

Electrosyntheses and Characterizations of a Soluble Blue Fluorescent Copolymer Based on Pyrene and Carbazole

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Poly(carbazole-co-pyrene) is successfully achieved by electrochemical oxidation of the monomer mixtures of carbazole (Cz) and pyrene in acetonitrile (ACN) containing sodium perchlorate (NaClO₄). FT-IR and ¹H NMR characterizations support that the obtained copolymers contain both pyrene and carbazole units. A series of experiments are carried out to investigate the properties of the copolymers obtained from 0.2 M NaClO₄/ACN. The electrochemical properties of the obtained copolymers are studied by cyclic voltammetry (CV). Compared with polypyrene, the copolymer shows good solubility in common organic solvents. The UV-vis absorption peak of the dedoped copolymer dissolved in DMF exhibits a significant red-shift. Fluorescence spectra studies reveal that the copolymer is a good blue-light emitter and the photoluminescence (PL) quantum yield (Φ) of the copolymer obtained at 1:1 is 89% in DMF solution. The obtained copolymer also presents properties of electrochromism and good thermal stability.

Keywords: Electrochemical copolymerization, conjugated polymer, polypyrene, polycarbazole, fluorescence

1. INTRODUCTION

π -conjugated polymers have been considered as promising materials holding unique optical and electrical properties [1], and have been widely applied in the fields of polymer solar cells (PSCs) [2], electrochromic devices [3, 4], sensors [5], polymer light emitting diodes (PLEDs) [6], and so on. These electroactive and photoactive polymers are usually based on thiophene, pyrrole, phenylene, fluorene, or carbazole moieties. The synthesis of these conjugated polymers can be carried out by either chemical or electrochemical method. The yield of products obtained from chemical routes is very low and the synthesis cost is very high, while electrochemical polymerization has been proved to be one of the most useful approaches for conjugated polymers synthesis [7]. Compared with the chemical routes,

electrochemical polymerization can obtain conjugated polymer films on conductive substrates directly. This not only enlarges the scope of candidate polymers [8, 9], but also omits the procedure of the film coating [10, 11].

Among the many investigations, structural modification of the polymer backbone has been used to control the resulting properties, e.g. incorporation of long alkyl chains in a given heterocyclic usually leads to the formation of soluble polymers [12, 13]. Copolymerization is also one of the widely accepted and feasible methods to modify various properties of the polymer films [14], such as photoelectronic properties, electronic properties and electroluminescence [15].

Among conjugated polymers, carbazole (Cz) containing polymers are of interest due to their applications in electrochromic devices, hole transport layers, and photovoltaic components [16,17]. These polymers obtained have various advantageous properties, such as high charge carrier mobility, electrochromic properties and photochemical stabilities [18]. Due to the ease of formation of relatively stable radical cations (polarons), carbazole can be readily polymerized at electrochemical polymerization process [15]. However, the direct electrooxidation of carbazoles in organic media such as CH₃CN leads to short oligomeric segments [19]. The principal properties of polycarbazole (PCz) might be improved by the introduction of a proper moiety in the backbone of the polymer, which can be facilely achieved by electrochemical copolymerization process. Here, electrochemical copolymerization is undertaken by direct oxidation of a mixture of carbazole and pyrene monomers in ACN solution. Pyrene is chosen as comonomer due to its good performance in solution [20], good fluorescence property and electron-acceptor nature [21]. As well known, polypyrene has been extensively studied as a blue-emission material with high photoluminescence quantum efficiency [22]. However, the synthesized polypyrene via anodic coupling is electrochemically irreversible and gets degraded easily [23]. In this paper, we expect that the electrochemical oxidation of a mixture of pyrene and carbazole could lead to the formation of the copolymers with improved characteristics (good solubility, optical and electric properties) compared with that of the polycarbazole or polypyrene. In addition, donor-acceptor copolymer would be prepared by incorporation pyrene units into carbazole-based main chains due to the electron-acceptor nature of pyrene moieties and the electron-donor property of carbazole units.

In this paper, we successfully electrosynthesize poly(carbazole-*co*-pyrene) films via the electrochemical oxidation of Cz/pyrene mixtures. The obtained copolymers are investigated by cyclic voltammetry (CV) and characterized by FT-IR, ¹H NMR, UV-vis and fluorescence spectra. The electrochromic property, thermal stability and morphology of the copolymer are also investigated in detail.

2. EXPERIMENTAL

2.1. Materials

Carbazole (Cz, Aldrich, analytical grade), pyrene (Acros Organics, 98%) and commercial high-performance liquid chromatography grade acetonitrile (ACN, Tedia Company, INC. USA) are used

directly without further purification. Sodium perchlorate (NaClO_4 , Shanghai Chemical Reagent Company, 98%) is dried in vacuum at 60 °C for 24 hours before use. N, N-Dimethyl formamide (DMF, AR) is a product of Beijing East Longshun Chemical Plant and is used directly. Other reagents are all used as received without further treatment. Indium-tin-oxide-coated (ITO) glass is washed with ethyl alcohol, acetone and deionized water successively, and then dry by N_2 flow.

2.2. Electrochemical synthesis and experiments

Electrochemical syntheses and experiments are performed in a one-compartment cell with a CHI 760 C Electrochemical Analyzer under computer control. The working and counter electrodes for cyclic voltammetric experiments are two platinum wires each with a diameter of 0.5 mm, placed 0.5 cm apart during the experiments, which are cleaned before each examination. An Ag/AgCl electrode (saturated KCl) is used as a quasi-reference electrode. All of the electrochemical experiments are performed at room temperature. All electrochemical polymerization and CV tests are taken in ACN solution containing 0.2 M NaClO_4 as a supporting electrolyte. And, monomer (or monomer mixtures) solutions are fixed at 2 ml, the depth of the working electrode immersed into the polymerization solutions is about 0.45 cm. After polymerization, the exact length of the obtained polymer film are measured and be taken into account in calculating the current densities. All solutions are deaerated by a dry N_2 stream and maintained at a slight N_2 overpressure during experiments.

To obtain a sufficient amount of polymer for characterization, stainless steel sheets with a surface area of 10 and 12 cm^2 each are employed as working and counter electrodes, respectively. Stainless steel electrodes are carefully polished with abrasive paper (1200 mesh), cleaned with deionized water and acetone successively, and then dried in air. After electrochemical polymerization at 1.25 V potentiostatically on stainless steel electrode, electrochemical dedoping is carried out at -0.1 V for 30 mins. In order to remove the electrolyte, oligomers and monomers, the polymers including PCz, polypyrene and copolymer (Cz-co-pyrene) films are peeled off, rinsed with ACN for 3 times, respectively. For spectral analysis and thermal analysis, these polymers are dried under vacuum at 60 °C for 24 hours.

The polymer films used for the UV-vis electrochromism are deposited on ITO (0.9 cm \times 2.0 cm) surface at 1.25 V potentiostatically with the charge of 2×10^{-2} C and washed with ACN. The polymer films used for morphology characterization are also electrodeposited on ITO (0.5 cm \times 0.5 cm) electrode at 1.25 V potentiostatically for 200s, and dedoped at -0.1 V for 30 s.

