Electropolymerization of Indole and Its 5- Position-Substituted Derivatives in the Mixed Electrolytes of Acetic Acid and Boron Trifluoride Diethyl Etherate

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The mixed electrolyte of acetic acid and boron trifluoride ethyl ether (BFEE), containing poly(ethylene glycol) with a molar mass of 1000 (PEG1000), was employed for the electrochemical synthesis of indole and its 5-position-substituted derivatives, such as 5-cyanoindole, 5-nitroindole, indole-5-carboxylic acid, and 5-hydroxyindole. The introduction of acetic acid into BFEE increased both the solubility of PEG1000 and the ionic conductivity of the well mixed electrolyte. In this medium, high-quality polyindole (PIN) and its derivatives were successfully electrodeposited via anodic oxidation of their corresponding monomers. The as-formed PINs exhibited good electrochemical behavior and good fluorescence properties.

1. INTRODUCTION

Promising applications of conducting polymers (CPs) have emerged in the field of electronic materials due to their unique properties and structures [1]. Based on general knowledge, the performance of CPs prepared by electrodeposition depend on their synthesis conditions, for instance the solvents used, supporting electrolytes, and temperature. Consequently, different solvents and electrolyte systems yield polymers with different properties. Boron trifluoride ethyl ether (BFEE) has been reported as a good solvent and supporting electrolyte for the electropolymerization of aromatic monomers and their derivatives, such as thiophene [2], carbazole [3], selenophene [4], pyrrole [5],

furan [6], and indole [7]. The polymerization potentials of monomers can be significantly lowered by utilizing the BFEE instead of the neutral solvents. Meanwhile, the mechanical properties of the resulting CPs films are greatly enhanced because of the formation of relatively long conjugated main chains. The use of BFEE significantly improves the properties of the CPs. However, BFEE has some drawbacks, such as its volatilizability and moisture-sensitivity. Altering the amount of BFEE in the electrolytes has a positive effect. Therefore, the electrolytes containing BFEE mixed with other organic solvents, including dichloromethane [8], ethyl ether [9], isopropyl alcohol [10], and tetrahydrofuran [11], were studied. For example, in acetic acid, the complex will be partly ionized to $CH_3COOH_2^+$ and $CH_3COOBF_3^-$, which are the main conducting species responsible for the increase in the ionic conductivity.

Acetic acid and BFEE can form a mixed electrolyte with high ionic conductivity [12]. Furthermore, the strong interaction between BF_3 and acetic acid enables renders good stability to the mixed electrolyte [13]. Based on these mechanisms, some CPs were successfully synthesized by electrodeposition in the mixed electrolyte of acetic acid and BFEE [14]. It has been determined that poly(ethylene glycol) (PEG) has a positive effect on electropolymerization of monomers [15]; however, its poor solubility in BFEE limits its application. The utilization of acetic acid could promote the dissolution of PEG, which may in turn control the properties of the as-formed CPs.

Among the inherently CPs, polyindole (PIN) and its derivatives have attracted much attention because of their high redox activities and fairly good thermal stabilities, which indicate their high potential for various applications, like electrochemical sensing, energy storage, and electrorheology [16-19]. In addition, the main attraction of PIN is that its properties can be well tuned by modifying the different functional groups on the benzene ring, such as 5-position substituents [20, 21].

In this study, the electrochemical polymerization of indole and its 5-position-substituted derivatives in the mixed electrolyte of acetic acid and BFEE, containing PEG1000, were investigated and high-quality PIN films were successfully electrodeposited. The structure, electrochemical properties, and fluorescence properties of this PIN formed from the mixed electrolyte were studied systematically.

2. EXPERIMENTAL

2.1. Materials

Indole, 5-methoxyindole (MOIN), indole-5-carboxylic acid (INAC), tetrabutylammonium tetrafluoroborate (TBATFB, 95%) and dimethyl sulfoxide (DMSO, analytical grade) were purchased from Acros Organics. 5-Cyanoindole (CNIN) and 5-nitroindole (NOIN) (Shandong Pingyuan Hengyuan Chemical Co. Ltd., China, analytical grade) were used as received. BFEE (Beijing Changyang Chemical Plant, China) was distilled before use. Acetic acid (Beijing Chemical Plant, analytical grade), PEG1000 (analytical grade) and dichloromethane (CH_2Cl_2, Tianjin Guangfu Fine Chemical Institute) were used as received.

