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Synthesis and electrochemical polymerization of 9,9-bis(carbazolylalkyl)fluorene and characterization of its conducting polymer film with high tensile strength

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Abstract Free-standing poly(9,9-bis(carbazolylalkyl)fluorene) (P2Cz-A-F, alkyl = hexyl or dodecyl) films with high tensile strength (185–200 kg cm^{-2}) were electrochemically synthesized by direct anodic oxidation of the monomer 9,9-bis(carbazolylalkyl)fluorene (2Cz-A-F) in a mixed electrolyte of boron trifluoride diethyl etherate containing 30% CH_2Cl_2 (by volume). The electrochemical and physical properties show that the quality of P2Cz-A-F films are much better than that of polycarbazole (PCz) and polyfluorene (PF) films due to the specially designed structure consisting of stiff bicarbazyl chromophores linked by a flexible long alkyl spacer at the fluorene unit. The structure of free-standing P2Cz-A-F films was investigated by UV–visible and infrared spectroscopy. Thermal analysis shows that the polymer films have good thermal stability. Fluorescent spectral studies indicate that polymer films in the solid state are blue-light emitters, which may meet potential applications in polymer light-emitting diodes.

Introduction

The pursuit of novel polymeric materials is still a very important topic in academic and industrial laboratories, especially the design and synthesis of smart materials combining the good mechanical properties of traditional materials together with interesting electrical, optical, or magnetic properties. During the past decade, conjugated polymers with different chemical structures emitting different colors in the entire visible range have been widely investigated [1–4]. Among them, increasing interest has been paid to polyfluorenes (PFs) [5, 6] and polycarbazoles (PCzs) [7, 8] for the following reasons: they both have fully aromatic units providing better chemical environmental stability; the nitrogen atom and C_9 atom can be easily substituted by a wide variety of functional groups to improve the polymer solubility and also to tune the optical and electrical properties. Furthermore, they possess a bridged biphenyl unit resulting in materials with a relatively large band gap, making them suitable for potential applications as blue-light emitting materials.

In previous studies, PFs and PCzs are mainly prepared by chemical approaches, and seldom on electrochemical polymerization has been reported. In comparison with chemical approaches, electrochemical polymerization has several distinct advantages such as being catalyst-free, having a requirement for only small amounts of monomers, one-step conducting film formation, ease of control of film thickness by controlling the deposition charge, ease of characterization, etc. [3, 9–11]. The electrochemical polymerization of carbazole and fluorene together with their derivatives at N and C_9 positions is not very successful in common organic solvents such as acetonitrile (ACN). On the other hand, over the past 10 years, boron trifluoride diethyl etherate (BFEE) has been found to be a good electrolyte for electrochemical polymerization of aromatic compounds. The interaction between BFEE and aromatic monomers can lower the monomer oxidation potentials, and high quality free-standing polymer films can easily be prepared [12–14]. The quality of PCz obtained from BFEE has been greatly improved compared to that obtained from ACN. The conductivity of PCz has increased from 5.0×10^{-4} [15] to 7.5×10^{-3} S cm^{-1} [16]. However, this improvement still cannot produce high quality free-standing films and their conductivity is still very low.

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Although highly soluble PFs [17–25], PCzs [26–37], and their copolymers [38–41] are considered as promising blue-light emitting materials, their color stability still is one problem needing improvement. A low-energy green emission band is generated during operation or annealing in air. Recent studies have proposed that the origin of the green emission band is from aggregation or formation of excimers [42–47] and organized structures (dense interchain packing) leading to significant long wavelength emission in the green band [48]. Several chemical modifications have been introduced with the aim of increasing the solid-state color purity of blue-emitting PCzs and PFs. They include the attachment of branched alkyl [20], aromatic [31, 32], or dendritic groups at the 9- and 9′-positions of fluorene [39], hyperbranching [41], blending [29], increasing the polymer's molecular weight [33], end-capping polymers with aromatic groups [36], and the introduction of anthracene on the backbone [21].

The PF was designed to have the carbazole group as the pendant group to offer the possibility of electrochemical polymerization and this was also reported to improve color stability [49]. The carbazole group was chosen because of the better band gap match between the anode and the polymer. We report here the synthesis of monomer 9,9-bis(carbazolylalkyl)fluorene (2Cz-A-F), for which one fluorene unit and two carbazole units are linked through a long alkyl spacer; such molecular structural design should overcome the drawbacks mentioned above and may give better performance. It was reported that carbazole is more easily polymerized than fluorene by cyclic voltammetry at lower potential. Therefore, according to the oxidation potential difference between carbazole and fluorene, when the monomer simultaneously possesses carbazole and fluorene cores, the oxidation process mainly occurs at the carbazole units while the fluorene unit would have no effect on that during the polymerization process. The presence of two carbazole units enables the generation of insoluble highly reticulated polymeric chains (Scheme 2, indicating polymer growth directions). The resulting polymer films should exhibit a cross-linked skeleton, and hence can improve the mechanical stability. In addition, this kind of polymer should be considered as an ambipolar carrier transporting material because PCz is a hole-transporting material, and functionalized fluorene is an electron-transporting material. A long alkyl spacer may give better hole-transporting and enhance electrical conductivity.