2.3. Characterizations

The obtained copolymers are studied by cyclic voltammetry. Infrared spectra are recorded on a Nicolet 5700 FT-IR spectrometer, where the samples are dispersed in KBr pellets. ^1H NMR spectra are collected on a Varian AMX 400 spectrometer. UV-vis spectra are measured with a Perkin-Elmer Lambda 900 UV-vis-near-infrared spectrophotometer. Thermal behavior of the polymers is investigated via a Pyris Diamond TG/DTA thermal analyzer (Perkin-Elmer) under nitrogen (N_2)

atmosphere in the temperature range of 40-800 °C with a heating rate of 10 °C min⁻¹. With an F-4500 fluorescence spectrophotometer (Hitachi), fluorescence spectra are determined. Scanning electron microscopy (SEM) measurements are taken by using a JEOL JSM-6380LV SEM. The images of electrochromic films and photoluminescence of soluble polymers are taken by a Fujifilm Shot (FinePix F200EXR). The fluorescence quantum yield (Φ) of dedoped copolymer obtained with the feed ratio of Cz/pyrene at 1:1 (Copolymer 1) in DMF is measured using anthracene in acetonitrile ($\Phi_{ref} = 0.27$) as the reference [24] and is calculated according to the well-known method given as Eq.(1):

$$\phi = \frac{n^2 A_{ref} I}{n_{ref}^2 A I_{ref}} \phi_{ref} \quad (1)$$

Here, n is the refractive index of the solvent, A is the absorbance at the excitation wavelength, and I is the intensity of the emission spectrum. The subscript *ref* denotes the reference, and no subscript denotes the sample. Absorbance of the samples and the standard should be similar [25].

3. RESULTS AND DISCUSSION

3.1. Electrochemical polymerization

Figure 1 shows the anodic polarization curves of 0.01 M carbazole, 0.01 M pyrene and the Cz/pyrene mixture at 1:1 in 0.2 M NaClO₄/ACN. The onset oxidation potential ($E_{pa \text{ onset}}$) of carbazole in the solution is about 0.99 V (Fig. 1b), while that of pyrene is 1.08 V (Fig. 1a).

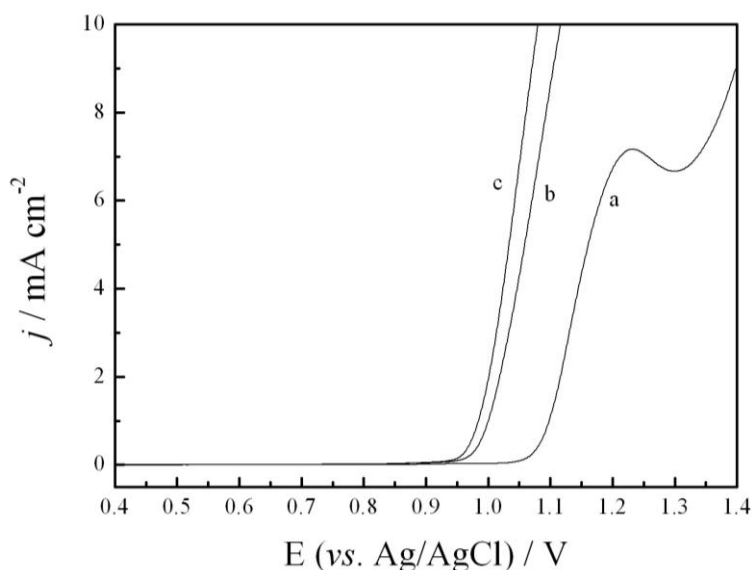
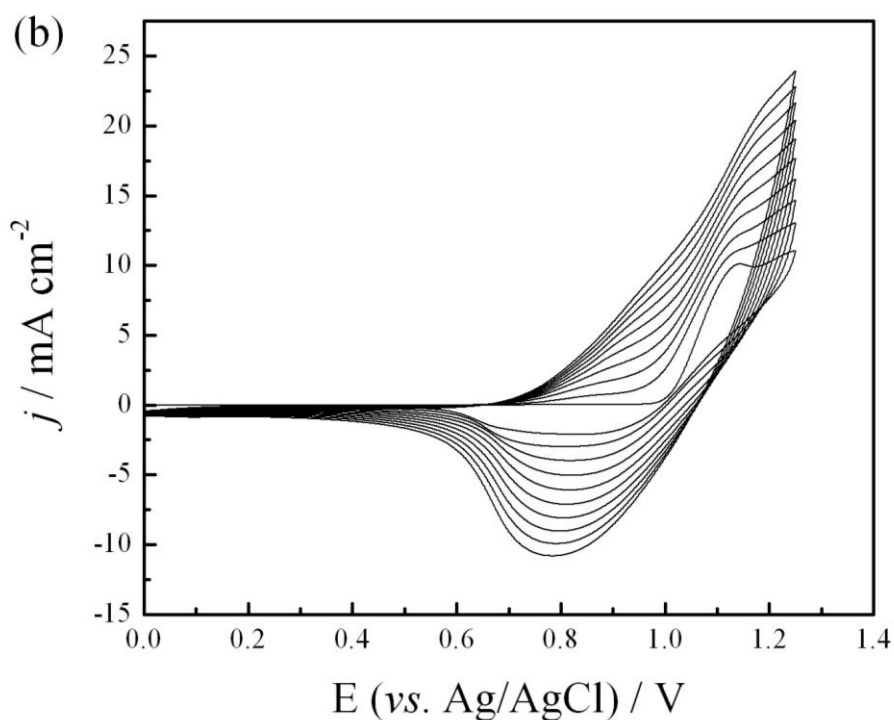
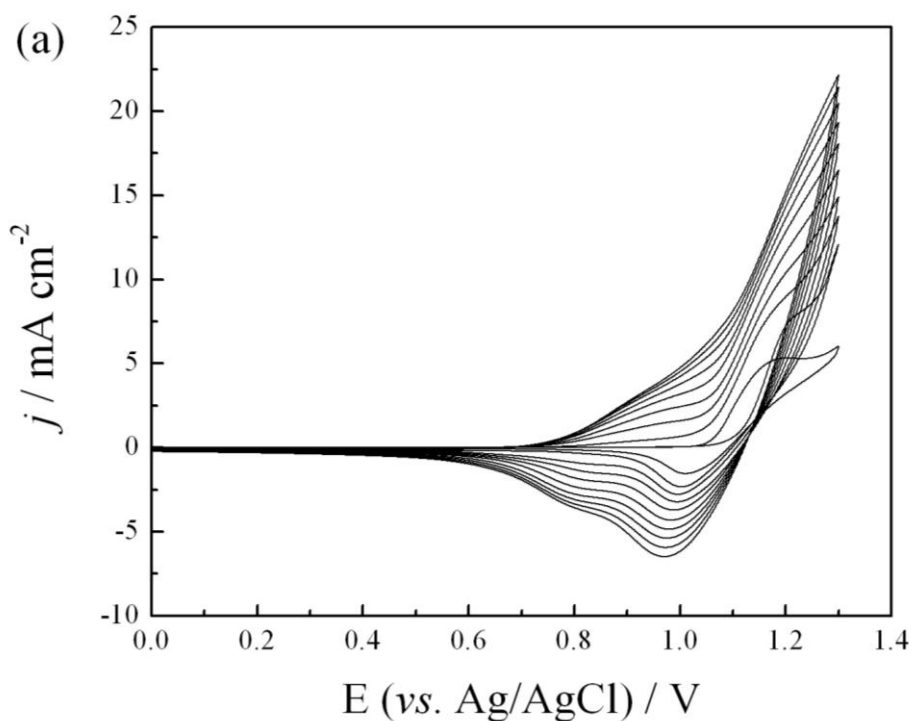


Figure 1. Anodic polarization curves of (a) 0.01 M pyrene, (b) 0.01 M carbazole, and (c) the monomer mixture of 0.01 M carbazole and 0.01 M pyrene (the feed ratios of Cz/pyrene at 1:1) in 0.2 M NaClO₄/ACN. The potential scan rate is 100 mV s⁻¹. j denotes the current density.