2.2. Electropolymerizations

Electropolymerizations were carried out in a three-electrode system using a CHI 660B potentiostat/galvanostat at room temperature. The working electrode and counter electrode were platinum and stainless steel sheets, respectively. The reference electrode was saturated calomel electrode (SCE). The mixed electrolyte of acetic acid and BFEE (1:1 by volume), containing 0.005 M PEG1000 was used as the electrolyte solution. PIN, poly(5-cyanoindole) (PCNIN), poly(5-nitroindole) (PNOIN), poly(indole-5-carboxylic acid) (PINCA),and poly(5-methoxyindole) (PMOIN) films were prepared at a constant applied potential 1.00, 1.23, 1.38, 1.28, and 1.23 V, respectively. The quantity of the polymer films was controlled by the polymerization time. For the de-doping process, the polymers were treated with ammonia (25%) for 72 hours, then washed with acetonitrile and water. Afterwards, the polymers were dried for 48 hours under vacuum at 60 °C.

2.3. Characterizations

UV–Vis spectra were obtained on a Perkin-Elmer Lambda 900. Fluorescence spectra were obtained on a Hitachi F-4500.

3. RESULTS AND DISCUSSION
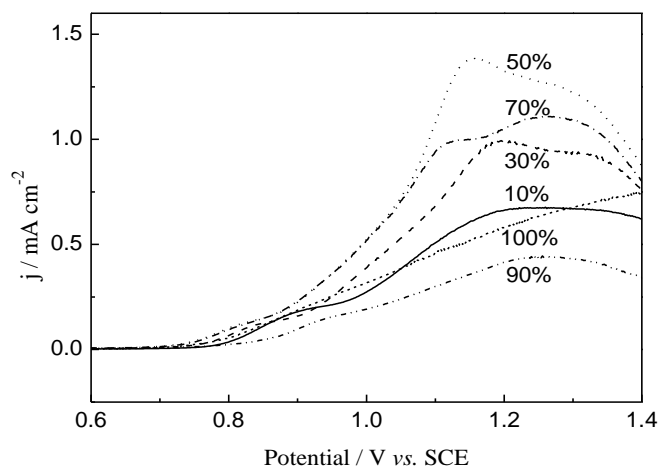
3.1. Electrolyte determination

Figure 1. Anodic polarization curves of 0.1 M indole in acetic acid containing different amount of BFEE by volume. Potential scan rate: 20 mV s^{-1}.

To determine a suitable ratio of acetic acid and BFEE (by volume), indole itself was chosen as the monomer. Figure 1 displays the anodic polarization curves of 0.1 M indole in acetic acid with different amount of BFEE. With increasing BFEE concentration, the onset oxidation potential of indole decreases and then increases after the lowest value, 0.70 V, corresponds to the mount of 50%

BFEE, is reached. Generally, the lower oxidation potential invariably indicates high-quality polymer films. Therefore, acetic acid containing 50% BFEE by volume is the most ideal. In addition, PIN films obtained from a mixed electrolyte of acetic acid and BFEE (1:1) without PEG1000 were in powder state, while those obtained from the mixed electrolyte containing 0.005 M PEG1000 exhibited significant improvement of film quality. Considering these results, the mixed electrolyte of acetic acid and BFEE (1:1) containing 0.005 M PEG1000 was employed as the suitable electrolyte for the electrochemical polymerizations of indole and its derivatives.