In this article, the 2Cz-A-F monomer with a hexyl or dodecyl spacer was synthesized and electrochemically polymerized in a mixed electrolyte of 30% CH_2Cl_2 + 70% BFEE (by volume). The electrochemical properties, spectroscopic properties, thermal stabilities, conductivities, morphologies, and especially the fluorescence properties in the solid state of the as-formed free-standing polymer films were investigated in detail. The cross-linkage between the carbazole units and the fluorene unit by the alkyl spacer was the main reason contributing to the formation of high quality free-standing P2Cz-A-F films.

Experimental

Reagents and treatment

Carbazole, fluorene, 1,6-dibromohexane, 1,12-dibromododecane, and *n*-butyllithium (*n*-BuLi) were purchased from Acros and used as received. Tetrahydrofuran (THF, analytical grade, Beijing Chemical Plant) was freshly distilled from sodium/benzophenone before use. The solvents CH_2Cl_2 and $CHCl_3$ were purified and dried over CaH_2 and distilled before use. BFEE (Beijing Changyang Chemical Plant, China) was distilled and stored at −20 °C before use. Tetrabutylammonium tetrafluoroborate (TBATFB, Acros Organics, 95%) was dried in vacuum at 60 °C for 24 h before use. Commercial high performance liquid chromatography grade ACN (Tianjin Guangfu Fine Chemical Research Institute), sulfuric acid (98%), 25% ammonia, and deuterium substituted dimethyl sulfoxide (d_6-DMSO) (Jinan Chemical Reagent Company) were used as received without further purification.

Characterization

The ^{1}H-NMR spectra were recorded on a Bruker AV 400 NMR spectrometer, and d_6-DMSO was used as the solvent. The infrared (IR) spectra were recorded using KBr pellets of the polymers on a Bruker Vertex 70 FT-IR spectrometer. UV–visible spectra were taken using a Perkin-Elmer Lamda 900 UV–vis–NIR spectrophotometer. Fluorescence spectra were determined with an F-4500 fluorescence spectrophotometer (Hitachi). Thermogravimetric (TG) analyses were performed with a Netzsch TG209 thermal analyzer. Scanning electron microscopy (SEM) measurements were taken using a JEOL JSM-6360 LA analytical SEM. Direct current electrical conductivity was measured with a conventional four-probe technique.

Monomer synthesis

Synthesis of 9-(6-bromohexyl)-9H-carbazole [50]

To a 250 mL three-necked flask containing carbazole (2 g, 12 mmol) in DMSO (30 mL), 1,6-dibromohexane (6.5 g, 12 mmol), and NaOH (13.75 g, 0.34 mol) were added. The mixture was stirred at room temperature for 4 h. Then the reaction mixture was poured into water, extracted with ether (60 mL), washed with brine and deionized water, and dried over $MgSO_4$. After filtration and evaporation of the solvent, the resulting light yellow solid was dissolved in hexane and purified by flash column chromatography using hexane as eluent. Yield: 1.95 g (65%).

Synthesis of 9-(12-bromododecyl)-9H-carbazole

This compound was synthesized according to a similar method as used for 9-(6-bromohexyl)-9H-carbazole using 6 mmol carbazole and 6 mmol 1,12-dibromododecane. The resulting white powder was dissolved in CH_2Cl_2 and purified by flash column chromatography using hexane/CH_2Cl_2 = 5:1 as eluent. Yield: 3.45 g (70%).

Synthesis of 9,9-bis(6-carbazole-hexyl)-fluorene(2Cz-H-F) [51]

Fluorene (1.55 g, 9.26 mmol) was reacted with 9-(6-bromohexyl)-9H-carbazole (7.65 g, 23.1 mmol) in a two-phase system composed of toluene (20 mL) and sodium hydroxide (50% w/w) aqueous solution using tetrabutylammonium bromide (0.3 g, 0.9 mmol) as the phase-transfer catalyst at 60 °C for 4 h. After the reaction mixture had been diluted with ethyl acetate, the organic layer was washed with water. The separated organic layer was dried over magnesium sulfate, and the solvent was evaporated. The crude product was recrystallized from ethanol to give 3.38 g of pale yellow needle crystals. Yield: 82%. ^{1}H-NMR: δ (ppm) 8.17–8.08 (d, 4H), 7.75–7.69 (d, 2H), 7.50–7.38 (m, 8H), 7.30–7.14 (m, 10H), 4.29–4.20 (t, 4H), 1.81–1.71 (p, 4H), 1.59–1.46 (p, 4H), 1.05–0.89 (m, 8H), 0.28–0.41 (m, 4H).

