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Electrochemical copolymerization of benzanthrone and 3-methylthiophene and characterization of their fluorescent copolymer

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Abstract Poly(3-methylthiophene-*co*-benzanthrone), a novel copolymer, was successfully achieved by electrochemical oxidation of the monomer mixtures of 3-methylthiophene (3MeT) and benzanthrone in the binary solvent system containing boron trifluoride diethyl etherate and acetonitrile. A series of experiments with different monomer feed ratios were carried out to investigate the influence of monomer feed ratio on the electrochemical copolymerization and the overall properties of the copolymer films. The resulting copolymer possesses the advantages of both polybenzanthrone and poly(3-methylthiophene), such as considerable fluorescence property, good redox activity, high thermal stability, and relatively high electrical conductivity. Ultraviolet–visible, FT-IR, and thermal analysis were used to characterize and investigate the structure and thermal stability of the copolymers. Fluorescence spectroscopic studies revealed that the copolymer dissolved in common organic solvents was a good green or yellow-green light emitter, with a strong emission at 499 nm in doped state and 529 nm in dedoped state.

Introduction

Conducting polymers, also being called “synthetic metals”, have been attracting considerable attention since they were discovered in the 1970s [1]. Nowadays, conducting polymers as functional materials hold a special and important position in the field of material science. With excellent fluorescence properties and other outstanding properties, conjugated polymers as part of conducting polymers have also been investigated for decades, such as poly(*p*-phenylenevinylene) (PPV) [2], poly(*p*-phenylene) (PPP) [3], polythiophene (PTh) [4], and polyfluorene (PF) [5]. Presently, high-quality green-light-emitting polybenzanthrone with electrical conductivity up to 2.2 S cm^{-1} and nice solubility in common organic solvents was successfully electrodeposited by direct anodic oxidation of benzanthrone in the binary solvent system consisting of acetonitrile (ACN) and additional boron trifluoride diethyl etherate (BFEE) acting as the supporting electrolyte [6]. However, the poor mechanical property and the relatively low electrical conductivity of the as-formed polybenzanthrone film have limited its applications in some certain practical domains [1, 7–15]. Therefore, it will be necessary and meaningful to further improve the mechanical property and electrical conductivity of the as-formed polybenzanthrone film, which may be competent to its future applications in some specific and sophisticated domains, such as polymer light-emitting diodes (PLEDs) [12] and electrochromic windows [16]. According to the literature, copolymerization is one feasible method to make the idea described above come true. Furthermore, copolymerization of different monomers no matter through chemical or electrochemical oxidation can effectively modify the structures and properties of conducting polymers, by which one could 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 and a blend [17]. Based on the above described, a proper copolymerized-partner should be found out for

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benzanthrone monomer before the copolymerization process carried out.

As an important derivative of PTh, poly(3-methylthiophene) (P3MeT) has the advantages of outstanding electrical conductivity as high as 750 S cm^{-1}, high tensile strength and environmental stability, excellent flexibility, and ease of anodic electrodeposited free-standing films [18–23]. Therefore, it can be a good candidate for applications in diverse domains like electronics, optoelectronics, and sensors. However, the relatively low photoluminescence quantum efficiency of P3MeT in the solid state, typically 1–3% and its poor solubility in common organic solvents have been inevitably limiting its applications in some domains, especially in PLED [24, 25]. As a matter of course, 3MeT is one of the best choices to copolymerize with benzanthrone in this experiment.

In this article, 3MeT and benzanthrone were successfully electrocopolymerized by direct anodic oxidation in the binary solvent system consisting of BFEE and ACN (2:1, by volume). For 3MeT and benzanthrone, BFEE can decrease their oxidation potentials, and ACN can increase the solubility of benzanthrone in this medium. The electrochemical properties of the copolymers of 3MeT and benzanthrone and the corresponding homopolymers were studied. The spectroscopic properties, fluorescence property, thermal stability, and electrical conductivity of the as-formed copolymers were investigated.

Experimental

Materials

3-Methylthiophene (3MeT, 99%, analytically pure; Acros Organics), benzanthrone (Alfa Aesar), and commercial high-performance liquid chromatography grade ACN (Beijing East Longshun Chemical Plant, China) were used directly without further purification. BFEE (Changyang Chemical Plant, Beijing, China) was purified by distillation and stored at −20 °C before use. Dimethyl sulfoxide (DMSO, analytically pure) was a product of Beijing East Longshun Chemical Plant and was used directly. Other reagents were all analytically pure and used as received without further treatment.

Electrochemical experiments

Electrochemical experiments were carried out in a one-compartment glass cell using a Model 263A potentiostat-galvanostat (EG&G Princeton Applied Research) connected to a computer. The working electrode and counter electrode for cyclic voltammetry experiments were two platinum (Pt) wires each with a diameter of 0.5 mm, placed 0.5 cm apart during the experiments. In the binary solvent system of BFEE and ACN, an Ag/AgCl electrode was directly immersed in the solution served as the reference electrode and all the potentials mentioned follow were versus the Ag/AgCl electrode. To obtain a sufficient amount of the copolymer films for characterization, two stainless steel sheets with surface areas of 10 and 12 cm^2 each were employed as the working electrode and counter electrode, respectively. Prior to each examination, the stainless steel electrodes mentioned above were carefully polished by abrasive paper (1500 mesh), cleaned with deionized water and acetone successively, and then dried in air. The polymer films deposited on an indium-tin-oxide (ITO) coated glass were used for the Ultraviolet–visible (UV–vis) spectral measurements. Moreover, the polymer films grew potentiostatically, and their thickness was controlled by the total charge passed through the cell that was read directly from the current–time (I–t) curves by computer. After polymerization, all the polybenzanthrone, P3MeT, and poly(3MeT-*co*-benzanthrone) films were rinsed repeatedly with ethyl ether to remove the electrolyte, monomers, and oligomers. To obtain neutral-state films, the doped films were treated with 25% ammonia for 3 days and then washed with pure water repeatedly. Finally, they were dried at 60 °C under vacuum for 2 days.

All the solutions were deaerated by a dry argon stream and maintained under a slight argon overpressure through all the experiments. To the binary solvent solution containing BFEE and ACN, the constant volume ratio of BFEE/ACN was 2:1. Additionally, the concentration of benzanthrone used through all the experiments was 0.01 mol L^{-1}.