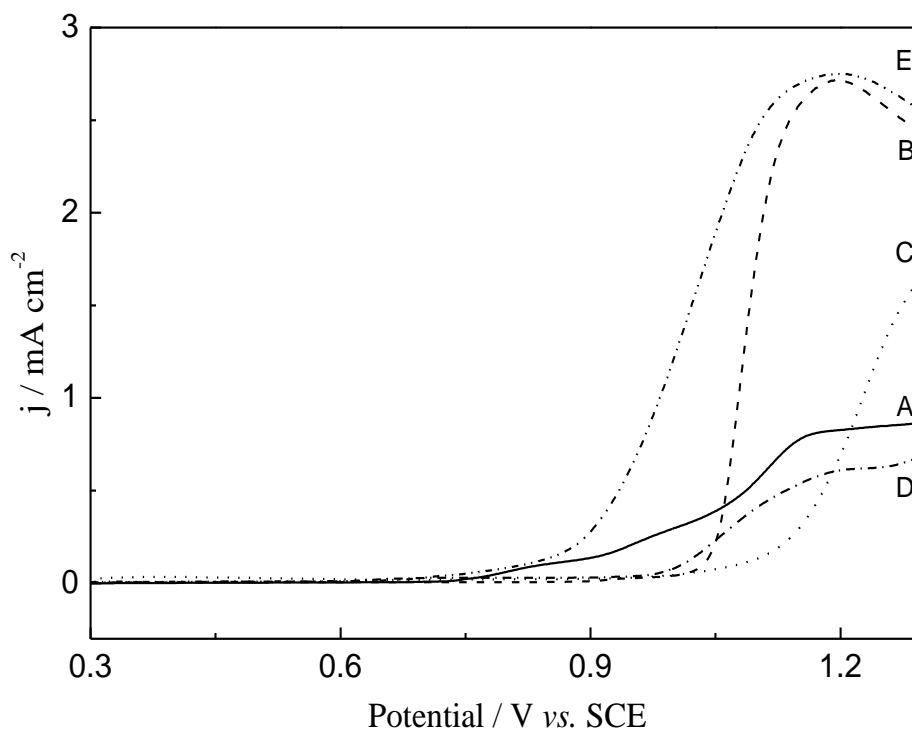## 3.2. Electrochemical polymerizations

Figure 2. Anodic polarization curves of 0.1 M indole (A), CNIN (B), NOIN (C), INCA (D), MOIN (E) in the mixed electrolyte of acetic acid and BFEE (1:1 by volume) containing 0.005 M PEG1000. Potential scan rate: 20 mV s^{-1}.

Figure 2 shows the anodic polarization curves for indole, CNIN, NOIN, INCA, and MOIN in the mixed electrolyte. The oxidation potential of indole is initiated at 0.75 V (Figure 2A). Electron-withdrawing groups lead to the increase in the onset oxidation potential of the monomers. The introduction of –CN, –NO$_2$, and –COOH groups on the 5-position result in the onset oxidation potential increasing to 1.03, 0.97, and 1.10 V, respectively (Figures 2B-D). On the contrary, the electron-donating group, –OCH$_3$ reduces the onset oxidation potential to 0.7 V (Figure 2E).
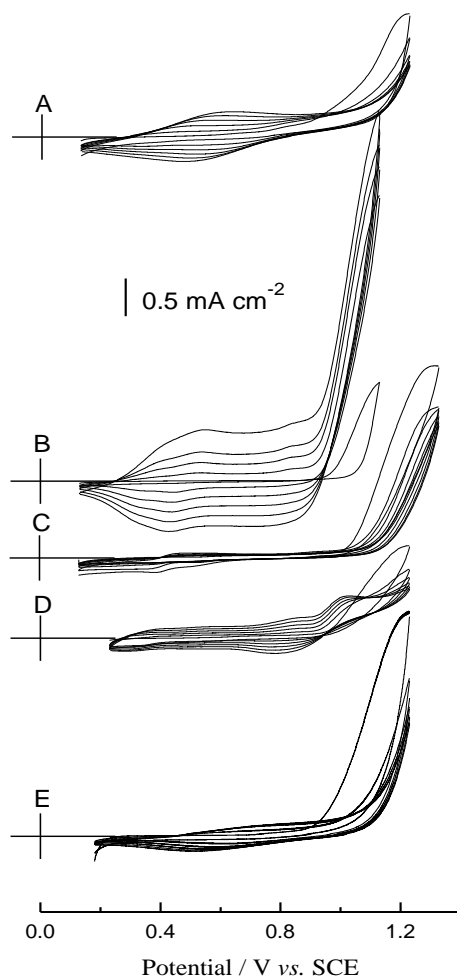
Figure 3. CVs of 0.1 M monomers, indole (A), CNIN (B), NOIN(C), INCA(D), MOIN(E) in the mixed electrolyte of acetic acid and BFEE (1:1 by volume) containing 0.005 M PEG1000. Potential scan rate: 100 mV s^{-1}.