Synthesis of 9,9-bis(12-carbazolyldodecyl)fluorene (2Cz-D-F)

Under a positive pressure of nitrogen, *n*-butyllithium (*n*-BuLi) (3.6 mL, 2.5 M solution, 9 mmol) was added dropwise to a solution of fluorene (0.66 g, 4.2 mmol) in THF (50 mL) at 0 °C. After stirring for 45 min, 9-(12-bromododecyl)-9H-carbazole (3.45 g, 8.4 mmol) was added at 0 °C. Then the mixture was stirred at 0 °C for 3 h, brought to room temperature and stirring continued for a further 24 h. Then the mixture was poured into water, extracted with CH_2Cl_2, washed with brine and deionized water, and dried over $MgSO_4$. After filtration and evaporation of the solvent, the resulting light yellow powder was dissolved in CH_2Cl_2 and purified by flash column chromatography using hexane/CH_2Cl_2 = 5:1 as eluent. Yield: 2.44 g (70%). ^{1}H-NMR (400 MHz $CDCl_3$): δ 8.1132–8.0940 (d, 6H), 7.5692–7.5486 (d, 6H), 7.4401–7.4029 (t, 6H), 7.1779–7.1408 (t, 6H), 4.3705–4.3364 (t, 4H), 1.8943–1.7241 (m, 8H), 1.1757–0.9768 (m, 36H).

Electrochemical polymerization

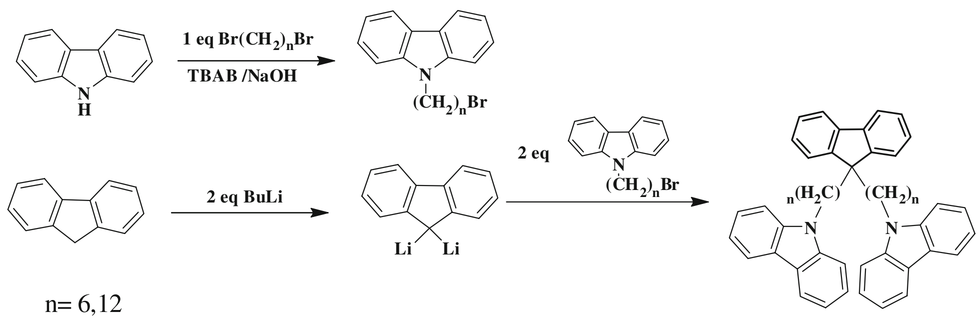
Electrochemical polymerization and examinations were performed in a one-compartment cell using a Model 263 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. The working and counter electrodes for cyclic voltammetric experiments were platinum wire and stainless steel wire with diameters of 0.5 and 1.0 mm placed 0.5 cm apart, respectively. For large-scale polymer film production, stainless steel sheets with surface areas of 1.5 and 2.0 cm^2 were employed as the working electrode and counter electrode, respectively. An Ag/AgCl electrode was used as the reference electrode, and all the obtained potentials were finally referred to a saturated calomel electrode (SCE).

The typical solutions were 0.05 mol L^{-1} monomer in 70% BFEE + 30% CH_2Cl_2. The use of mixed electrolytes was mainly because the solubility of the monomers in pure BFEE was relatively low while they showed better solubility in CH_2Cl_2. Furthermore, the ionic conductivity of pure BFEE was about 880 μS cm^{-1}. With the increase in CH_2Cl_2 concentration, the ionic conductivity of the mixed electrolyte decreased gradually. When the volume ratio of BFEE/CH_2Cl_2 was 7:3, the ionic conductivity decreased to 712 μS cm^{-1}, which was still enough for electrochemical polymerization in this medium. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during experiments. The amount of polymer deposited on the electrode was controlled by the integrated current passing through the cell. For dedoping, the polymer films were rinsed with 30% ammonia for 3 days then washed repeatedly with acetone. For spectral analysis, the polymer was dried under vacuum at 60 °C for 2 days. The polymer films were deposited on an indium tin oxide (ITO) coated glass for UV–visible, fluorescence spectral and SEM measurements in the solid state. Neutral (dedoped) polymer films were obtained by applying a constant potential of 0 V until the current passing through the cell became nearly zero.

Results and discussion

Monomer synthesis

Fluorene and carbazole have reactive remaining protons at the C_9 atom and N atom that can be activated by a strong base such as sodium hydride or *n*-butyllithium. After forming the sodium complex or lithium complex, carbazole or fluorene can readily react with the α,ω-dibromoalkane. Based on this idea, carbazole was treated with equimolar amounts of 1,6-dibromohexane and 1,12-dibromododecane,



Scheme 1 Synthesis routes of 9,9-bis(carbazolylalkyl)fluorene (P2Cz-A-F, alkyl = hexyl or dodecyl) monomer

respectively. Compounds 9-(6-bromohexyl)-9H-carbazole and 9-(12-bromododecyl)-9H-carbazole were obtained. Then, fluorene was reacted with two equivalents of 9-(6-bromohexyl)-9H-carbazole and 9-(12-bromododecyl)-9H-carbazole, respectively. The end products 9,9-bis(6-carbazole-hexyl) fluorene (2Cz-H-F) and 9,9-bis(12-carbazolyldodecyl)fluorene (2Cz-D-F) were formed, as shown in Scheme 1.