Characterization

The electrical conductivity of as-formed polymer and copolymer films was determined by applying the conventional four-probe technique with the pellets of the samples. UV–vis spectra were measured with a Perkin-Elmer Lambda 900 UV–vis-near-infrared spectrophotometer. Infrared spectra were recorded on a Varian 3100 FT-IR spectrometer, where the samples were dispersed in KBr pellets. Thermal behavior of the samples was investigated via a Pyris Diamond TG/DTA thermal analyzer (Perkin-Elmer) under nitrogen (N_2) atmosphere. With an F-4500 fluorescence spectrophotometer (Hitachi), fluorescence spectra were determined.

Results and discussion

Electrochemical copolymerization

It is well known that the oxidation potentials of the starting monomers are relatively close with intention to prepare copolymer chain with alternating monomer units [26, 27].

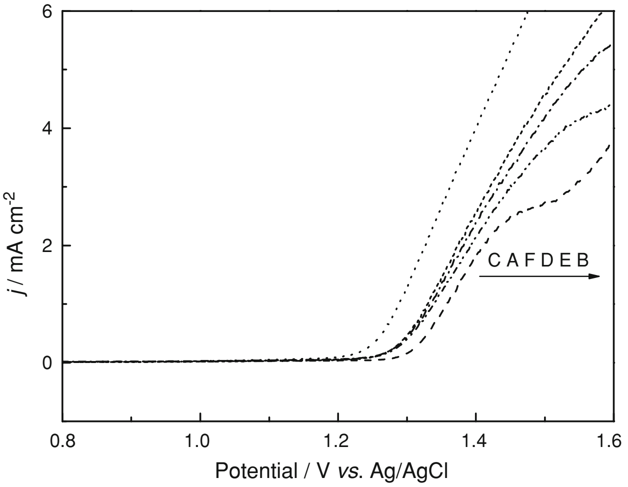


Fig. 1 Anodic polarization curves of 0.05-mol L^{-1} 3MeT (*A*), 0.01-mol L^{-1} benznanthrone (*B*), and the monomer mixtures with the feed ratios of 3MeT/benzanthrone—3:1 (*C*), 2:1 (*D*), 1:1 (*E*), and 1:2 (*F*) in BFEE + ACN (2:1, by volume). The potential scanning rate was 50 mV s^{-1}. *j* denotes the current density

In order to investigate the influence of different monomer feed ratios on the electrochemical copolymerization and properties of the copolymer films, and ensure the occurrence of the copolymerization between 3MeT and benzanthrone, this experiment was carried out in four subordinate groups based on the molar ratio of the monomers. It should be noted here that the background electrolyte is electrochemically inert in the whole potential range. Figure 1 shows the typical anodic polarization curves of the monomers and monomer mixtures with different feed ratios in the binary solvent solution of BFEE and ACN. The onset oxidation potential of 3MeT in the binary solvent solution was approximately 1.24 V (Fig. 1A), while that of benzanthrone was 1.28 V (Fig. 1B). The small distinction (0.04 V) implies that the copolymerization of benzanthrone and 3MeT is quite feasible [27–29]. Four groups of the monomer mixtures with feed ratios of 3MeT/benzanthrone—3:1, 2:1, 1:1, and 1:2 were investigated. As can been seen from Fig. 1, there is no regular variation trend of the oxidation potential onsets for monomer mixtures with different feed ratios. When the feed ratio of 3MeT/benzanthrone was 3:1, the corresponding onset oxidation potential of the monomer mixture was initiated at 1.23 V (Fig. 1C). While when the feed ratio was 2:1, curve D was obtained and the onset oxidion potential was initiated at 1.26 V (Fig. 1D), which was quite close to those of the monomer mixtures with the feed ratio of 3MeT/benzanthrone—1:1 (Fig. 1E) and 1:2 (Fig. 1F). However, with a decrease in the concentration of 3MeT in the system, the onset oxidation potentials did not shift regularly. For this circumstance, there might be several influencing factors, such as the tiny distinction between the onset oxidation potentials of 3MeT and benzanthrone, a drift of the potential of the reference electrode, or the unavoidable differences among the electrochemical environments or the environments of outside [30, 31], in which a series of electrochemical experiments were carried out.

Figure 2 shows the successive cyclic voltammograms (CVs) of benzanthrone, 3MeT, and the monomer mixtures with different feed ratios (3MeT/benzanthrone = 3:1, 2:1, 1:1, 1:2), recorded in the binary solvent system on platinum electrodes at the potential scan rate of 100 mV s^{-1}. As the cyclic voltammetry scan continued, conducting polymer films were formed on the working electrode surface. The increase in the redox wave current densities implied that the amount of conducting polymers deposited on the electrode was increasing. Moreover, the obvious potential shift of the wave current density maximum provided information about the increase in the electrical resistance in the polymer film and the overpotential needed to overcome the resistance [32]. For the CVs recording in the solution of benzanthrone (Fig. 2a), their redox peaks were unsymmetrical and located at about 1.6 and 1.1 V. On the contrary, the CVs of 3MeT recorded in the same medium was quite plump, and 3MeT monomer or oligomer could be oxidized and reduced from 0.8 to 0 V, just as shown in Fig. 2f. For comparison, the CVs of the copolymers deposited in the monomer mixtures with feed ratio of 3MeT/benzanthrone—1:2 (Fig. 2b), 1:1 (Fig. 2c), 2:1 (Fig. 2d), and 3:1 (Fig. 2e) were also illustrated. When the monomer feed ratio of 3MeT/benzanthrone reached 1:1 (Fig. 2c), the mixtures could be oxidized and reduced from 0.7 to 0.2 V. When the concentration of 3MeT was dominated in the monomer mixtures, the CV curves of them were much more similar to those of pure 3MeT, indicating that more 3MeT units were incorporated into the copolymer film (Fig. 2e). As the monomer feed ratio (3MeT/benzanthrone) of the monomer mixtures changed, new redox peaks of the CVs of the copolymer appeared compared with those of 3MeT and benzanthrone, which indicated that a new copolymer of 3MeT and benzanthrone might formed in the system [33] and an appropriate feed ratio of 3MeT/benzanthrone—1:1 was chosen for their copolymerization.

