

Electrochemical Synthesis of Poly(1,12-bis(carbazolyl)dodecane) on Pure Organic PEDOT:PSS Nanofilm Electrode and its Characterizations

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PEDOT:PSS nanofilm as a pure organic working electrode has been used for the electrochemical synthesis of poly(1,12-bis(carbazolyl)dodecane) (P2Cz-D) films. The electropolymerization was carried out in the mixed electrolytes of dichloromethane and 5%~50% boron trifluoride ethyl ether (BFEE). The structure and properties of the PEDOT:PSS/P2Cz-D bilayered nanofilms were investigated by FT-IR, UV-vis, fluorescence, and SEM characterizations. The as-formed bilayered films combined the advantages of PEDOT:PSS and P2Cz-D, especially the electrical conductivity, with the maximum value of 41.2 S cm^{-1} , six orders of magnitude higher than that of P2Cz-D films ($2.7 \times 10^{-5} \text{ S cm}^{-1}$). It was considered that the improvement could be ascribed to the high conductivity of the PEDOT:PSS layer. It is expected that pure organic PEDOT:PSS nanofilm as the working electrode may provide a novel thought for the electrochemical synthesis of conducting polymers.

Keywords: PEDOT:PSS electrode; electrochemical synthesis; P2Cz-D; electrical conductivity

1. INTRODUCTION

The last few decades have been marked by the growing importance taken by conducting polymers, which combine the advantages of conventional polymers, such as low density, processability, and flexibility, with the functional physical properties of conventional semiconductors, such as a tunable conductivity, and absorption and emission of light, providing innovative materials for electronic devices [1].

Electrochemical synthesis has been proved to be one of the most effective approaches to prepare conducting polymers, with several merits including one-step film formation, small amounts of monomer, easily controlled reaction rate and product amount [2]. It is well known that the

electrochemical synthesis depends strongly on experimental conditions, such as solvents, concentration of reagents, supporting electrolytes, nature of the electrodes, applied electrical conditions, and temperature. Among them, the electrode is a critical variable since it may affect both the polymerization process and the properties of the resulting polymer [3]. Traditional electrodes for electrochemical synthesis are generally noble metals (platinum, gold), stainless steel, carbon materials, or optically transparent electrodes such as indium tin oxide (ITO) coated glass [4-8]. They are of high stability and conductivity in common, but with their respective defects, taking ITO for example, it has problems of scarce indium on earth, high temperature processing, and poor adhesion to polymeric materials [9, 10]. Hence, it is of great importance to explore new electrode materials.

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), well-known as the most successful conducting polymer, has been widely applied as conductive electrode in organic electronics such as field-effect transistors, light-emitting diodes, and solar cells, mainly due to its high stability and enhanced electrical conductivity by post-treatment [10-14]. Moreover, Groenendaal et al. predicted that the PEDOT:PSS was promising to substitute ITO as the next-generation transparent electrode material of optoelectronic devices [15]. Lately, our group for the first time reported the pure organic PEDOT:PSS nanofilm as working electrode during the electrochemical synthesis of polythiophene and its derivatives [16]. Compared with the traditional working electrodes, the PEDOT:PSS electrode possesses the advantages of low cost, simple process, easy degradation, especially non-pollution without the introduction of metals.

Among eligible conducting polymers, polycarbazole (PCz) and its derivatives have rapidly become the subject of considerable interest, due to their potential applications in hole-transporting layers, electrochromic devices, and electroluminescence efficiency units [17-19]. From a theoretical viewpoint, carbazole can be easily functionalized at its 3,6-, 2,7- or N- positions and then covalently linked to a polymer, either in the main chain as a block or in the side chain as a pendant group [19-21]. Additionally, dicarbazoles connected with various ether oxide spacers or carbon chains have also been investigated [22, 23]. It was found that the length of flexible bridging chain connected with the two carbazole units played an important role on the polymer films, that is, the longer the bridging chain, the higher mechanical strength and longer conjugated chains of polymer films [24]. Furthermore, free-standing P2Cz-D films with high mechanical properties and outstanding blue-light emitting properties have been obtained by electrochemical synthesis on the platinum electrode. However, the as-formed films possessed poor electrical conductivity, which impede their practical applications [25, 26].