Electrochemical polymerization

Figure 1 shows the anodic polarization curves of 2Cz-H-F (A), 2Cz-D-F (B), carbazole (C), and fluorene (D) in 70% BFEE + 30% CH_2Cl_2 solutions. The initial onset of oxidation of fluorene (1.10 V vs. SCE) is much higher than that of carbazole (0.71 V vs. SCE). Therefore, during the electrochemical polymerization of the monomer 9,9-bis (carbazolylalkyl)fluorene (2Cz-A-F), the carbazole units were mainly oxidized. This was very different to the reported chemical polymerization of monomer 9,9-bis (carbazolylalkyl)-2,7-dibromofluorene, in which only the fluorene unit was polymerized or copolymerized through the Suzuki coupling reaction by activating the 2,7 positions with bromine atoms [49]. The onset of oxidations of 2Cz-H-F and 2Cz-D-F were at 0.68 and 0.70 V vs. SCE, and the onset of oxidation of 2Cz-D-F was slightly higher than that of 2Cz-H-F. This may be due to the fact that the substitution of the long alkyl chain at the N position increased the steric interactions on the polymer backbone. The longer the alkyl chain, the higher the onset of oxidation. All of these phenomena indicated that the 2Cz-A-F monomers can be easily oxidized during electrochemical polymerization and the alkyl spacer substitution has little effect on this process.

The successive cyclic voltammograms (CVs) of 0.05 M 2Cz-H-F (A) and 2Cz-D-F (B) in 70% BFEE + 30% CH_2Cl_2 solution at a potential scanning rate of 100 mV s^{-1} are illustrated in Fig. 2. As the CV scans continued, conducting polymer films were formed on the working electrode surface, with characteristics of other conducting polymer films during potentiodynamic synthesis. The increase in the redox wave currents implied that the amount of polymer on the electrode was increasing. The potential

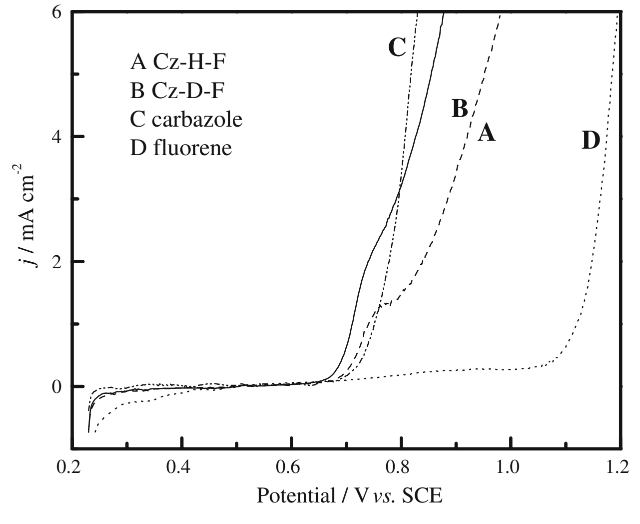


Fig. 1 Anodic polarization curves of 0.05 M 2Cz-H-F (*A*), 2Cz-D-F (*B*), carbazole (*C*), and fluorene (*D*) in 70% BFEE + 30% CH_2Cl_2 solution. Potential scan rate: 20 mV s^{-1}

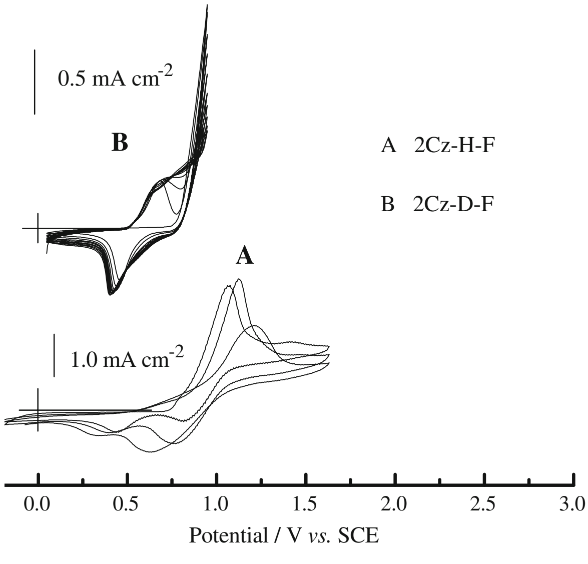


Fig. 2 CVs of 0.05 M 2Cz-H-F (*A*) and 0.05 M 2Cz-D-F (*B*) in 70% BFEE + 30% CH_2Cl_2 (by volume) solutions, respectively. Potential scan rate: 100 mV s^{-1}