Electrochemistry of the copolymer films

Based on the above observation, further studies were carried out for P3MeT, polybenzanthrone, and the copolymer films generated from the monomer mixtures of 3MeT and benzanthrone. To obtain high-quality polymer or copolymer films and facilitate the experiments, we used the potentiostatic method for the conductive film deposition, and the optimized constant-potential was 1.5 V. The

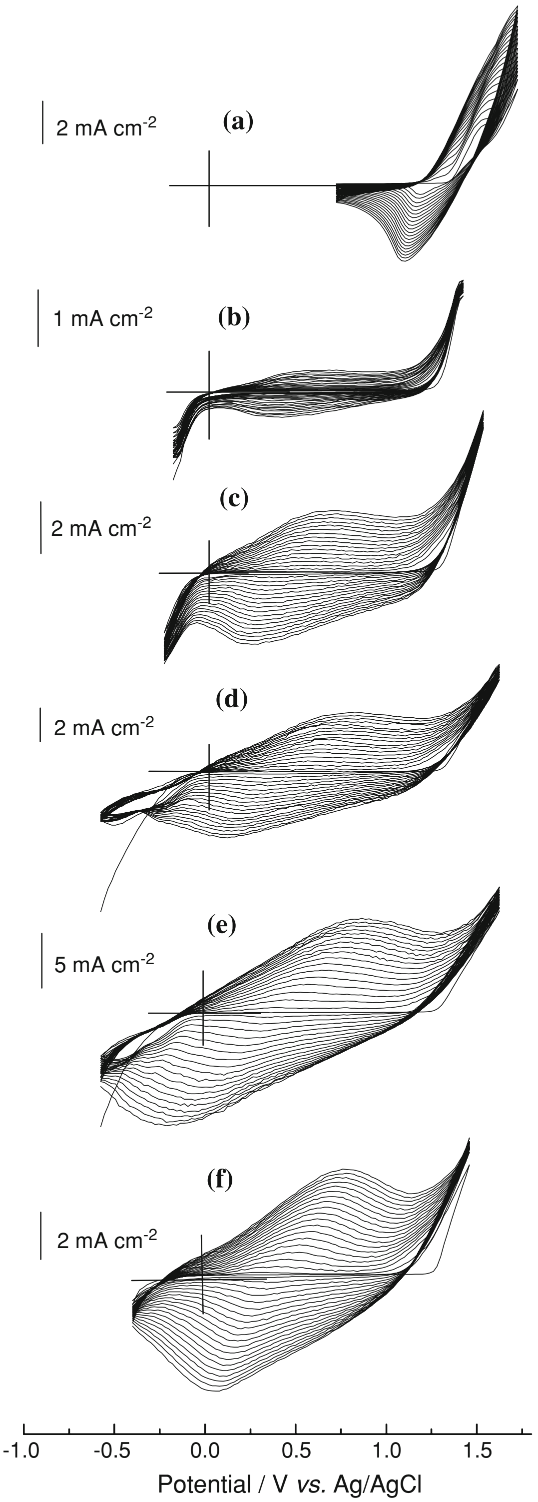


Fig. 2 Cyclic voltammograms of 0.01-mol L^{-1} benzanthrone (**a**), 0.05-mol L^{-1} 3MeT (**f**), and the monomer mixtures with the feed ratios of 3MeT/benzanthrone—1:2 (**b**), 1:1 (**c**), 2:1 (**d**), 3:1 (**e**) in BFEE + ACN (2:1, by volume). The potential scanning rate was 100 mV s^{-1}

electrochemical properties of these films mentioned above were characterized by CVs both in the monomer-free binary solvent solution (Fig. 3) and in BFEE (Fig. 4). Obviously, these polymer films were cycled repeatedly between conducting and insulating states without significant decomposition. Furthermore, exhibited by the insets of Figs. 3 and 4, the current densities were proportional to the potential scan rates, indicating a redox couple fixed on the electrode. As can be seen from Fig. 3, P3MeT synthesized from the binary solvent system with the concentration of 3MeT being 0.05 mol L^{-1}, was oxidized and reduced from 0.90 to 0 V (Fig. 3e). For polybenzanthrone film, polymerized in the binary solvent system containing 0.01 mol L^{-1} benzanthrone monomer, much higher potentials were needed to oxidize or reduce the film (from 1.48 to 0.90 V) (Fig. 3a). Figure 3b–d showed the CVs of the copolymer films electrodeposited with feed ratios of 3MeT/benzanthrone—1:1, 2:1, 3:1, successively. Specifically, the copolymer film with the feed ratio of 3MeT/benzanthrone—1:1, could be oxidized or reduced from 0.63 to 0.30 V (Fig. 3b). With a feed ratio of 3MeT/benzanthrone—2:1, the copolymer showed a couple of redox waves at 0.68 and 0.25 V, as shown in Fig. 3c. When the feed ratio changed to 3:1, the redox peaks located at around 0.83 and 0.08 V (Fig. 3d), quite close to the values of P3MeT. Based on the comparison described above and new pairs of redox peaks appearing in the CVs of the copolymers, it was reasonable to arrive at the conclusion that the two monomers, 3MeT and benzanthrone, were oxidized together to some extents, and the copolymer chain was composed of both 3MeT and benzanthrone units. Similar results were also observed about the CVs of these polymers in BFEE, just as shown in Fig. 4. A detailed summary of the oxidation and reduction potentials of these polymer films in different electrolytes is listed in Table 1.

The CVs of the bilayer films (polybenzanthrone–P3MeT composite) prepared successively in the binary solvent solutions containing benzanthrone or 3MeT at the same applied potential of 1.5 V, were also studied in the monomer-free binary solvent solution and pure BFEE, as shown in Figs. 3f and 4f. Apparently, they were quite different from those of polybenzanthrone, P3MeT, and the copolymer films. For each CVs of the bilayer films recorded in the monomer-free binary solvent solution (Fig. 3f) and in the pure BFEE (Fig. 4f), two reduction peaks could be easily observed, which were ascribed to the corresponding peaks of pure polybenzanthrone and P3MeT; however, the two oxidation peaks were not so clear-cut. This suggested that the two polymers were oxidized and reduced alternately, implying the copolymers were different from the mixtures of pure polybenzanthrone and P3MeT. On the contrary, there was only one pair redox peaks in the CVs of the copolymer (Figs. 3, 4b–d) recorded in the same medium, further confirming the occurrence of copolymerization of 3MeT and benzanthrone in the binary solvent system containing BFEE and ACN [34].