It is well known that successful electrochemical copolymerization of different monomers is due to the fact that the $E_{pa \text{ onset}}$ of the monomers are close to each other [26]. The small distinction of the $E_{pa \text{ onset}}$ between carbazole and pyrene is 0.09 V, implying that the electrochemical copolymerization is quite feasible. As can be seen from Fig. 1c, the $E_{pa \text{ onset}}$ of the Cz /pyrene at 1:1 mixture is 0.97 V, which is lower than that of carbazole or pyrene, indicating the existence of the interaction between two monomers in 0.2 M NaClO₄/ACN [23].



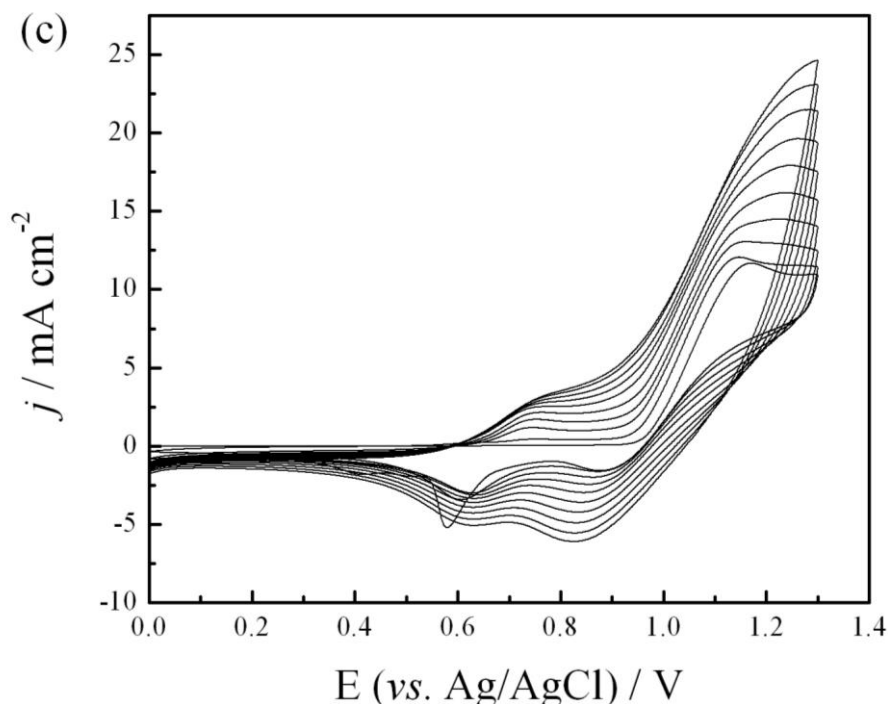


Figure 2. Successive CV curves of (a) 0.01 M pyrene, (b) 0.01 M carbazole and 0.01 M pyrene, (c) 0.01 M carbazole in 0.2 M NaClO₄/ACN. Scan rates: 50 mV s⁻¹. *j* denotes the current density.

The successive CV curves of 0.01 M pyrene, 0.01 M carbazole and the Cz/pyrene mixture at 1:1 (0.01 M pyrene and 0.01 M carbazole) in 0.2 M NaClO₄/ACN are illustrated in Fig. 2. As the CV scan continued, polymer films are formed on the working electrode surface. The increases in the redox wave current densities imply that the amount of conducting polymers deposited on the electrode are increasing. As shown in Fig. 2a, the CV curves of pyrene show distinct reduction waves of the oligomer located at 0.97 V, while the corresponding oxidation waves are overlapped with the oxidation waves of the pyrene monomer and cannot be observed clearly [27]. In Fig. 2c, the cyclic voltammetry of carbazole in this system exhibits two redox processes with the onset of oxidation at 0.61 and 0.94 V. the oxidation and reduction peak of the first redox process appears at 0.79 and 0.63 V, respectively. The reduction peak of the second redox process is located at 0.83 V, and the corresponding oxidation peak is overlapped with the oxidation waves of the carbazole monomer. However, the CV curve of the Cz/pyrene mixture at 1:1 exhibits a reduction peak at 0.72 V (Fig. 2b), which is different from those of pyrene and carbazole, indicating the formation of a new polymer consisting of both carbazole and pyrene units [28].

3.2. Electrochemistry of the copolymer films

The films of polycarbazole, polypyrene and copolymers are prepared on platinum wires by sweeping the potentials for ten scan cycles for CV tests. Figure 3 and 4 show the CV curves of polycarbazole (prepared from 0.01 M carbazole), polypyrene (prepared from 0.01 M pyrene), and

copolymers obtained with the feed ratio of carbazole /pyrene at 1:2, 1:1, and 2:1 (the concentration of pyrene is always 0.01 M), respectively.

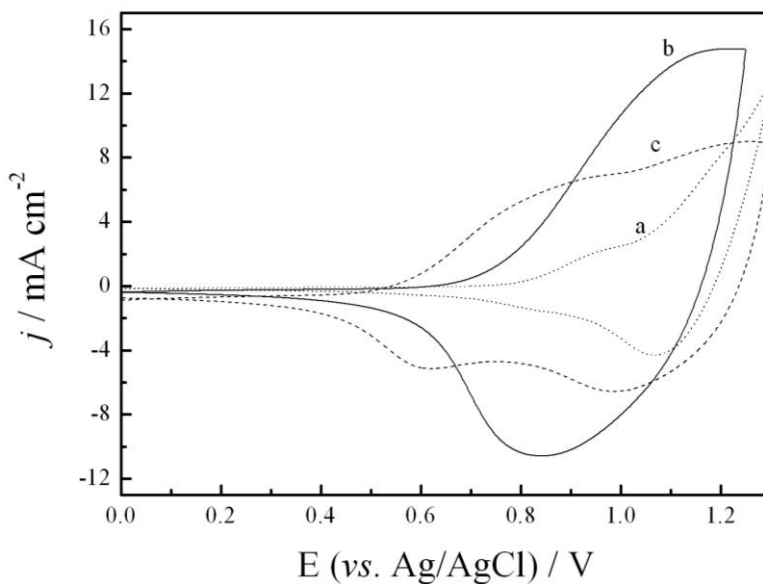


Figure 3. CV curves of (a) polypyrrole, (b) the copolymer prepared by sweeping the potentials between 0 and 1.25 V with the feed ratio of Cz/pyrene at 1:1, and (c) polycarbazole in 0.2 M $\text{NaClO}_4/\text{ACN}$. Polypyrrole and polycarbazole are prepared by sweeping the potentials between 0 and 1.30 V. Scan rates: 50 mV s^{-1} .

