recorded^[26], macroscopically, PTh films with metallic surfaces appeared to be smooth, homogeneous, and compact, no matter in doped or de-doped states and they could be peeled off from the electrode directly by hand as free-standing films. However, for polybenzanthrone, it was so brittle that it was hard to form free-standing films. Similar with PTh, the copolymer of benzanthrone and Th could be easily deposited on working electrode surface and form black free-standing films, but with rough surface. As expected, the electrochemical copolymerization of Th and benzanthrone was helpful to improve the film quality of the copolymers.

CONCLUSIONS

In this paper, Th and benzantrone were copolymerized by direct anodic oxidation in BFEE + ACN (9:1, vol). The optimal feed ratio of benzantrone/Th = 1:1 together with the best applied potential of 1.3 V versus Ag/AgCl were determined from the experiments. The as-formed copolymer film showed properties intermediate between those of PTh and polybenzantrone, such as high electrochemical and redox activity, good mechanical properties, relatively high electrical conductivity and thermal stability. Fluorescence studies revealed that the obtained copolymers in solid state show maximum emissions at about 525 nm, and their fluorescence property can be controlled by changing the monomer feed ratio, or the applied potential *etc.* The resultant copolymer could partly dissolve in DMSO and the dissolved part exhibited yellow-green light-emitting property under 365 nm UV light.

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