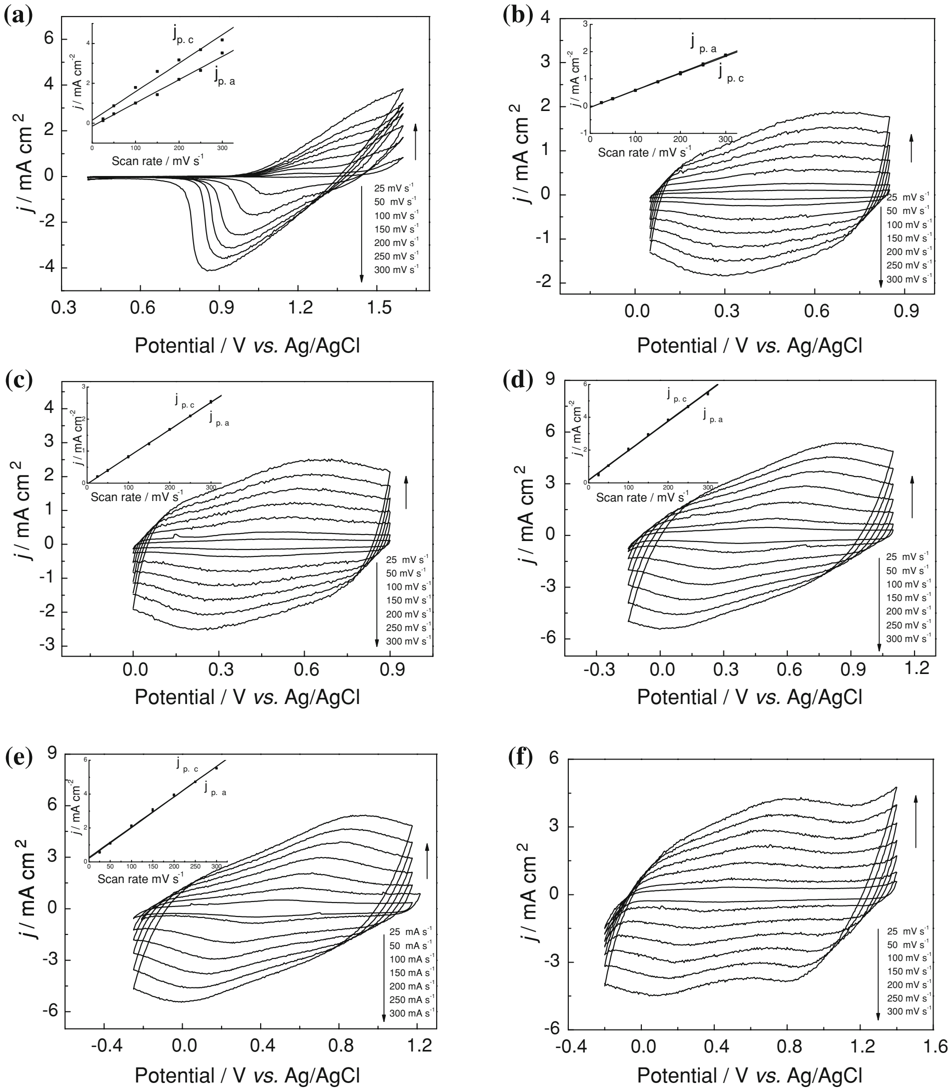


Fig. 3 Cyclic voltammograms of polybenzanthrone (**a**), poly(3MeT-*co*-benzanthrone) with the feed ratios of 3MeT/benzanthrone—1:1 (**b**), 2:1 (**c**), and 3:1 (**d**), P3MeT (**e**), and the mixed bilayer films (**f**), recorded in the monomer-free BFEE + ACN (2:1, by volume), at different potential scan rates. The mixed bilayer films (polybenzanthrone/P3MeT) were electrodeposited in solutions of benzanthrone and 3MeT at the same applied potentials of 1.5 V versus Ag/AgCl for 30 s. j is the current density, and $j_{\mathrm{p.a}}$ and $j_{\mathrm{p.c}}$ denote the anodic and cathodic peak current densities, respectively

Structural characterization

During the potentiostatic process, the original solutions darkened step by step as the polymerization went on. This indicated that the soluble oligomers might have formed during the anodic oxidation. With the propagation of the polymerization, partly soluble oligomers became insoluble and were deposited on the working electrode surface with the elongation of the polymer main chain. However, there were still some oligomers, which diffused from the electrode into the bulk solution. As a result, the color of the bulk solution darkened.

P3MeT is well known as electrochromic and semiconducting materials, because the polymers can be repeatedly driven from insulating to conducting states electrochemically with high contrast in color [35–37] and this electrochromic property cannot be observed for polybenzanthrone at all. In detail, P3MeT film electrogenerated in the binary solvent system changed its color from dark blue in doped state to brown in dedoped state. However, the color of polybenzanthrone film is golden yellow both in doped and dedoped states. For copolymers, their colors changed from dark green in doped state to dimgray in dedoped state, being similar to P3MeT as they exhibited electrochromic property to some extent, which indicated that there were 3MeT units inserting into the copolymer chain. On the other hand, according to the literature [6], polybenzanthrone has nice solubility that it can dissolve in common organic solvents, such as methanol, ethanol, acetone, DMSO, ACN, ethyl ether, etc. On the contrary, the solubility of P3MeT prepared electrochemically was too poor to dissolve in any organic solvents. For the copolymers, as be expected to possess the combination properties of the pure polybenzanthrone and P3MeT, they could partly dissolved in some organic solvents (e.g., DMSO, ACN, and diethyl ether). Based on the phenomenon described above,