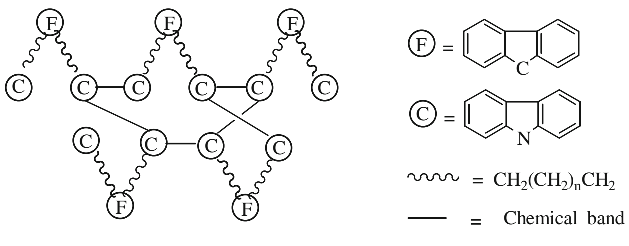
shift of this maximum provided information about the increase in the electrical resistance in the polymer film and an over-potential was required to overcome the resistance [52]. It was worth noticing that there are two pairs of redox systems in CVs of P2Cz-H-F. The first oxidation peak was not very clear and centered at about 0.78 V, which is lower than the necessary potential for monomer oxidation. The second oxidation peak appeared at about 1.1 V, which is more anodic than the monomer oxidation, and its intensity grew with the number of scans. This second merging step could also be ascribed to the polymer response. Such a peak could be attributed to the formation of new species as a result of creation of new linkages between the 3,6 positions of adjacent polymer chains within other carbazole units.

Nature of linkages in the polymers

According to the literature, in the case of dicarbazoles [53–60], beyond the preliminary formation of dimers, the linkage of carbazyl units under anodic electron transfer may give rise to polymers. The presence of two carbazole units in a monomer made the difference in electrochemistry of the polymer films together with the mechanism of oxidative coupling. Increasing the number of carbazole units may increase the polymerization positions and consequently, high quality polymer films can be obtained. When taking into account monomer 2Cz-A-F, only the carbazole units were polymerized. Scheme 2 shows the possible polymerization paths for this dicarbazole monomer. Due to the symmetry of the monomer, the polymer chains can grow through the C–C bond. Most of the monomers were cross-linked by both carbazole units. However, some monomer units, mainly in chain terminals, only have one carbazole being polymerized. This internal cross-linked structure made the electrodeposition of free-standing P2Cz-A-F films with high strength be possible.

Electrochemistry of P2Cz-A-F

The electrochemical behavior of as-formed P2Cz-H-F and P2Cz-D-F films deposited electrochemically from 70% BFEE + 30% CH_2Cl_2 solution was studied in pure BFEE (Fig. 3) and ACN + 0.1 M TBATFB (Fig. 4). The anodic and cathodic current densities were both proportional to the scan rates (Figs. 3A, B, 4A, B, insets), indicating the reversible redox behavior of P2Cz-H-F and P2Cz-D-F. The CVs of the polymers in BFEE and ACN + 0.1 M TBATFB all showed two obviously reversible peaks with redox potentials listed in Table 1. The first anodic peak has been assigned to one-electron oxidation of the dicarbazyl units into the radical cation. Similarly, when higher potentials were reached, dicationic forms might be obtained in the polymer. Furthermore, these polymer films could be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition of the materials, indicating the high structural stability of the polymer films.



Scheme 2 Possible coupling sites of P2Cz-A-F

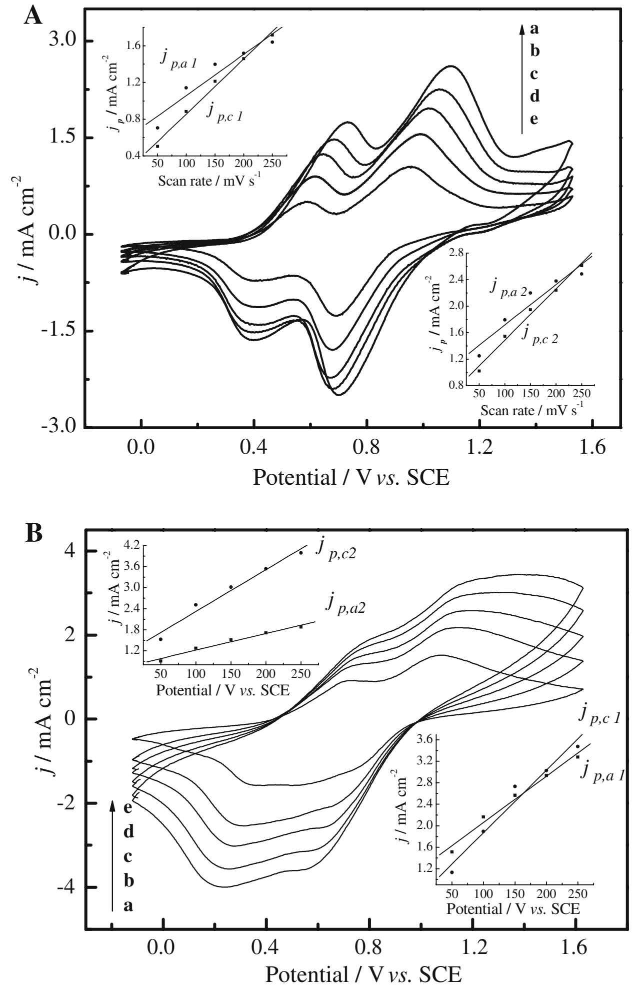


Fig. 3 CVs of P2Cz-H-F (**A**) and P2Cz-D-F (**B**) films in monomer free BFEE solution at potential scan rates of 250 (a), 200 (b), 150 (c), 100 (d), and 50 (e) mV s^{-1}. P2Cz-H-F and P2Cz-D-F films were synthesized electrochemically in 70% BFEE + 30% CH_2Cl_2 (by volume) at a constant applied potential of 1.15 and 1.08 V vs. SCE, respectively