The cyclic voltammograms (CVs) for these monomers indicated a typical potentiodynamic process. The increase in current densities of the redox wave during the CV scan process implies that the obtained polymer films increase. The potential shift evidently indicates the increase of the electrical resistance in the polymer, and an overpotential is needed to overcome this resistance [22]. The PIN shows a pair of redox peaks at 0.46 and 0.62 V (Figure 3A). The broad redox peaks may be attributed to the distribution of polymer chain [23] or the conversion from the neutral state to metallic state of the as-prepared polymer [24]. Analogous CV results could be obtained for the other monomers. Among the CVs recorded, those of CNIN and INCA are quite alike in shape, while that of NOIN is very different, which mainly results from the different electron-withdrawing abilities of–CN, –COOH and –NO$_2$, well in accordance with the results from the onset oxidation potential–analysis. It can be concluded that the substituents at the 5-position on indoles have a significant effect on the electropolymerization of the monomers in the mixed acetic acid and BFEE electrolyte containing PEG1000.

3.3. Electrochemistry of the polymer films

The electrochemical performances of the as-prepared polymer films were studied in CH_2Cl_2 + 0.1 M TBATFB (Figure 4). The CVs of PIN display broad anodic and cathodic peaks. With the increase in the scan rates, the redox potentials significantly shifted positively and negatively. The peak current densities are both proportional to the scan rates, indicating that a redox couple fixed on the PIN films [25]. In comparison with the PIN, the CVs of the other four polymers are similar, but the oxidation and reduction potentials of PCNIN, PNOIN, and PINCA shift positively and negatively with better reversibility, while the reduction peaks of PMOIN are not very clear. This is influenced by the substituent at the 5-position. Unlike –OCH₃, –CN, –NO₂, and –COOH are electro-withdrawing groups, useful for electropolymerization.
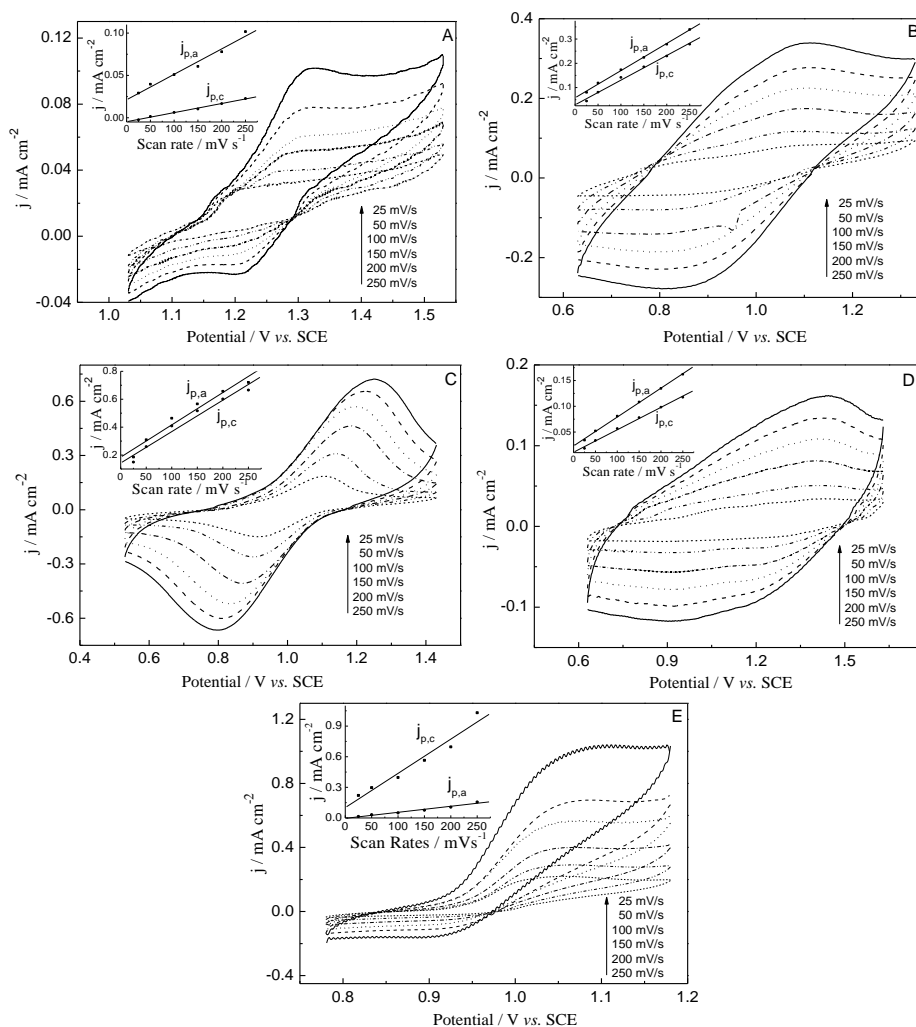