Herein, we adopted the pure organic PEDOT:PSS nanofilm as working electrode to electrochemically synthesize P2Cz-D films in the mixed electrolytes of $\text{CH}_2\text{Cl}_2/\text{BFEE}$. The as-formed bilayered nanofilms combined the advantages of PEDOT:PSS and P2Cz-D, showing enhanced electrical conductivity and blue-light emitting properties.

2. EXPERIMENTAL DETAILS

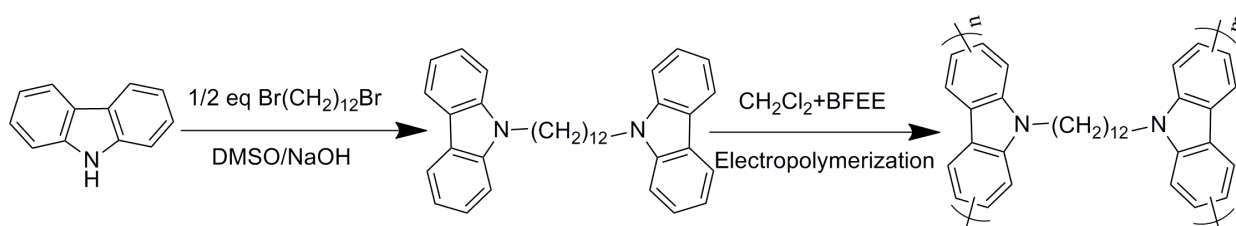
2.1 Materials

PEDOT:PSS (PH1000; Baytron), carbazole (99%; J&K Chemical Ltd), 1,12-bisbromododecane (99%; Isomersyn Technology CO; LTD), and DMSO (AR; Beijing Chemical Works) were

used directly as received. CH_2Cl_2 (Beijing Chemical Plant) and BFEE (Beijing Changyang Chemical Plant) were refluxed with CaH_2 and distilled before use. 2Cz-D was synthesized according to the general procedure already described in the literature [27].

2.2 Preparation of PEDOT:PSS/P2Cz-D bilayered nanofilms

Firstly, PEDOT:PSS/5% DMSO (herein referred to as PEDOT:PSS) nanofilms was prepared by spin-coating at speed of 2000 rpm. Then, the as-formed PEDOT:PSS nanofilm was used as the working electrode in a three-electrode cell configuration for the electropolymerization of 2Cz-D in a mixed CH_2Cl_2 /BFEE solution to fabricate the bilayered structures. Meanwhile, a stainless steel sheet and home-made Ag/AgCl were used as the counter and reference electrode. All solutions were deaerated by bubbling argon gas and were maintained at a low overpressure during the polymerization process. Detailed preparation processes were shown in Schema 1.



Scheme 1. The synthesis of 2Cz-D and P2Cz-D.

2.3 Characterizations

The electropolymerization was conducted by a Model 263 potentiostat/galvanostat (EG&G Princeton Applied Research, Oakridge, TN) under the control of a computer. Infrared spectra were recorded on a Bruker Vertex 70 Fourier Transform Infrared Spectrometer. UV-vis absorption spectra were conducted by a Perkin-Elmer Lambda 900 UV-Vis-near-infrared (NIR) spectrophotometer. The fluorescence properties were determined with a Hitachi F-4600 fluorescence spectrophotometer. The morphologies were observed on a JEOL JSM-6701F field emission scanning electron microscope. Electrical conductivity was measured by a homemade shielded four-point probe apparatus along with a Keithley 2700 Multimeter (Cleveland, OH) in conjunction with the Labview (National Instruments, Austin, TX) after four metal lines were patterned with silver paint.