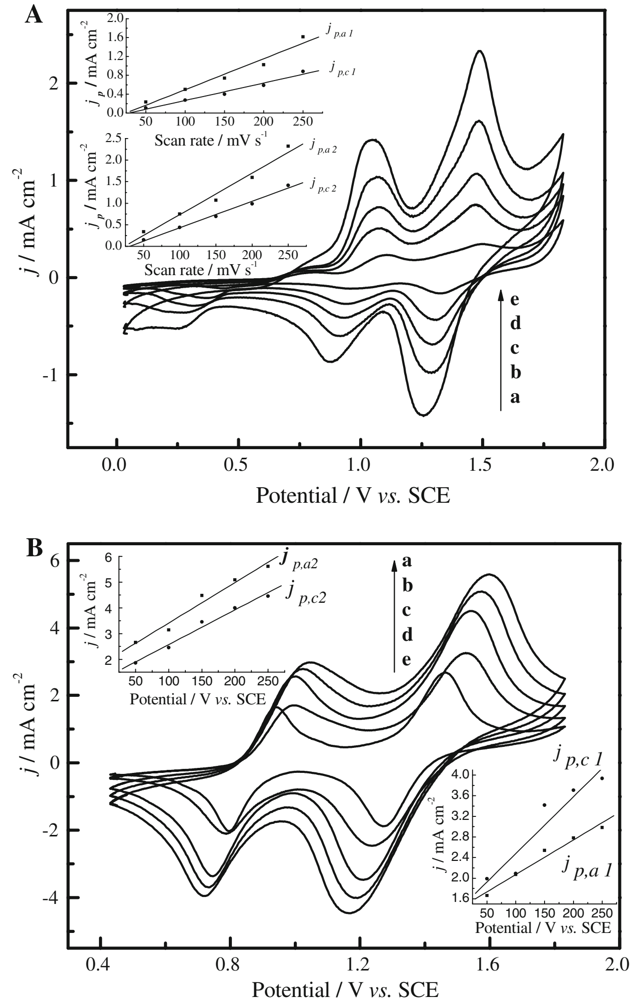


Fig. 4 CVs of P2Cz-H-F (**A**) and P2Cz-D-F (**B**) films in ACN + 0.1 M TBATFB solution at potential scan rates of 250 (a), 200 (b), 150 (c), 100 (d), and 50 (e) mV s^{-1}. P2Cz-H-F and P2Cz-D-F films were synthesized electrochemically in 70% BFEE + 30% CH_2Cl_2 (by volume) at a constant applied potential of 1.15 and 1.08 V vs. SCE, respectively

Table 1 Redox peak potentials of P2Cz-H-F and P2Cz-D-F films determined in pure BFEE and ACN + 0.1 M TBATFB solutions, respectively

	Pure BFEE		ACN + 0.1 M TBATFB	
	E_{pa} (V)	E_{pc} (V)	E_{pa} (V)	E_{pc} (V)
P2Cz-H-F	0.61	0.40	1.06	0.94
	0.95	0.68	1.47	1.30
P2Cz-D-F	0.70	0.31	0.93	0.79
	1.07	0.65	1.45	1.27

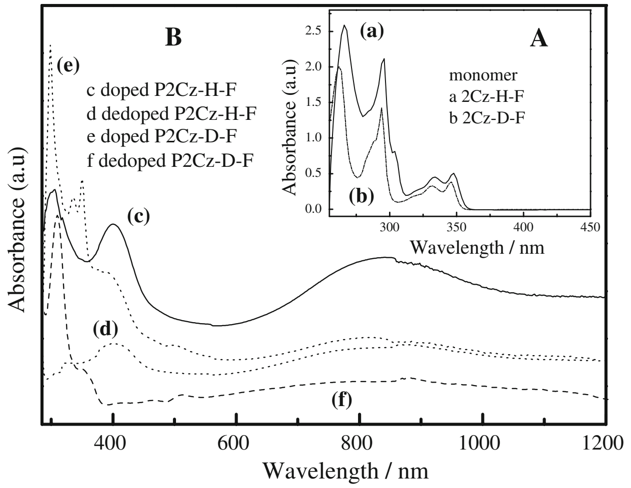


Fig. 5 UV–vis spectra of the monomers in $CHCl_3$ (inset *A*), the doped and dedoped polymer films deposited on ITO electrodes (*B*): 2Cz-H-F (a), 2Cz-D-F (b), doped P2Cz-H-F (c), dedoped P2Cz-H-F (d), doped P2Cz-D-F (e), and dedoped P2Cz-H-F (f)