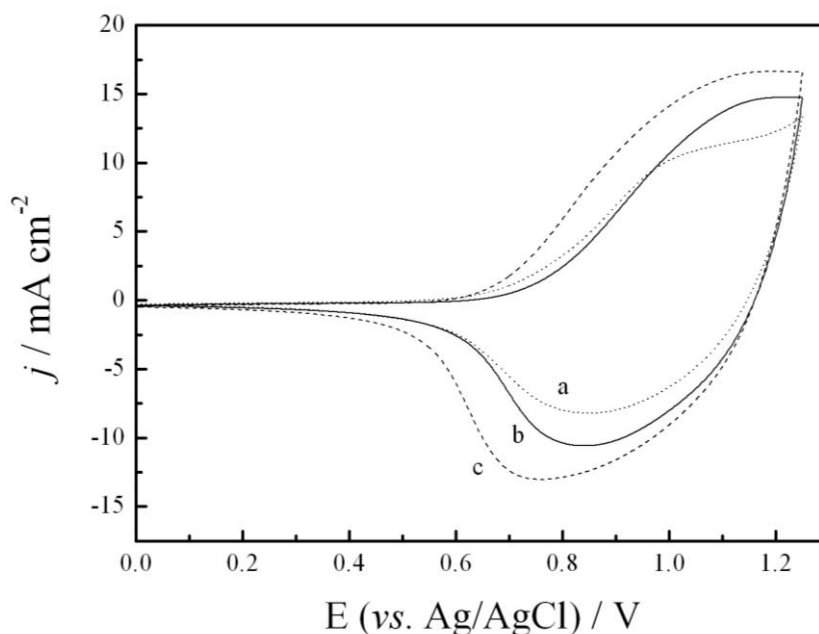


Figure 4. CV curves of the copolymers obtained from 0.2 M $\text{NaClO}_4/\text{ACN}$ with the feed ratio of Cz/pyrene at: (a) 1:2, (b) 1:1, (c) 2:1. Polymerization by sweeping the potentials between 0 and 1.25 V. scan rates: 50 mV s^{-1} .

In Fig. 3, polypyrrene shows irreversible redox waves in 0.2 M NaClO₄/ACN, which are oxidized or reduced between 1.3 and 1.07 V (Fig. 3a). While polycarbazole exhibits two couple of redox peaks, one couple is located at 0.82 and 0.62 V and another at 1.26 and 0.99 V (Fig. 3c). The copolymer film obtained at 1:1 performs a strong response with a reversible redox process between 0.84 and 1.20 V (Fig. 3b), which can be attributed to the existence of both pyrene and carbazole units into the polymer chain [3, 26].

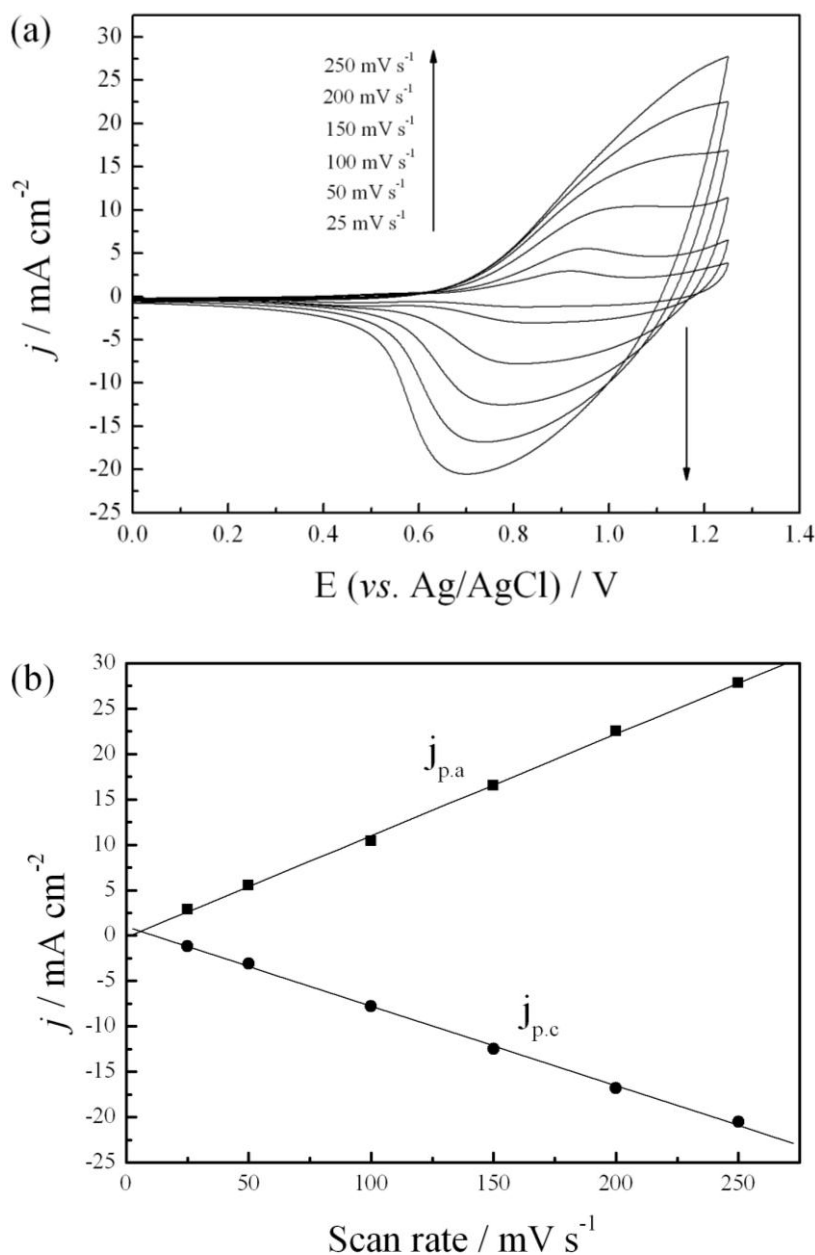


Figure 5. (a) CV curves of the copolymer (prepared with the feed ratio of Cz/pyrene at 1:1 on platinum wires by sweeping the potentials from 0 and 1.25 V for three cycles) at different scan rates between 25 mV s⁻¹ and 250 mV s⁻¹ in the monomer-free 0.2 M NaClO₄/ACN. (b) scan rate dependence of the copolymer. j_{pa} and j_{pc} denote the anodic and cathodic peak current densities, respectively.

As can be seen from Fig. 4, when the Cz/pyrene feed ratio is 1:2, the copolymer shows anodic peak potential (E_{pa}) at 0.98 V and cathodic peak potential (E_{pc}) at 0.85 V. As the feed ratio increases to 1:1, the copolymer presents a pair of redox peaks (E_{pa} at 1.20 V and E_{pc} at 0.84 V). When the feed ratio becomes 2:1, the copolymer presents E_{pa} at 1.21 V and E_{pc} at 0.76 V. The positive shift of E_{pa} and the negative shift of E_{pc} are caused by the fact that more carbazole units are incorporated into the copolymer chain when the carbazole concentration increases in the mixture [23]. Based on new E_{pc} and E_{pa} appearing in the CV curves of the copolymers (shown in Fig. 3 and Fig. 4), it is reasonable to arrive at the conclusion that the two monomers, carbazole and pyrene are oxidized together to some extents, and the copolymer chain is composed of both carbazole and pyrene units.