Figure 4. CVs of PIN (A), PCNIN (B), PNOIN (C), PINCA (D), PMOIN (E) films recorded in CH_2Cl_2 at potential scan rates of 250, 200, 150, 100, and 50 mV s^{-1}.

3.4. UV-Vis spectra

Figure 5 displays the UV-Vis spectra of the monomers, doped, and de-doped polymers in DMSO solution. The indole monomer show a λ_{max} at 281 nm, a significant shoulder at 289 nm, and the

absorption band reaching 307 nm (Figure 5A). The spectra of the other monomers show similar results, a λ_{max} ranging from 270 to 285 nm and a significant shoulder.
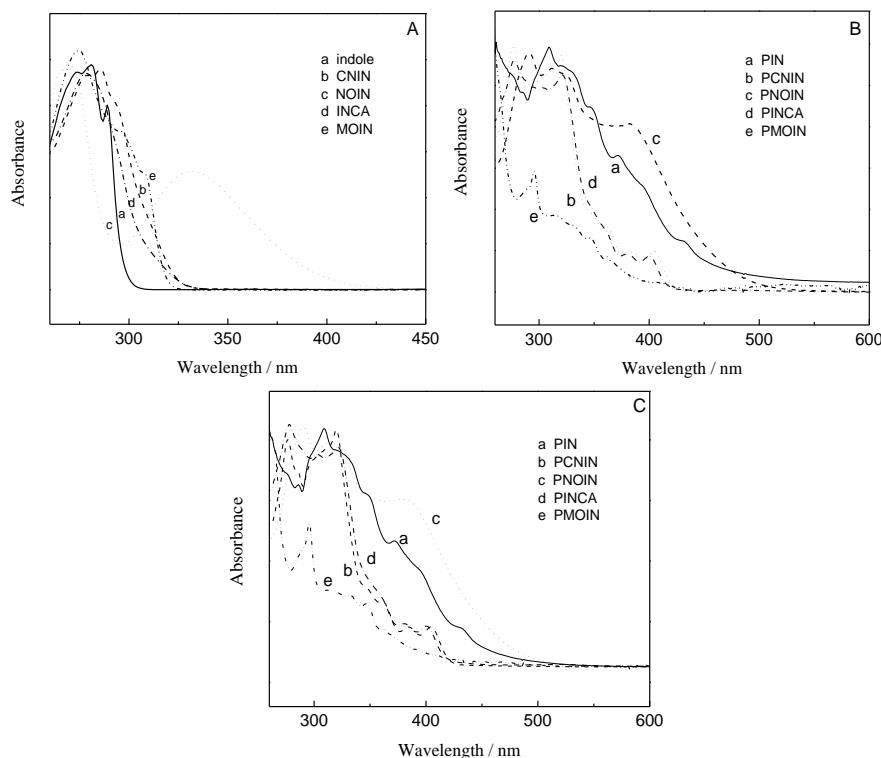

Figure 5. UV–Vis spectra of the monomers (A): indole (a), CNIN (b), NOIN (c) INCA (d) MOIN (e); the doped polymer (B): PIN (a), PCNIN (b), PNOIN (c) PINCA (d) PMOIN (e); the dedoped polymer films (C): PIN (a), PCNIN (b), PNOIN (c) PINCA (d) PMOIN (e) in DMSO.