3. RESULTS AND DISCUSSION

Fig. 1 represents the anodic polarization curves of 2Cz-D in the solvents of CH_2Cl_2 mixed with 5% (a), 10% (b), 20% (c), 30% (d), and 50% (e) BFEE (by volume). It should be noted that BFEE was used as the supporting electrolyte in CH_2Cl_2 without the addition of any other salts. As the BFEE content increased from 5% to 50%, the onset oxidation potential of the monomer reduced gradually,

and the values were 0.54, 0.51, 0.49, 0.47, and 0.43 V, respectively. They were all much lower than that of 2Cz-D in CH_2Cl_2 containing 0.1 M Bu_4NBF_4 as the supporting electrolyte (1.10 V vs. Ag/AgCl) [26]. The lower oxidation potential was due to the fact that the Lewis acid BFEE with good electrophilic property would strongly catalyze the deprotonation of aromatic monomers on the electrodes [5].

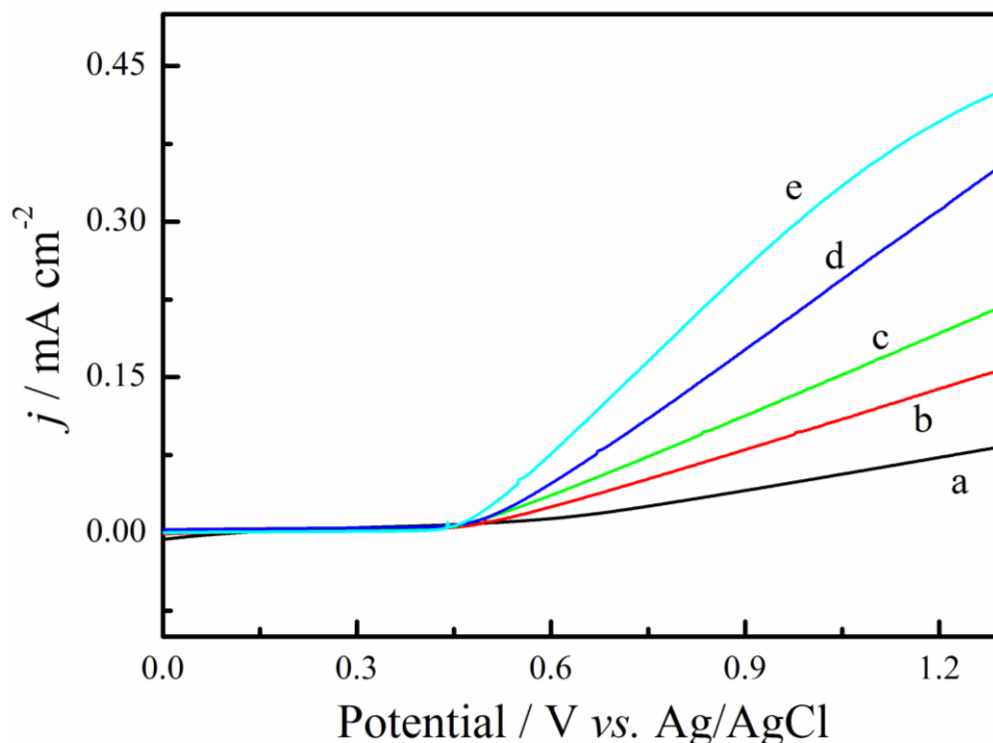


Figure 1. Anodic polarization curves of 2Cz-D in $\text{CH}_2\text{Cl}_2/\text{BFEE}$ mixed solution with different BFEE contents: (a) 5%, (b) 10%, (c) 20%, (d) 30%, (e) 50%. The potential scanning rate was 50 mV s^{-1} . j denotes the current density. The working electrode is PEDOT:PSS nanofilm, the counter electrode is stainless steel sheet, and the reference electrode is home-made Ag/AgCl.