Figure 5 shows the electrochemical behavior of the copolymer (prepared with the feed ratio of Cz/pyrene at 1:1 on platinum wires by sweeping the potentials from 0 and 1.25 V for three cycles) at different scan rates between 25 mV s^{-1} and 250 mV s^{-1} in $0.2\text{M NaClO}_4/\text{ACN}$. As can be seen from Fig. 5a, the copolymer film is cycled repeatedly between doped and dedoped states without significant decomposition. The peak current densities (j) are proportional to the potential scan rates (Fig. 5b), indicating a reversible redox process of the copolymer adhered well to the platinum wire electrode. This also demonstrates that the electrochemical processes of the copolymers are reversible and not diffusion limited [29]. In addition, the difference between E_{pa} and E_{pc} becomes more obvious as the scanning rate increases.

3.3. Structural characterizations

The FT-IR spectrum can provide evidence for the characterization of the conjugated polymer. Polypyrene (Fig. 6A), polycarbazole (Fig. 6E), and copolymers prepared at 1.25 V potentiostatically with the feed ratio of Cz/pyrene at 1:2 (Fig. 6B), 1:1 (Fig. 6C) and 2:1 (Fig. 6D) are analyzed by FT-IR spectra, as shown in Fig. 6. According to the spectrum of polycarbazole (Fig. 6E), the intense band located at 1190 and 1207 cm^{-1} are attributed to valence vibration of C-N bond of carbazole cycle [30]. In the spectrum of polypyrene (Fig. 6A), the peaks at 843 and 814 cm^{-1} reflected the 1,2,3,4-substituted benzene ring. The above mentioned bands of PCz and polypyrene could also be found in the FT-IR spectra of the copolymers. Compared with corresponding homopolymers, the band at 1196 cm^{-1} in the spectrum of the copolymer at 1:1 (Fig. 6C) originates from valence vibration of C-N bond of PCz, indicating the presence of carbazole units in the copolymer. The bands at 847 and 815 cm^{-1} in the copolymer at 1:1 (Fig. 6C) can also be found, which are ascribed to the 1,2,3,4-substituted benzene rings in the polypyrene. The same bands can also be found in the spectrum of copolymers at 1:2 (Fig. 6B) and 2:1 (Fig. 6D). All the above features indicate that copolymers contain both pyrene and carbazole units.

In order to get deep insight into the structure of copolymers, the ^1H NMR spectra of the copolymer prepared at 1.25 V potentiostatically with the feed ratio of Cz/pyrene at 1:1 (Copolymer 1) is recorded in DMSO-d_6 , as shown in Fig. 7B. For comparison, the ^1H NMR spectra of polypyrene and PCz prepared at 1.30 V potentiostatically are also recorded in DMSO-d_6 (Fig. 7A,C). As illustrated in Fig. 7A, the spectra of polypyrene show several groups of protons between 8.0 and 8.7 ppm, which are

located within the low field compared with pyrene due to the high conjugation length of the polymer chain. In the spectrum of PCz (Fig. 7C), there are three groups of protons at 11.0, 11.3, and 11.7 ppm, which are assigned to the N-H of carbazole rings in the PCz chain.

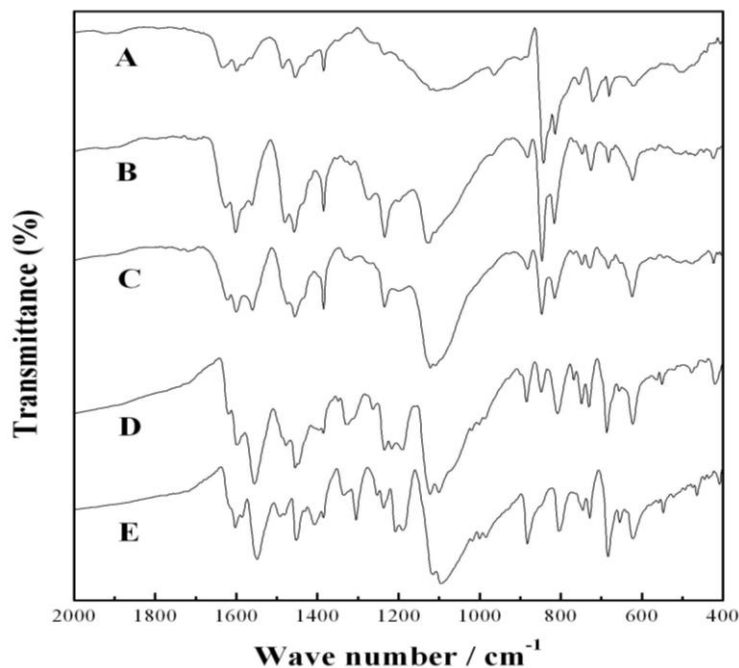


Figure 6. The FT-IR spectra of (A) polypyrene, (E) PCz, and copolymers prepared at 1.25 V potentiostatically with the feed ratios of Cz/pyrene at (B) 1:2, (C) 1:1, and (D) 2:1, respectively.

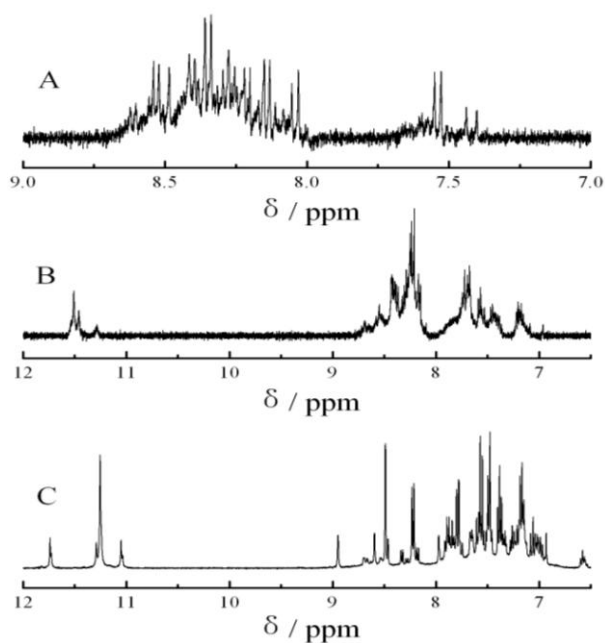


Figure 7. The ¹H NMR spectra of (A) polypyrene, (B) Copolymer 1 and (C) PCz prepared from 0.2 M NaClO₄/ACN solution potentiostatically are recorded in DMSO-d₆.

As shown in Fig. 7B, the three groups chemical shift at 11.28, 11.46 and 11.5 ppm can be assigned to the N-H bond of carbazole rings in the spectrum of copolymer 1, which means that carbazole units consist in the copolymer main chain. The several group peaks presented in the copolymer spectra between 8.0 and 8.8 ppm mainly arise from the C-H of pyrene units, and the peaks between 7.0 and 8.0 ppm are assigned to the C-H of carbazole units. It's obvious that the polymer obtained from Cz/pyrene mixture is a copolymer, not a composite of polypyrene and PCz [23].

3.4. Optical Properties

Copolymer 1 is soluble in DMF and dimethyl sulfoxide (DMSO). The UV-visible spectra of PCz, polypyrene and Copolymer 1 in DMF solutions are shown in Fig. 8.