Table 1. The adsorption and emission of the monmers and polymers.

Monmers and polymers	UV-Vis spectra		Emission spectra	
	λ_{max} (nm)	tail off to (nm)	λ_{max} (nm)	tail off to (nm)
indole	281	307	333	440
CNIN	285	335	366	504
NOIN	270	435	432	560
INAC	279	335	378	520
MOIN	274	325	332	407
PIN	309	543	441	583
PCNIN	320	425	425	550
PNOIN	291	543	437	576
PINAC	276	425	438	550
PMOIN	295	420	- [a]	- [a]

[a] Some properties of PMOIN were not recorded for its poor solubility.

The absorptions of CNIN, NOIN, INCA, and MOIN tailed off at 335, 436, 335, and 325 nm, respectively (Table 1). This is obviously influenced by the conjugation lengths of the substituents at 5-position [26]. $-NO_2$ increases the visibility of the red shift of the absorption peak more than $-CN$, $-COOH$, and $-OCH_3$, accounting for the visible peak at 330 nm. Compared with those of the monomers, the spectra for both the doped and de-doped polymers show much broader absorption bands (Figures 5B and C), which can be ascribed to the longer conjugated main chains [27]. The comparability of $-CN$ and $-COOH$ results in similar absorption peak shapes, and the $-NO_2$ accounts for the much broader absorption of PNOIN. Due to the poor solubility of PMOIN, its spectrum is not satisfactory. However, compared with the monomer, the absorption band tails off at 420 nm also implies the increase of the conjugated chain length.