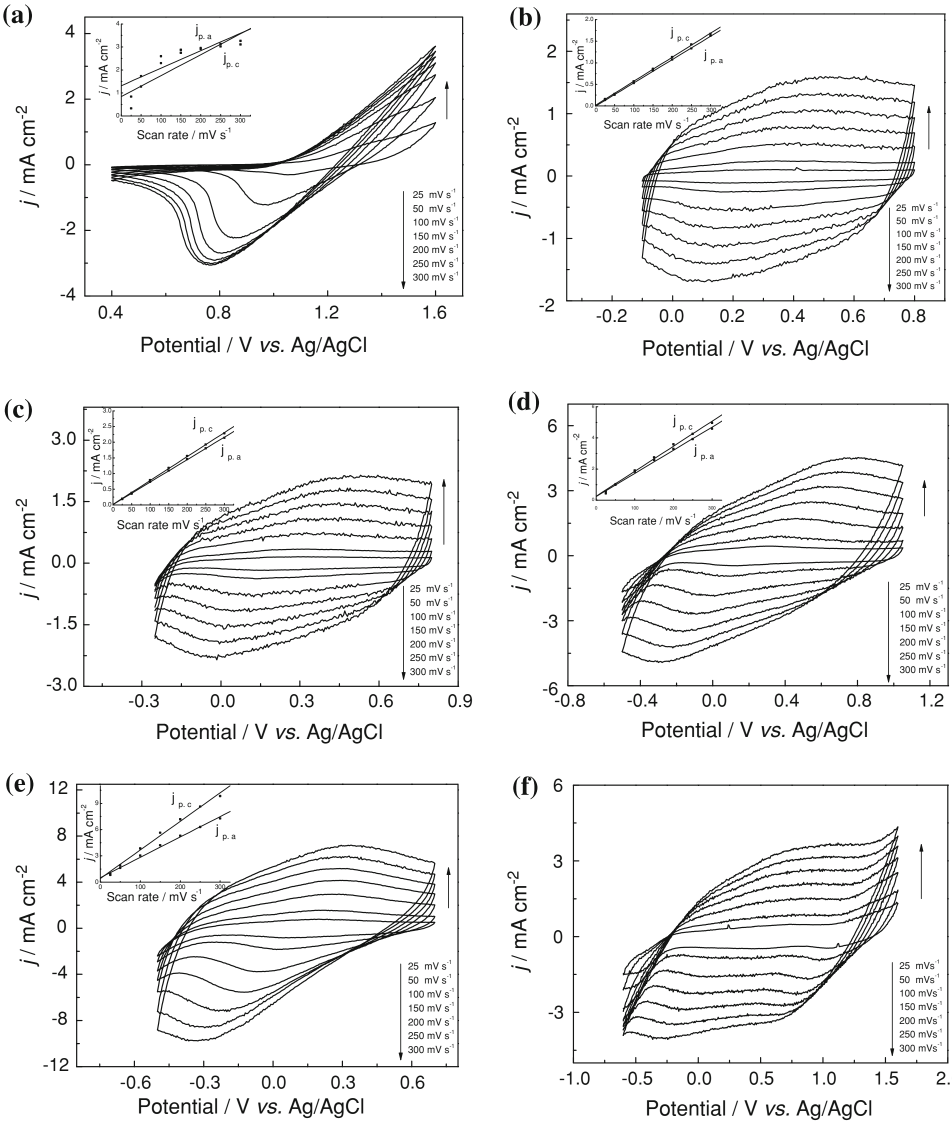


Fig. 4 Cyclic voltammograms of polybenzanthrone (**a**), poly(3MeT-*co*-benzanthrone) with the feed ratios of 3MeT/benzanthrone—1:1 (**b**), 2:1 (**c**), and 3:1 (**d**), P3MeT (**e**), and the mixed films (**f**) recorded in monomer-free BFEE at different potential scan rates. The mixed bilayer films (polybenzanthrone/P3MeT) were electrodeposited in solutions containing benzanthrone and 3MeT, respectively, at the applied potential of 1.5 V versus Ag/AgCl for 30 s. j is the current density, $j_{p.a}$ and $j_{p.c}$ denote the anodic and cathodic peak current densities, respectively

there might be some reactions occurred between the two monomers during the potentiostatic process. As a result, the insertion of benzanthrone units into P3MeT could improve the solubility of the copolymers.

The UV–vis spectra of the copolymer films, electrodeposited on ITO electrodes from the monomer mixtures with different monomer feed ratios, are shown in Fig. 5. The spectrum of polybenzanthrone film showed characteristic absorptions at 435 nm (Fig. 5A), which could be assigned to the valence band–conductive band (π–π) transition. However, there was a slight red shift of the main absorption of polybenzanthrone film deposited on ITO electrode in comparison with that of polybenzanthrone dissolved in DMSO (423 nm) [6]. The reasonable explanation for this phenomenon might be that among the solid state polybenzanthrone, there were some polymers with longer conjugated chains, which were insoluble in DMSO. As a result, the aromaticity of solid state polybenzanthrone was higher than that of polybenzanthrone dissolved in common organic solvents. For P3MeT film, there was a broad absorbtion at 550–950 nm, with a maximum at 750 nm (Fig. 5B). Similar to those of P3MeT and polybenzanthrone, the spectra of the copolymers (Fig. 5C–F) showed the characteristic absorptions of both P3MeT and polybenzanthrone, which further confirmed the occurrence of the copolymerization between 3MeT and benzanthrone.

Figure 6 shows the vibrational spectra of polybenzanthrone, P3MeT, and poly(3MeT-*co*-benzanthrone) with the feed ratios of 3MeT/benzanthrone—1:2, 1:1, 2:1, and 3:1. The vibrational spectra can provide structure information of these polymers. A comparison of the evolution of the vibrational modes appearing in the conducting polymers usually shed light on the interpretation of the polymerization process. According to the spectrum of polybenzanthrone

Table 1 Redox peak potentials of the CVs of P3MeT, polybenzanthrone, and the copolymer films prepared with different feed ratios of 3MeT/benzanthrone at the constant-potential of 1.5 V, recorded in the monomer-free BFEE + ACN (2:1, by volume) and BFEE, respectively

	BFEE		BFEE + ACN (2:1)	
	E_{pa} (V)	E_{pc} (V)	E_{pa} (V)	E_{pc} (V)
Polybenzanthrone	1.42	0.73	1.48	0.90
Poly(3MeT-*co*-benzanthrone) 1:1	0.47	0.01	0.63	0.30
Poly(3MeT-*co*-benzanthrone) 2:1	0.50	0.00	0.68	0.25
Poly(3MeT-*co*-benzanthrone) 3:1	0.68	−0.29	0.83	0.08
P3MeT	0.35	−0.30	0.90	0.00