Spectral characterization

The UV–visible spectra of the monomers in $CHCl_3$ and the doped and dedoped polymer films in the solid state on an ITO electrode are illustrated in Fig. 5. In $CHCl_3$ solution, 2Cz-H-F had an absorption maximum at 266 nm and with four significant shoulders at 295, 303, 333, and 346 nm (Fig. 5a, inset). The spectra of monomers 2Cz-D-F and 2Cz-H-F were very similar. The maximum absorption of 2Cz-D-F was located at 264 nm, with three significant shoulder peaks at 294, 331, and 347 nm (Fig. 5b, inset). They both have the absorption peaks of carbazole and fluorene. According to the literature [16, 61], the absorption peak at around 266 nm originated from the fluorene unit. The remaining absorption peaks belong to the carbazole unit. Therefore, for a monomer constructed of carbazole and fluorene, the absorption peaks were an amalgamation of peaks from carbazole and fluorene units. On the other hand, the UV–visible spectra of the doped and dedoped polymer films on ITO glass were also examined. In the doped state, P2Cz-H-F film showed absorption peaks located at 305, 403, and 600–1,200 nm (Fig. 5c), and P2Cz-D-F film showed absorption peaks at 296, 334, 349, 398, and 600–1,200 nm (Fig. 5e). The absorption peaks of doped P2Cz-H-F at 305 nm and doped P2Cz-D-F at 294, 334, and 349 nm originated from the unpolymerized carbazole units. However, the absorption peaks of P2Cz-H-F at 403 nm and P2Cz-D-F at 398 nm were due to a valence band–conduction band (π–π*) transition of the polymers. The broad bands from 600 to 1,200 nm were characteristic of conductive species such as the existence of polarons or bipolarons. After being electrochemically dedoped, the absorption peaks of P2Cz-H-F at 403 nm and P2Cz-D-F at 398 nm still existed and the absorption at 600–1,200 nm was reduced (Fig. 5d, f). The similarity of the absorption spectra of the P2Cz-A-F films in both doped and dedoped states indicated that the structures of the polymers were very similar.

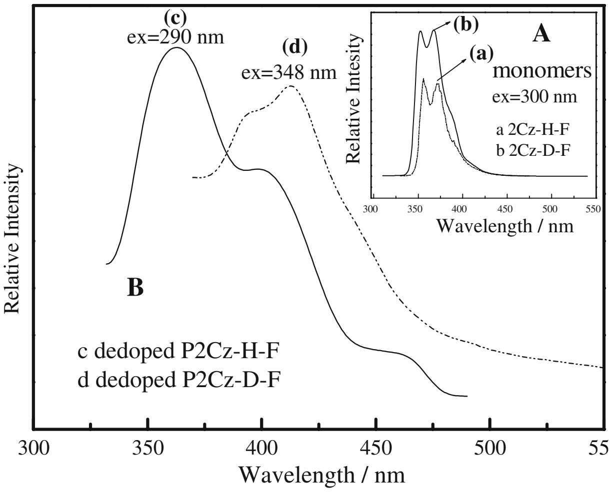


Fig. 6 Fluorescence spectra of the monomers 2Cz-H-F (a), 2Cz-D-F (b) in $CHCl_3$ (inset *A*) and the dedoped state P2Cz-H-F (c), P2Cz-D-F (d) films deposited on ITO glasses (*B*)

The fluorescence spectra of the monomers in $CHCl_3$ and the doped and dedoped polymer films in the solid state on an ITO electrode are illustrated in Fig. 6. The monomers 2Cz-H-F exhibited strong peaks at 356 and 370 nm when excited by 300 nm light (Fig. 6a, inset) while 2Cz-D-F exhibited strong peaks at 353 and 367 nm when excited by 300 nm light (Fig. 6b, inset). Compared to the monomers, the fluorescence spectrum of the polymer P2Cz-H-F in dedoped state (Fig. 6c) showed maximum emissions at 366 nm with shoulder peaks at 401 and 461 nm when excited by 290 nm light. The maximum emissions can be assigned to the untouched fluorene and unconnected carbazole units. At the same time, the weak emission peak at 401 nm was the result of the carbazole oligomers or short conjugated PCz chains, while the emission peak at 461 nm originated from longer conjugated PCz chains formed during the electropolymerization. The fluorescence spectra of dedoped P2Cz-D-F (Fig. 6d) showed maximum emissions at 394 and 411 nm when excited by 348 nm light. This can be assigned to the conjugated polymer chains. These results implied that as-formed P2Cz-A-F films in solid state were good blue-light emitters.