3.5. Fluorescence spectra

The fluorescence spectra of monomers, doped, and de-doped polymers in DMSO are illustrated in Figure 6. Due to its poor solubility, PMOIN peaks were not detected. Strong peaks from the monomers indole and MOIN were detected at ~333 nm (Figure 6A). This is mainly because the $-OCH_3$ has a weak influence on the conjugated system. In comparison, $-CN$, and $-COOH$ influence the λ_{max} shift to 363 and 377 nm, while $-NO_2$ influences the λ_{max} shift to 430 nm (Table 1). The polymers with electron-withdrawing group substitutions show similar shapes in DMSO solution, and their major emissions center is between 417–447 nm, indicating that these polymers are blue-light-emitters (Figures 6B and C). These peaks, representing the emission properties of the PIN backbone, are very close to each other, mainly because the increase in the conjugation main chain debases the influence of the substitution [28]. There is an obvious red shift between the monomers and the corresponding polymers, proving that the formation of the conjugated backbone. The slight differences between the doped and de-doped polymers could imply the existence of a counterion [29]. In addition, the excitation and emission of the polymers took place in this region, indicating their favorable photoluminescence properties. Figure 7 shows the photoluminescence properties of monomers of indole, CNIN, and INAC when exposed to 365-nm UV light. As noted, the three monomers did not exhibit emissions while the doped and de-doped polymers all exhibited a blue light emitting property. This shows that $-CN$ enhances the fluorescence, while $-COOH$ reduces it. From our experiment, we noted that the almost indiscerptible PMOIN also launched a faint blue light while PNOIN did not exhibit any emissions. These fluorescent spectral results indicate that these polymers are blue-light emitters with potential applications in the field of optoelectronics.
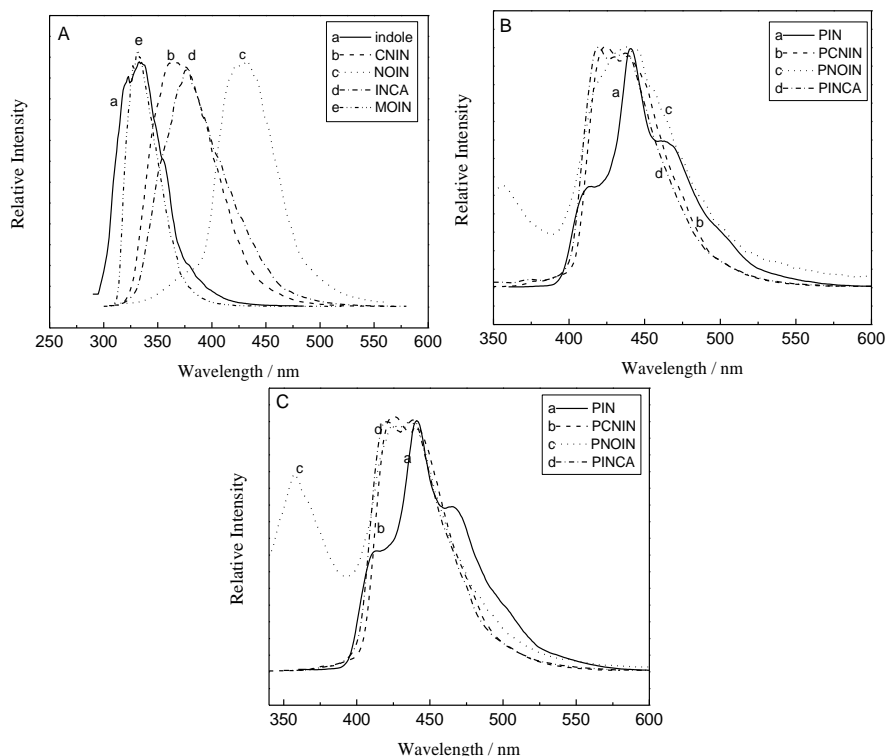
Figure 6. Fluorescence spectra of monomers (A): indole (a), CNIN (b), NOIN (c), INCA (d), MOIN (e); doped polymers (B): PIN (a), PCNIN (b). PNOIN (c), PINCA (d); dedoped polymers (C): PIN (a), PCNIN (b), PNOIN (c), PINCA (d) in DMSO.
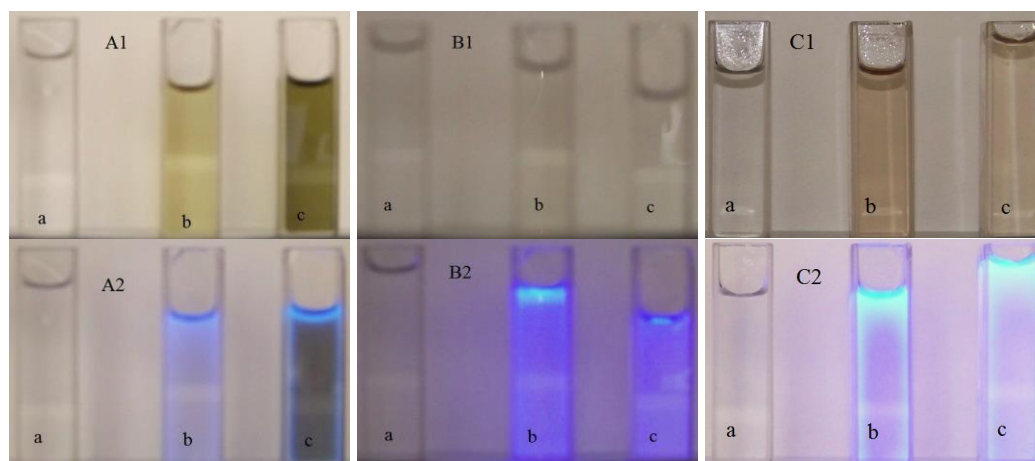

Figure 7. Photoluminescence of the monomer (A1), doped polymers (B1), dedoped polymers (C1) under natural light in DMSO; (A2), (B2), (C2) under UV light irradiation of 365 nm in DMSO. Indole (a); CNIN (b); INCA (c).

4. CONCLUSIONS

A set of indole-based CPs were prepared by electrochemical polymerization of indole and its 5-position-substituted derivatives in the well mixed electrolyte of acetic acid and BFEE. PEG1000 was

also introduced into the mixed electrolyte, which exhibited a positive effect on electropolymerization. Indole and its derivatives all exhibited low onset oxidation potential in this mixed electrolyte solution. The as-formed polymers displayed favorable redox behavior and blue-light-emitting properties. The substituents at the 5-position had varying effects on the polymers. The successful electropolymerizations of indoles in the mixed electrolyte of acetic acid and BFEE containing PEG1000 may increase applications of the mixed electrolyte in the field of electrochemistry and materials science.

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