All the potentials were versus an Ag/AgCl electrode

E_{pa} anodic peak potential, E_{pc} cathodic peak potential

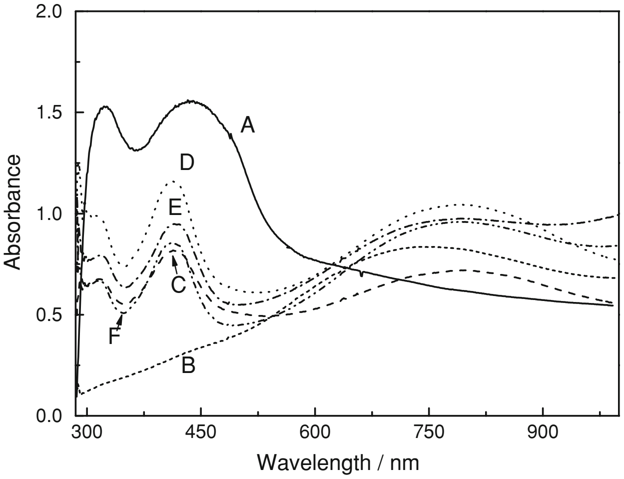


Fig. 5 UV–Vis spectra of doped polybenzanthrone (*A*), P3MeT (*B*), and the copolymer films with feed ratios of 3MeT/benzanthrone—1:2 (*C*), 1:1 (*D*), 2:1 (*E*), 3:1 (*F*) deposited on ITO glasses. The polymer films mentioned above were electrodeposited in BFEE + ACN (2:1, by volume) at a constant applied potential of 1.5 V versus Ag/AgCl

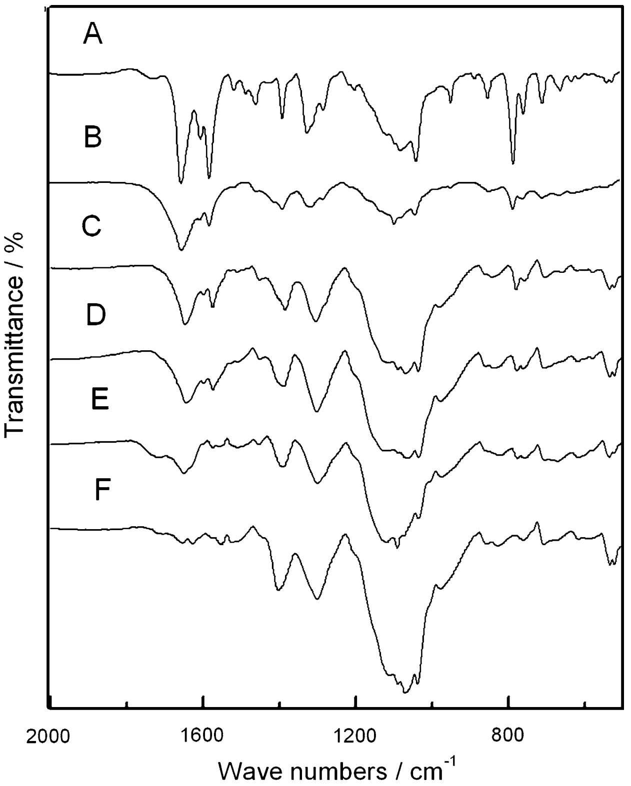


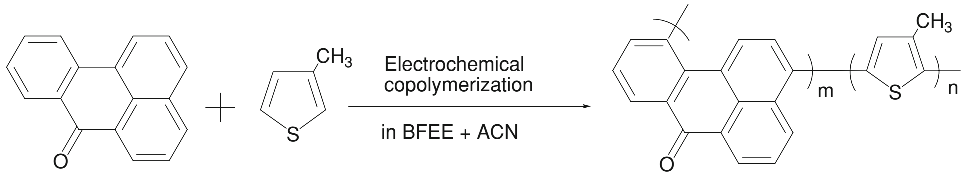
Fig. 6 FT-IR spectra of polybenzanthrone (*A*), P3MeT (*F*), and poly(3MeT-*co*-benzanthrone) in dedoped state, prepared in BFEE + ACN (2:1, by volume), with the feed ratios of 3MeT/benzanthrone—1:2 (*B*), 1:1 (*C*), 2:1 (*D*), and 3:1 (*E*) at an applied potential of 1.5 V versus Ag/AgCl

(Fig. 6A), the bands at 1650 and 1580 cm^{-1} were ascribed to C=O stretching vibration and C=C ring stretching vibration, respectively. The bands at 1320 and 1276 cm^{-1} were related to the C–C–C (aryl ketones) asymmetric stretching vibration. The bands at 1077 and 1030 cm^{-1} were ascribed to the C–H in-plane bending of 1,2,3-trisubstituted phenyl and C–H in-plane bending of 1,2,3,4-tetrasubstituted phenyl, respectively. Furthermore, the bands at 847, 777, and 700 cm^{-1} were assigned to the 1,2,3,4-tetrasubstituted C–H wagging, 1,2,3-trisubstituted C–H wagging, and 1,2,3-trisubstituted ring deformation, respectively. The above-mentioned bands could also be found in the vibrational spectra of the copolymers. For P3MeT (Fig. 6F), the bands at 1628 and 1130 cm^{-1}, originating from the stretching modes of C=C in the thiophene ring [38], together with the band at 824 cm^{-1} were ascribed to the out-of-plane C–H bands, which could be found in the spectra of the copolymers (Fig. 6B–E). The bands at 1401 and 1302 cm^{-1} were assigned to the deformation of the methyl group. The weak absorption band at about 609 cm^{-1} was the characteristic absorption of the C–S bond. On the basis of the above discussion, the characteristic peaks in the vibrational spectra of polybenzanthrone and P3MeT could also be found out in the spectra of the copolymers of 3MeT and benzanthrone. The proposed copolymerization mechanism 3MeT and benzanthrone is illustrated in Scheme 1.