The successive cyclic voltammograms (CVs) in the course of electrochemical polymerization of 10 mM 2Cz-D in $\text{CH}_2\text{Cl}_2/\text{BFEE}$ solution on a PEDOT:PSS nanofilm electrode are exhibited in Fig. 2. The CVs of 2Cz-D show characteristic features as other conducting polymers, such as polythiophene and polypyrrole, during potentiodynamic syntheses. As the CVs scan continued, green colored P2Cz-D films were formed gradually on the PEDOT:PSS nanofilm electrode. The increase of anodic and cathodic peak current densities in CVs also implied that the amount of the polymer deposited on the working electrode increased. The shift of redox peak potentials implied the increase of the electrical resistance in the polymer and the overpotential needed to overcome the resistance. Similar phenomenon was reported in the electrochemical polymerization of this monomer in mixed electrolytes of 60% BFEE and 40% CHCl_3 [25].

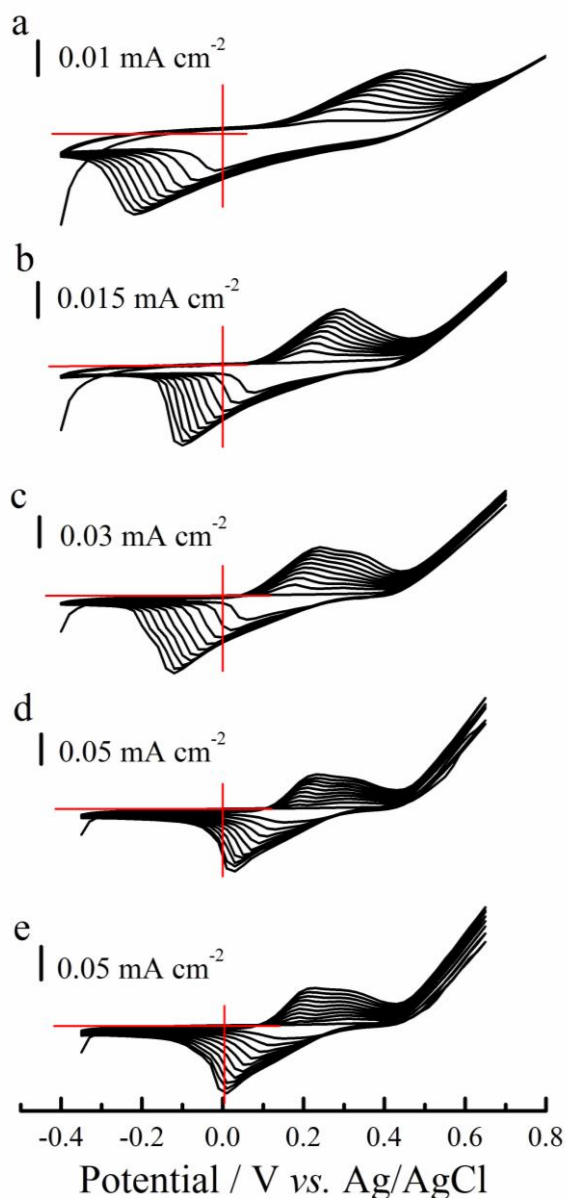


Figure 2. CVs of 2Cz-D in $\text{CH}_2\text{Cl}_2/\text{BFEE}$ mixed solution with different BFEE contents: Sample a–e. Potential scanning rate: 50 mV s^{-1} .

In order to elucidate the structure of the PEDOT:PSS and PEDOT:PSS/P2Cz-D films, FT-IR spectra were recorded, as shown in Fig. 3. According to the inset spectrum, PEDOT:PSS nanofilms exhibited the vibrations at 1325 and 1515 cm^{-1} , which are caused by the C–C and C=C stretching of the quinoidal structure and the ring stretching of the thiophene ring of PEDOT chains. The band at about 835 cm^{-1} is related to the C–S bond vibration in the thiophene ring [28]. According to the spectrum of PEDOT:PSS/P2Cz-D films, the aliphatic C–H stretching vibration appeared at 2926 and 2847 cm^{-1} , indicating the stability of the dodecyl chain during the polymerization process. The band at 730 cm^{-1} suggested the existence of a 1,2-disubstituted benzene ring. The results were in well consistent with the previous studies [24].