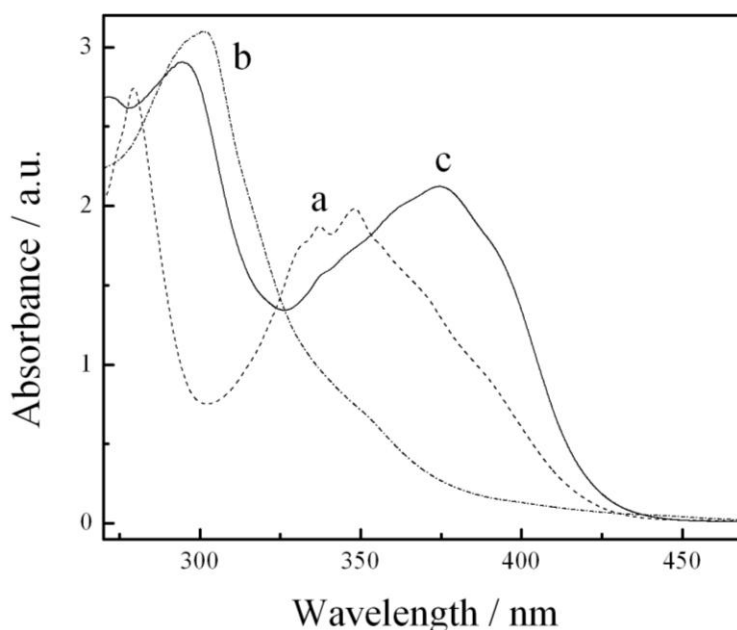


Figure 8. UV-vis spectra of (a) polypyrene, (b) PCz and (c) Copolymer 1 dissolved in DMF.

As can be seen from Fig. 8, the UV-visible spectrum of polypyrene shows two strong and sharp absorption peaks at 337 and 348 nm and a weak shoulder at 331 nm (Fig. 8a), while the spectrum of PCz shows a strong absorption peak at 302 nm, which may be derived from the π - π^* transition of the short conjugated chain (Fig. 8b) [7, 30]. However, it is interesting that the spectrum of Copolymer 1 shows unique characteristic absorption band at 375 nm (Fig. 8c), which is shifted by about 27 nm to a longer wavelength compared to that of polypyrene. It has been well known that the peak position of the lowest energy absorption (π - π^*) transition is determined by the distribution of conjugation lengths in the polymer: increasing delocalization of π -electrons leads to a red-shifted spectrum [31]. The red-shifted spectrum of Copolymer 1 indicates the presence of longer conjugated sequences in the copolymer backbone compared with those of PCz and polypyrene [32]. On the other hand, due to the

electron-acceptor property of pyrene moieties and the electron-donor property of carbazole moieties, the donor-acceptor copolymer should be obtained by incorporation pyrene units into carbazole-based polymer main chains.

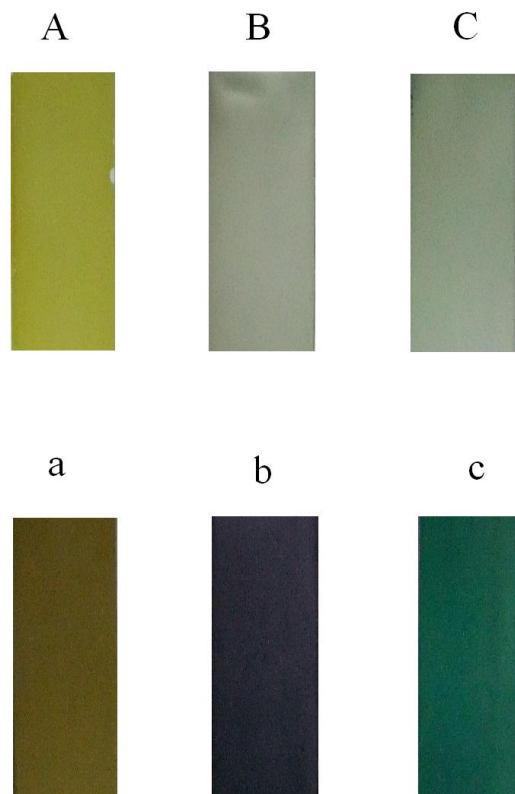


Figure 9. The electrochromism of polymer films: (a) (dark yellow), (b) (purple), (c) (bluish green), are doped films, and (A) (yellowgreen), (B) (light yellow), (C) (achromatic color) are dedoped films of polypyrene, Copolymer 1 and PCz, respectively

In case of this, the intra-chain charge transfer from donor (carbazole moieties) to acceptor (pyrene moieties) might also be responsible for the red-shifted spectrum of the copolymer 1 [33]. The low energy edge of the absorption spectra of Copolymer 1 is at 435 nm corresponding to a band gap of 2.85 eV, which lowers that of polypyrene (2.95 eV) or PCz (3.18 eV). The reduction of the band gap indicates a good conjugation between the pyrene and carbazole moieties, which further confirms the occurrence of the copolymerization between carbazole and pyrene monomers.

It has been well known that conjugated polymers are promising materials for electrochromic applications. Figure 9 shows the electrochromism of PCz, polypyrene and Copolymer 1, which are electrodeposited on ITO at 1.25V potentiostatically for the same charge 9.1×10^{-2} C. As can be seen from Fig.9, PCz is bluish green in doped state and achromatic color in dedoped state (Fig. 9c and Fig. 9C), and polypyrene is an dark yellow or yellowgreen polymer in its doped or dedoped state (Fig. 9a and Fig. 9A), respectively. While Copolymer 1 changes colour from purple in the doped state (Fig. 9b) to light green in the dedoped state (Fig. 9B). The electrochromism phenomenon of Copolymer 1 is

significantly different from those of two individual homopolymers, further confirming the formation of copolymer consisting of both pyrene and carbazole units.

3.5. Thermal analysis

The thermal stability of a conjugated polymer is very important for its potential application [34]. The thermal stability of polypyrene, PCz and Copolymer 1 in dedoped state are analyzed under nitrogen atmosphere in the temperature range of 40–800 °C with a heating rate of 10 °C min⁻¹. The thermogravimetry (TG) curves of all polymers are shown in Fig. 10.

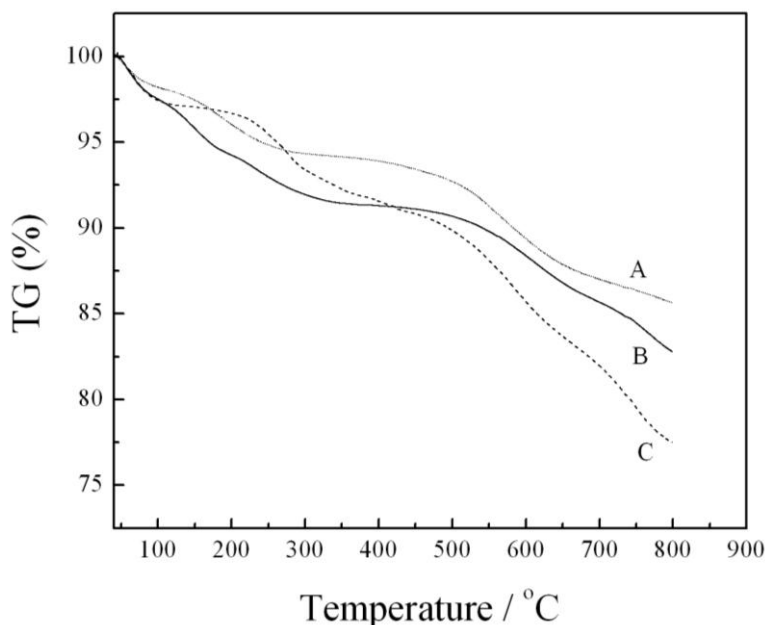


Figure 10. TG curves of (A) polypyrene, (B) Copolymer 1, and (C) PCz under nitrogen atmosphere in the temperature range of 40–800 °C with a heating rate of 10 °C min⁻¹.