Fluorescence property

It is well known that polybenzanthrone with nice solubility in common organic solvents, is a good green-light emitter, while P3MeT showed almost no emission in the whole wavelength range. For P3MeT prepared electrochemically by direct anodic oxidation, it possesses the advantages of facile electrodeposition of free-standing polymer film with excellent mechanical property and high electrical

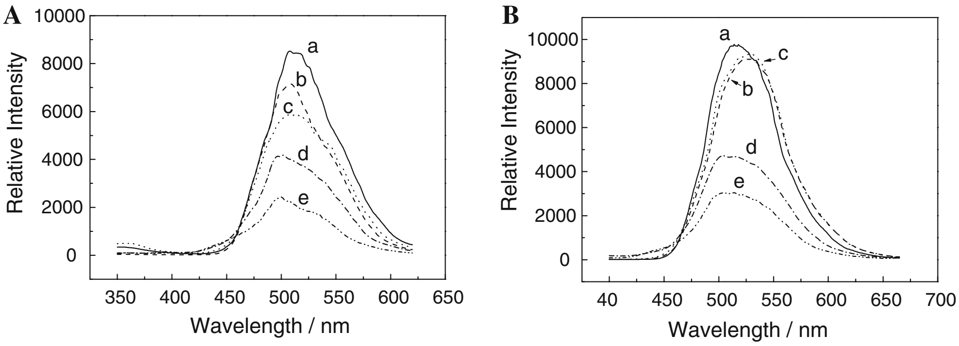
Scheme 1 Proposed electrochemical copolymerization mechanism of 3MeT and benzanthrone in BFEE + ACN (2:1, by volume)



conductivity [17–22]. It will be interesting if all the advantages of these two polymers can be combined together, and the novel copolymers with the property intermediate between those of P3MeT and polybenzanthrone may find application in the PLEDs field as light-emitting films. The fluorescence spectra of polybenzanthrone and the copolymers in the doped state with monomer feed ratios of 3MeT/benzanthrone—1:2, 1:1, 2:1, and 3:1, dissolved in DMSO were illustrated in Fig. 7A. Polybenzanthrone exhibited a strong emission peak at about 512 nm (Fig. 7A-a). For the copolymers, the corresponding fluorescence spectra were a little blue shift with the maximum emission peaks at about 499 nm. Moreover, the intensity of the emission of the copolymers was still very strong, and deceased gradually with an increase in the P3MeT concentration in the copolymers (Fig. 7A-b–e). The same phenomenon could also be observed in the fluorescence spectra of polybenzanthrone and the copolymers in dedoped state dissolved in DMSO at excitation of 335 nm UV light, just as shown in Fig. 7B. At 515 nm, polybenzanthrone exhibited a strong emission peak (Fig. 7B-a). For the copolymers with the feed ratios of 1:2 (Fig. 7B-b) and 1:1 (Fig. 7B-c), they showed strong emission peaks centering at 529 nm, a little red shift compared to that of polybenzanthrone. With an increase in the 3MeT concentration in the copolymers, the emission intensity of these copolymers decreased gradually. All the above phenomena indicated that there were benzanthrone units inserting into the copolymer or oligomer chains, and the intrachain energy transfer in the copolymer or the intrachain interaction between poly(3MeT-*co*-benzanthrone) chains dissolved in DMSO, were less efficient [24].

Moreover, the photoluminescence property of polybenzanthrone and poly(3MeT-*co*-benzanthrone) dissolved in DMSO both in doped (Fig. 8A) and dedoped states (Fig. 8B) are shown in Fig. 8, when exposed to 365 nm UV light. As shown in Fig. 8, polybenzanthrone both in doped and dedoped states exhibited a bright-green-light-emitting property. As the concentration of 3MeT in the copolymers increased, the luminescent intensity of the copolymers decreased gradually, which might be attributed to that less benzanthrone units incorporated into the polymer chains

Fig. 7 Fluorescence spectra of polybenzanthrone (*a*), poly(3MeT-*co*-benzanthrone) prepared in BFEE + ACN (2:1, by volume) at constant applied potential of 1.5 V versus Ag/AgCl, with 3MeT/benzanthrone—1:2 (*b*), 1:1 (*c*), 2:1 (*d*), and 3:1 (*e*), in doped state (**A**) and dedoped state (**B**) dissolved in DMSO



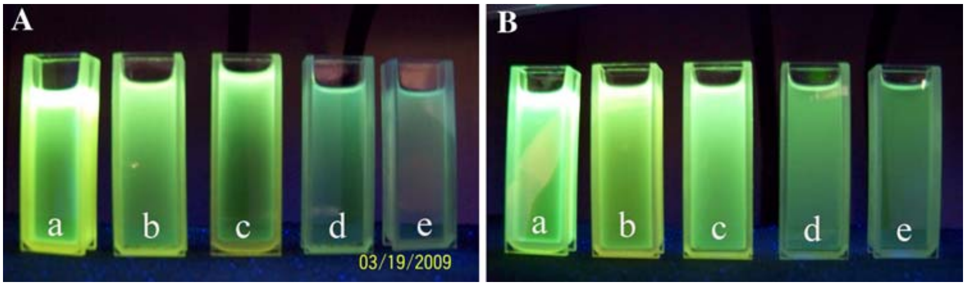


Fig. 8 Photoluminescence of polybenzanthrone (*a*) and the copolymers of 3MeT and benzanthrone electrodeposited in BFEE + ACN (2:1, by volume) with feed ratios of 3MeT/benzanthrone—1:2 (*b*), 1:1 (*c*), 2:1 (*d*), and 3:1 (*e*), in doped (**A**) and dedoped states (**B**), under UV light irradiation of 365 nm at an applied potential of 1.5 V versus Ag/AgCl, solvent: DMSO

and the quenching of the copolymer emission occurred at the same time, as shown in Fig. 8A, B(b–e) with the monomer feed ratios of 3MeT/benzanthrone—1:2 (b), 1:1 (c), 2:1 (d), and 3:1 (e). Moreover, it should be noted here that polybenzanthrone and the copolymers in doped state (Fig. 8A) showed slight weaker emission light than the dedoped ones (Fig. 8B), which mainly because that the dopants in the doped polybenzanthrone and copolymers led to fluorescence quenching among the polymer matrix, in accordance with the literature [6]. On the basis of these striking fluorescent results, as excellent green-light-emitting polymers, the copolymer films of 3MeT and benzanthrone may exploit applications in various fields, such as optoelectronics, and may be promising candidates for the hole-transporting materials in LEDs.