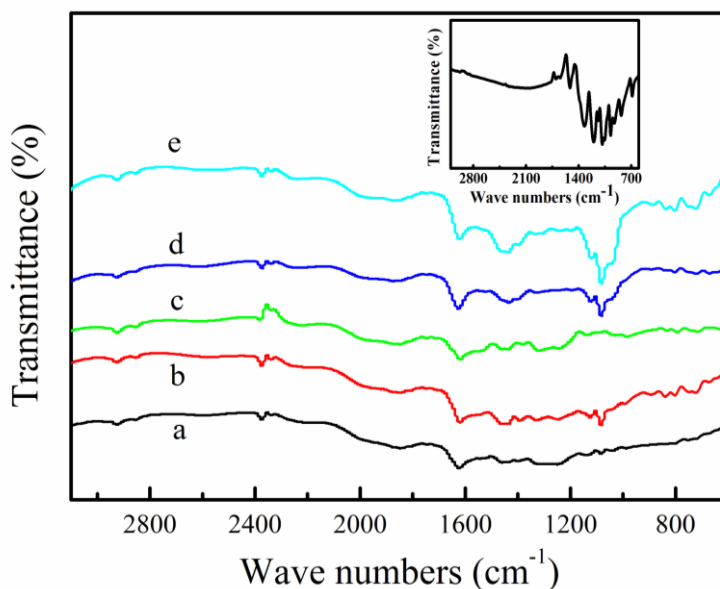


Figure 3. FT-IR spectra of the samples: a–e. The inset refers to PEDOT:PSS nanofilms.

UV-vis spectra of the PEDOT:PSS and PEDOT:PSS/P2Cz-D films were carefully examined, as shown in Figure 4. The measurements were carried out at room temperature in the wavelength range from 300 to 1000 nm. The inset of the PEDOT:PSS films possess an increasing absorption after 500 nm [29]. The spectrum of PEDOT:PSS/P2Cz-D films displayed characteristic absorption peaks at 395 nm, which was caused by the valence band–conduction band (π - π^*) transition. While the wide absorption bands centered at 830 nm indicating the presence of conductive species such as polaron or bipolaron and the long conjugated chain [26].

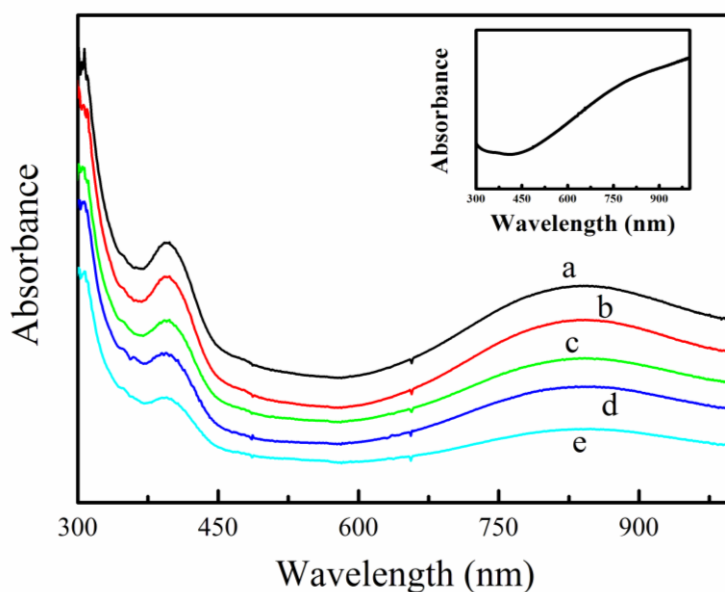


Figure 4. UV-Vis absorption spectra of the samples: a–e. The inset refers to PEDOT:PSS electrodes.

The SEM images of PEDOT:PSS and PEDOT:PSS/P2Cz-D films were exhibited in Fig. 5. Macroscopically, as can be seen in the inset, PEDOT:PSS (a) nanofilms with smooth and homogeneous surface were colored in light blue, and the color changed to be green after the electropolymerization of 2Cz-D. The PEDOT:PSS/P2Cz-D films obtained from the electropolymerization condition of 5% (b), 10% (c), and 20% (d) BFEE represented the smooth surface, while some crevices can be observed on that of 30% (e) and 50% (f) BFEE. On the basis of these phenomena, microscopically, the samples b–d showed a smooth surface morphology, similar to that of PEDOT:PSS nanofilms, which has an extremely beneficial effect on their electrical conductivity. On the contrary, the samples e and f exhibited a much rougher morphology.