According to Figure 10, before 120 °C, a light weight loss of all polymers are about 3%, mainly due to evaporation of water trapped in the polymers. And two obvious weight losses of all polymers are observed. The first is located between 120 and 410 °C and the weight loss is about 6 %, which could be attributed to the evaporation of the corresponding oligomers. The further increase in temperature results in the significant weight losses for all polymers, which is due to the degradation of the backbone of the polymers. PCz, polypyrene and Copolymer 1 show the onset temperature of second weight loss at about 500 °C, 497 °C and 520 °C, with the weight loss rate at 0.44 % min⁻¹, 0.31% min⁻¹ and 0.30% min⁻¹, respectively. When the temperature increase to 800 °C, the total weight losses of PCz, polypyrene and Copolymer 1 are 22.51%, 14.36%, 17.22%, respectively, indicating that all the polymers present good thermal stability. On the basis of the above analysis, the thermal stability of the Copolymer 1 is between that of polypyrene and PCz.

3. 6. Fluorescence property

The fluorescence spectra of PCz, polypyrene and copolymer 1 dissolved in DMF are recorded, as shown in Fig. 11.

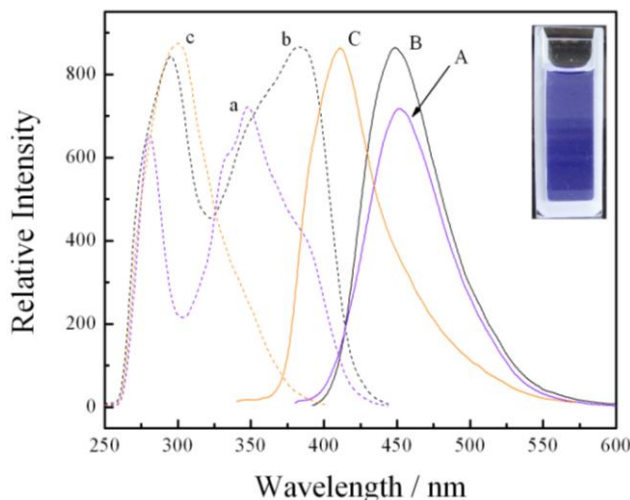


Figure 11. Fluorescence spectra of PCz, polypyrene and Copolymer 1 dissolved in DMF. Emission spectra of (A) polypyrene, (B) Copolymer 1 and (C) PCz. Excitation spectra of (a) polypyrene, (b) Copolymer 1 and (c) PCz. Inset: Photoluminescence of Copolymer 1 dissolved in DMF when exposed in natural daylight.

It is well known that polypyrene is a good blue-light emitter [23]. At 348 nm, polypyrene exhibits a maximum excitation peak in invisible region (Fig. 11a). And a strong emission peak of polypyrene is at 452 nm in the blue region (Fig. 11A). PCz also shows a strong emission peak at 411 nm in the purple range (Fig. 11C) when excited by 301 nm (Fig. 11c). For Copolymer 1, the maximum excitation peak is at about 383 nm located at visible region, which is a obvious red shift compared with that of polypyrene (Fig. 11b). Copolymer 1 shows a strong emission peak centering at 449 nm (Fig. 11B), a slight blue shift compared to that of polypyrene, which shows that Copolymer 1 is a good blue-light emitter. It is interesting that Copolymer 1 dissolved in DMF emits strong blue fluorescence when exposed in natural daylight (inset of Fig. 11), implying favorable photoluminescence properties of soluble copolymer based on pyrene and carbazole. The fluorescence quantum yield (Φ) of Copolymer 1 in DMF is measured to be 0.891 according to the Eq. (1). These striking fluorescent results show that the copolymer based on pyrene and carbazole may exploit applications in various fields, such as organic lasers.

3.7. Morphology

Scanning electron micrographs (SEM) of PCz, Copolymer 1 and polypyrene deposited on ITO electrode at 1.25 V potentiostatically for 200s provides their clear surface and bulk morphologies,

which are closely related to their optical and electrical properties [34], as shown in Fig. 12. In this case, Polypyrene shows a crinkly morphology dispersed small crinkly globular structure with diameter at around 5 μm (Fig. 12c). PCz exhibits a dendrite structure with a great deal of cavities (Fig. 12a).

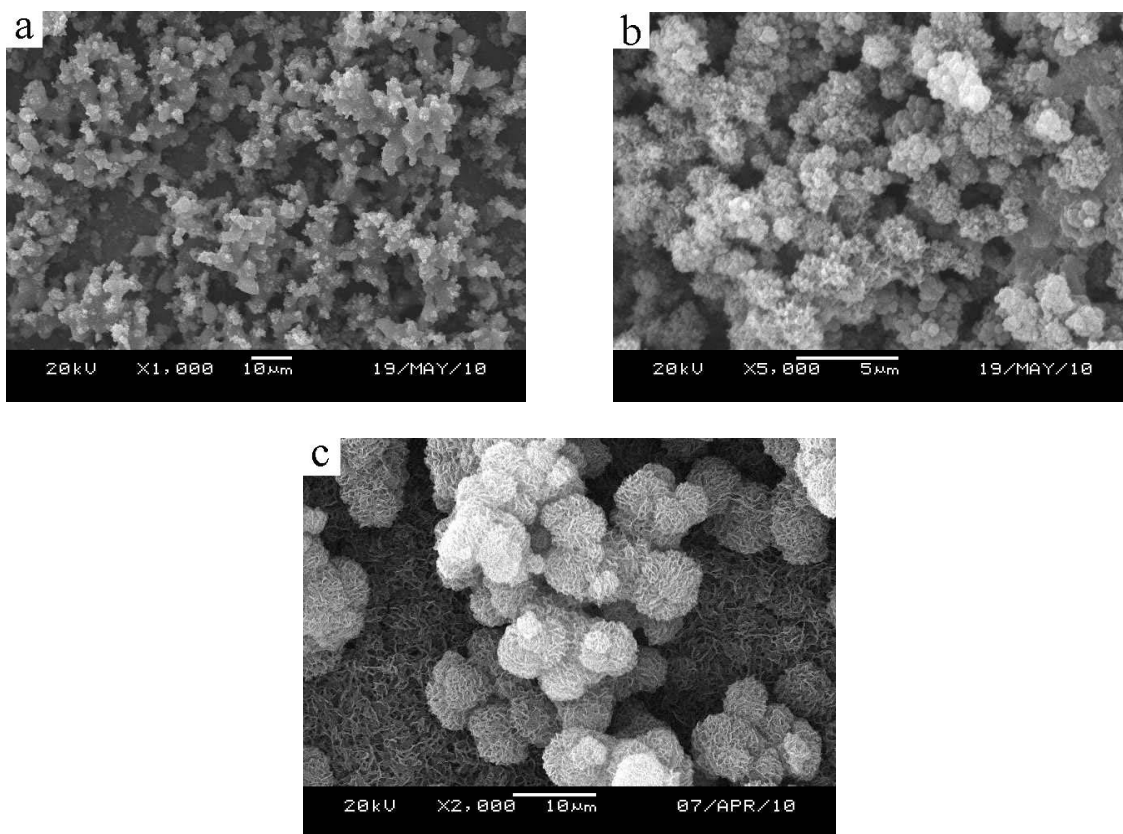


Figure 12. SEM images of (a) PCz, (b) Copolymer 1 and (c) polypyrene deposited on ITO electrode at 1.25 V potentiostatically.