Thermal analysis

It is well known that the thermal property of conducting or semiconducting polymers is quite important for their potential applications. To investigate the thermal property of these polymers and copolymers, thermogravimetric analytical experiments were performed under a nitrogen stream at a heating rate of 10 K min^{-1}, as shown in Fig. 9. As recorded in the literature [6, 24, 39], both P3MeT and polybenzanthrone have good thermal stability. For P3MeT (Fig. 9A), there were two prominent decompositions at 537 and 759 K. The former might be attributed to the degradation of some oligomers and the latter one was caused by the decomposition of the skeletal P3MeT back bone structure. On the other hand, polybenzanthrone (Fig. 9D) underwent its maximum degradation when the temperature reached about 714 K, and the preceding degradation might be attributed to the decomposition of the oligomer or moisture concealed in the polymer. For the copolymers, with the feed ratios of 2:1 (Fig. 9B) and 1:1 (Fig. 9C), there were some improvements in their thermal property compared with their corresponding homopolymers. However, because of the high concentration of 3MeT in the medium with monomer feed ratio of 2:1, the thermal behavior of the copolymer was similar to that of P3MeT. The above mentioned implied that the incorporation of 3MeT and benzanthrone units with different feed ratios into the copolymer chains had influence on the thermal property of the copolymers, which were intermediate between those of P3MeT and polybenzanthrone. All these results demonstrated that the copolymers had good thermal stability.

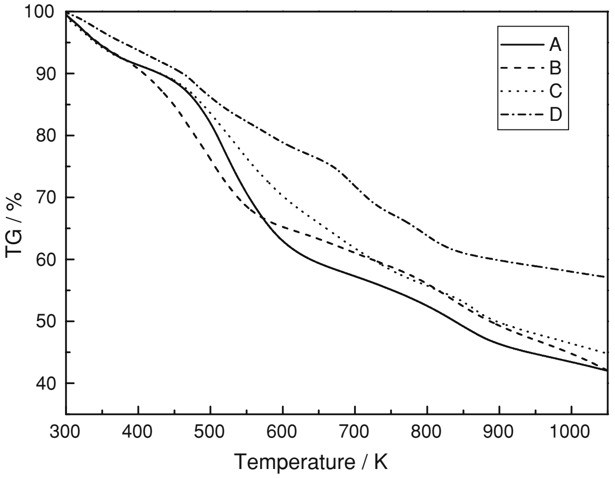


Fig. 9 Thermogravimetric (TG) curves of P3MeT (*A*), and poly (3MeT-*co*-benzanthrone) electrodeposited in BFEE + ACN (2:1, by volume) at an applied potential of 1.5 V versus Ag/AgCl, with the feed ratios of 3MeT/benzanthrone—2:1 (*B*) and 1:1 (*C*), and polybenzanthrone (*D*)

Electrical conductivity and morphology

The electrical conductivities of P3MeT, polybenzanthrone, and poly(3MeT-*co*-benzanthrone) films were measured and listed in Table 2. The conductivity of P3MeT was up to 63.6 S cm^{-1}, while that of polybenzanthrone was about 1.7 S cm^{-1}. For the copolymers electrodeposited in the binary solvent solution with the feed ratio of 3MeT/benzanthrone—1:1 at different potentials, the conductivities were between those of P3MeT and polybenzanthrone, as shown in Table 2, indicating that the incorporation of 3MeT units into the polybenzanthrone chains was helpful to improve the conductivity of polybenzanthrone. In detail, when 1.5 V was used as the applied potential, the resulting copolymer showed higher conductivity (about 7.9 S cm^{-1}) compared with those of the other copolymers prepared at different applied potentials. Therefore, 1.5 V was the best choice as an applied potential for the copolymerization of 3MeT and benzanthrone with the feed ratio of 3MeT/benzanthrone—1:1 in the binary solvent system of BFEE and ACN.

Table 2 Electrical conductivities of P3MeT, polybenzanthrone, and poly(3MeT-*co*-benzanthrone) films prepared in BFEE + ACN (2:1, by volume) with the monomer feed ratio of 3MeT/benzanthrone—1:1 at applied potentials of 1.3, 1.4, 1.5, and 1.6 V versus Ag/AgCl, respectively

Polymer	Conductivity (S cm^{-1})
P3MeT	63.6
Poly(3MeT-*co*-benzanthrone) (1:1), 1.3 V	3.7
Poly(3MeT-*co*-benzanthrone) (1:1), 1.4 V	5.2
Poly(3MeT-*co*-benzanthrone) (1:1), 1.5 V	7.9
Poly(3MeT-*co*-benzanthrone) (1:1), 1.6 V	4.3
Polybenzanthrone	1.7

On the other hand, the mechanical property of P3MeT was so good that it could be peeled off from the electrode into free-standing film state. On the contrary, the polybenzanthrone film was brittle, and it had some difficulty to obtain polybenzanthrone in free-standing film state. As a result, the copolymerization of 3MeT and benzanthrone improved the quality of the copolymer film significantly. These copolymer films could also be peeled off from the electrode surface carefully, as free-standing films.

Conclusions

The electrochemical copolymerization of 3MeT and benzanthrone in the binary solvent system containing BFEE and ACN (2:1, by volume), was successfully realized by direct anodic oxidation of the monomer mixtures. The properties of the as-formed poly(3MeT-*co*-benzanthrone) films depended on the mixture feed ratios and the applied potential. The incorporation of 3MeT units into the polymer chain could overcome the low electrical conductivity derived from the poor quality of the polybenzanthrone film. On the other hand, too much 3MeT units into the copolymer chain could result in the quenching of the copolymer emission. Based on the above experiments and comparisons, the copolymer film electrodeposited in the binary solvent solution containing 0.01-mol L^{-1} 3MeT and 0.01-mol L^{-1} benzanthrome possessed better properties comparing with the other copolymers. The as-formed copolymer films exhibited the advantages of both P3MeT and polybenzanthrone, such as good redox activity, nice solubility, and relatively high mechanical property and electrical conductivity. The copolymers dissolved in DMSO were good green-light emitters, with a maximum emission at about 499 nm in doped state and at 529 nm in dedoped state. The successful copolymerization of 3MeT and benzanthrone may be helpful to exploit their application extent in PLEDs as the light-emitting material.

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