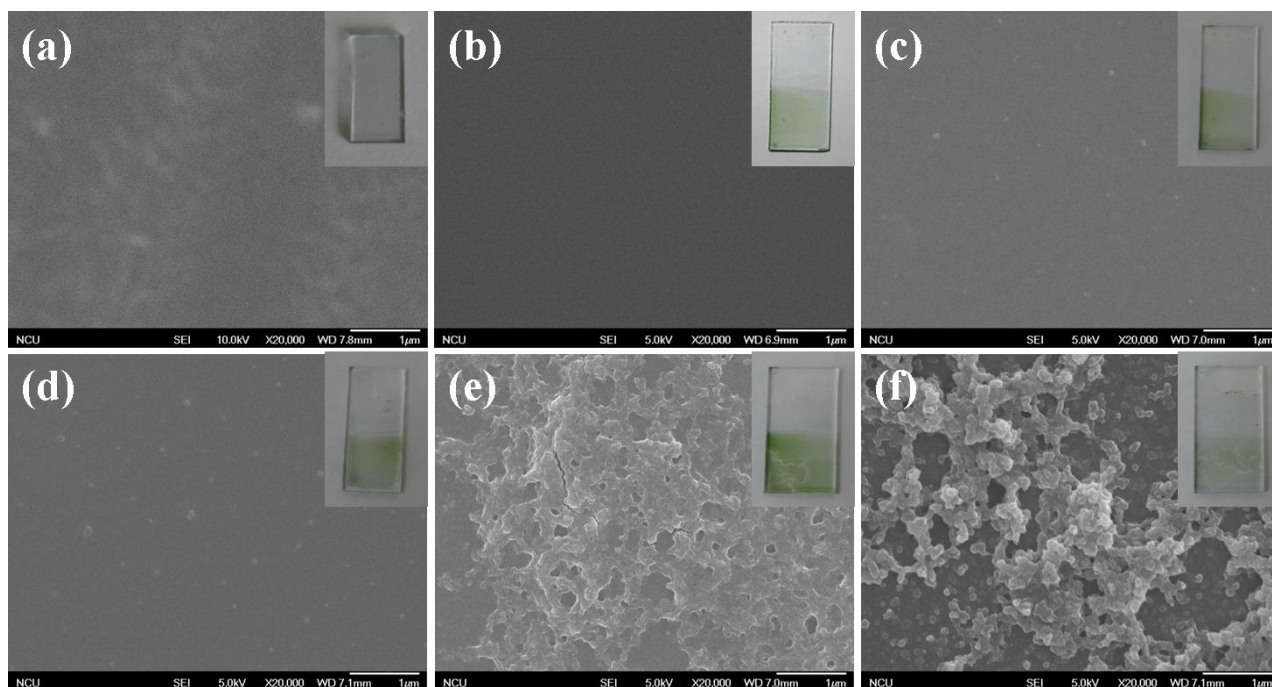


Figure 5. SEM images of the samples: a–f. Sample a refers to PEDOT:PSS electrodes.

The electrical conductivity of the PEDOT:PSS and PEDOT:PSS/P2Cz-D films were carefully investigated, as listed in Table 1. The electrical conductivity of PEDOT:PSS nanofilm electrode was 393 S cm^{-1} . It is known that the electropolymerization conditions have an effect on the quality of PEDOT:PSS/P2Cz-D films, therefore, the electrical conductivity. Generally, the electrical conductivity would be increased with the increasing BFEE content during the electrochemical synthesis. However, the maximum electrical conductivity reached up to be 41.2 S cm^{-1} when the BFEE content was 20%. The electrical conductivity for 5% BFEE was relatively low with the value of 6.9 S cm^{-1} . The electrical conductivity of the films fabricated with 10%, 30%, and 50% BFEE was 31.8 , 26.3 , and 25.9 S cm^{-1} , respectively. The results were in good agreement with the surface morphology of the films. Accordingly, the electrical conductivity of the PEDOT:PSS/P2Cz-D films was improved by 5~6 magnitude higher than that of P2Cz-D films reported previous ($2.7 \times 10^{-5} \text{ S cm}^{-1}$) [26]. It has been reported and proved in our earlier work that the substrate contribution to the electrical resistivity is