While Copolymer 1 shows angular small granules stacked together with many porous structures, which are significantly different from two corresponding homopolymers (Fig. 12b). This morphology of Copolymer 1 may facilitate the movement of doping anions into and out of the polymer film during doping and dedoping process, in good agreement with the good redox activity of Copolymer 1. The difference of morphology between Copolymer 1 and homopolymers also confirms the occurrence of copolymerization between pyrene and carbazole.

4. CONCLUSIONS

The electrochemical copolymerization of carbazole and pyrene in 0.2 M $\text{NaClO}_4/\text{ACN}$ solution is successfully realized by direct anodic oxidation of the monomer mixtures. The obtained copolymer has good solubility in common organic solvents such as DMSO, DMF. FT-IR, ^1H NMR spectra reveal the presence of both carbazole and pyrene monomer units in the copolymer, indicating the formation

of the copolymers. The obtained copolymer based on carbazole and pyrene possess good redox activity and thermal stability. The UV-vis spectra show that the absorption peaks of the obtained copolymers presents a significant red-shift compared with that of polypyrene. The fluorescence spectra indicate that the soluble copolymer is a good blue-light emitter and processes high fluorescence quantum yield. These properties of copolymers may extend the applications of both carbazole and pyrene.

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References

1. M. Hanif, P. Lu, M. Li, Y. Zheng, Z.Q. Xie, Y.G. Ma, D. Li, J.G. Li, *Polym. Int.*, 56 (2007) 1507-1513.
2. J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, A. J. Heeger, *Science*, 317 (2007) 222-225.
3. Y. Pang, X. Li, G. Shi, L. Jin, *Int. J. Electrochem. Sci.*, 2 (2007) 681-688.
4. M. Ak, E. Sahmetlioglu, L. Toppare, *J. Electroanal. Chem.*, 621 (2008) 55-61.
5. H. Zhang, J. Zhao, H. Liu, H. Wang, R. Liu, J. Liu, *Int. J. Electrochem. Sci.*, 5 (2010) 295-301.
6. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, W. R. Salaneck, *Nature*, 397 (1999) 121-128.
7. Z.H. Wei, J.K. Xu, G.M. Nie, Y.K. Du, S.Z. Pu, *J. Electroanal. Chem.*, 589 (2006) 112-119.
8. J. Chen, C. Too, G. Wallace, G. Swiegers, B. Skelton, A. White, *Electrochim. Acta*, 47 (2002) 4227-4238.
9. C. C. Chang, L. J. Her, J. L. Hong, *Electrochim. Acta*, 50 (2005) 4461-4468.
10. S. Inaoka, D. B. Roitman, R. C. Advincula, *Chem. Mater.*, 17 (2005) 6781-6789.
11. M. Li, S. Tang, F. Shen, M. Liu, W. Xie, H. Xia, L. Liu, L. Tian, Z. Xie, P. Lu, M. Hanif, D. Lu, G. Cheng, Y. Ma, *Chem. Commun.*, (2006) 3393-3395.
12. H. Masuda, S. Tanaka, K. Kaeriyama, *J. Chem. Soc. Chem. Comm.*, (1989) 725-732.
13. B. Thémans, W.R. Salaneck, J.L. Brédas, *Synth. Met.*, 28 (1989) C359-364.
14. M. Rani, R. Ramachandran, S. Kabilan, *Synth. Met.*, 160 (2010) 678-684.
15. S. Koyuncub, B. Gultekina, C. Zafera, H. Bilgili, M. Cana, S. Demica, İ. Kayab, S. Icli, *Electrochim. Acta*, 54 (2009) 5694-5702.
16. P.J. Low, M.A.J. Paterson, D.S. Yufit, J.A.K. Howart, J.C. Cherryman, D.R. Tackley, R. Brook, B. Brown, *J. Mater. Chem.*, 15 (2005) 2304-2315.
17. P. Tranekar, T. Fulghum, A. Baba, D. Patton, R. Advincula, *Langmuir*, 23 (2007) 908-917.
18. A. Kimoto, J.S. Chao, K. Ito, D. Aoki, T. Miyake, K. Yamamoto, *Macromol. Rapid Commun.*, 26 (2005) 597-601.
19. L. Beouch, F.T. Van, O. Stephan, J.C. Vial, C. Chevrot, *Synth. Met.*, 122 (2001) 351-358.
20. J. Ohshita, K. Yoshimoto, Y. Tada, Y. Harima, A. Kunai, Y. Kunugi, K. Yamashita, *J. Organomet. Chem.*, 678 (2003) 33-38.
21. Y.Y. Xing, X.J. Xu, P. Zhang, W.J. Tian, G. Yu, P. Lu, Y.Q. Liu, D.B. Zhu, *Chem. Phys. Lett.*, 408 (2005) 169-173.
22. G. Zotti, G. Schiavon, *Synth. Met.*, 47 (1992) 193-202.

23. C. Zhang, Y. Xu, N. Wang, Y. Xu, W. Xiang, M. Ouyang, C. Ma, *Electrochim. Acta*, 55 (2009) 13-18.
24. C. Zimmermann, M. Mohr, H. Zipse, R. Eichberger, W. Schnabel, *J. Photochem. Photobiol. A. Chem.*, 125 (1999) 47-56.
25. F.C. Tasi, C.C. Chang, C.L. Liu, W.C. Chen, S.A. Jenekhe, *Macromolecules*, 38 (2005) 1958-1966.
26. G.M. Nie, L.Y. Qu, Y. Zhang, J.K. Xu, S.S. Zhang, *J. Appl. Polym. Sci.*, 109 (2008) 373-381.
27. G. W. Lu, G. Q. Shi, *J. Electroanal. Chem.*, 586 (2006) 154-160.
28. C. Kvarnstrom, H. Kulovaara, P. Damlin, T. Vuorinen, H. Lemmetyinen, A. Ivaska, *Synth. Met.*, 149 (2005) 39-45.
29. B. Yigitsoy, S. Varis, C. Tanyeli, I.M. Akhmedov, L. Toppare, *Electrochim. Acta*, 52 (2007) 6561-6568.
30. K. Khama, S. Sadki, C. Chevrot, *Synth. Met.*, 145 (2004) 135-140.
31. O. Stéphan, F. Tran-Van, C. Chevrot, *Synth. Met.*, 131 (2002) 31-40.
32. B. Fan, L.T. Qu, G.Q. Shi, *J. Electroanal. Chem.*, 575 (2005) 287-292.
33. E. Bundgaard, F. C. Krebs, *Sol. Energ. Mater. Sol. C.*, 91 (2007) 954-985.
34. W. Ma, C. Yang, X. Gong, K. Lee, A.J. Heeger, *Adv. Funct. Mater.*, 15 (2005) 1617-1622.