considered negligible when the resistivity ratio between substrate and film is larger than 10000:1 [30]. Thus, it is considered that the layer of PEDOT:PSS with high conductivity is beneficial for the electrical conductivity enhancement of the PEDOT:PSS/P2Cz-D bilayered nanofilms.

Table 1. Electrical conductivity of the PEDOT:PSS/P2Cz-D bilayered nanofilms.

BFEE (%)	5	10	20	30	50
σ (S cm ⁻¹)	6.9	31.8	41.2	26.3	25.9

The fluorescence spectra of PEDOT:PSS and PEDOT:PSS/P2Cz-D nanofilms were investigated and illustrated in Fig. 6. It is well known that P2Cz-D is a good blue-light emitter, while PEDOT:PSS films has almost no emission peaks in the whole visible region, as shown in Fig. 6a. [26] In the spectra of PEDOT:PSS/P2Cz-D films (b–f), an emission peak at ca. 440 nm is observed. The results indicated that the as-formed bilayered nanofilms combined the high electrical conductivity of PEDOT:PSS and the good blue-light emitting properties of P2Cz-D.

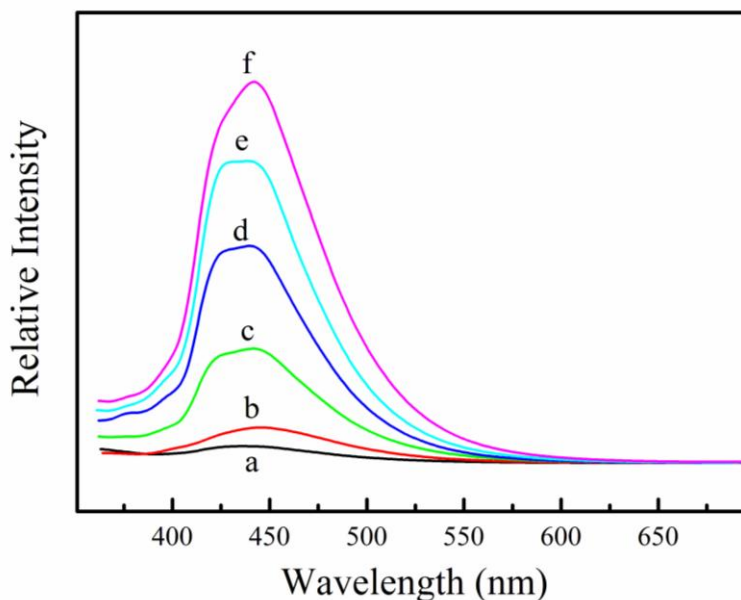


Figure 6. Fluorescence spectra of the samples: a–f. Sample a refers to PEDOT:PSS electrodes.

4. CONCLUSIONS

In conclusion, PEDOT:PSS nanofilm electrodes have been used to fabricate P2Cz-D films via electrochemical synthesis carried out in the mixed electrolytes of CH₂Cl₂ and BFEE. Owing to the high conductivity of the PEDOT:PSS layer, the maximum electrical conductivity of PEDOT:PSS/P2Cz-D films was 41.2 S cm⁻¹, improved by six orders of magnitude compared with the P2Cz-D films. Fluorescence studies revealed that the PEDOT:PSS/P2Cz-D films showed emission at

about 440 nm. The enhanced electrical properties together with good blue-light emitting properties made the bilayered nanofilms a good candidate for applications in organic electronic devices such as light emitting diodes. Furthermore, it is considered that the pure organic PEDOT:PSS as the working electrode may provide a novel approach for the electrochemical synthesis of conducting polymers.

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