Thermal analysis

The thermal stability of polymers is very important for their potential applications. In order to investigate the degradation behavior of polymer films prepared in mixed BFEE + CH_2Cl_2 solution, thermal analyses of P2Cz-H-F and P2Cz-D-F were performed, as shown in Fig. 7. All thermal analyses were performed under a nitrogen stream with a heating rate of 10 K/min. It can be seen from this figure that, for P2Cz-H-F film (A), the first weight loss about 2.3% occurred from 323 to 569 K; P2Cz-D-F film (B) lost its weight of 3.3% when the temperature reached 460 K, which were ascribed to moisture trapped into the polymer matrix. The second decomposition step of

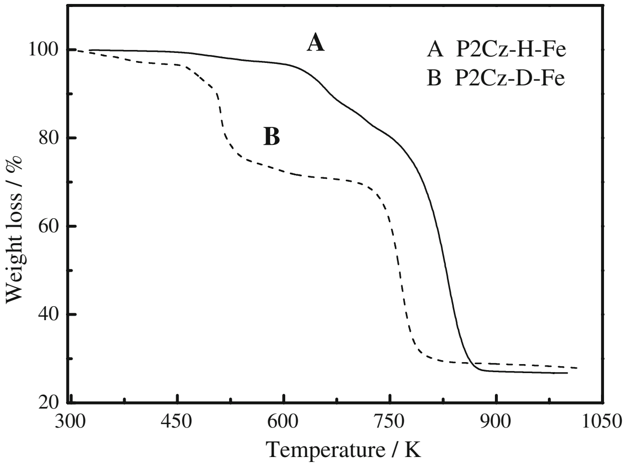


Fig. 7 TG curves of dedoped P2Cz-H-F and P2Cz-D-F films

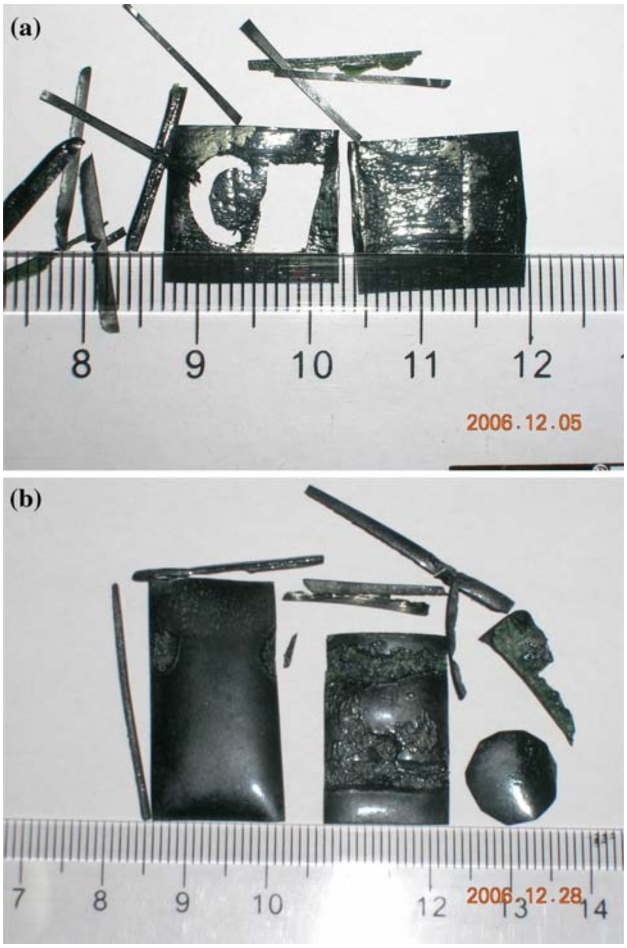


Fig. 8 Images of the free-standing P2Cz-H-F and P2Cz-D-F films prepared from 70% BFEE + 30% CH_2Cl_2 (by volume) solutions directly peeled off the working electrode

P2Cz-H-F occurred at 597–780 K (A), and that of P2Cz-D-F occurred at 460–612 K (B), respectively. This weight loss can be attributed to the degradation of the oligomers or other short chain structures. The third decomposition steps for the polymers occurred at 780 K (P2Cz-H-F) (A) and 706 K (P2Cz-D-F) (B), respectively, and these weight losses were ascribed to the degradation of the skeletal backbone chain structure of the polymers. All of the results indicated that the thermal stability of P2Cz-A-F films obtained from 70% BFEE + 30% CH_2Cl_2 was reasonably good.

Conductivity, morphology, and mechanical properties

The P2Cz-H-F and P2Cz-D-F films deposited on the electrode surface were all shiny, metallic, compact, and smooth. Moreover, the polymer films could be peeled off from the electrode surface as a free-standing films and could be cut into various shapes with a knife. Figure 8 shows images of the P2Cz-H-F and P2Cz-D-F films prepared from 70% BFEE + 30% CH_2Cl_2. The conductivity of the P2Cz-H-F film was measured to be 1.1×10^{-2} S cm^{-1}, while P2Cz-D-F film was as high as 1.91 S cm^{-1}, which was significantly higher than that of PCz (7.5×10^{-3} S cm^{-1}) prepared from BFEE [16].

SEM images of P2Cz-H-F and P2Cz-D-F films are shown in Fig. 9. The doped polymer films were very flat and compact (Fig. 9a, c). After dedoping at a constant applied potential of −0.2 V, the surfaces of the dedoped films are still compact and flat with regular granules (Fig. 9b, d). This was due to migration of counteranions out of the polymer surface. This morphology indicated that movement of doping anions into and out of the polymer is easy.

The polymer films were very flexible and had reasonably good mechanical properties. The tensile strengths of P2Cz-H-F and P2Cz-D-F films were measured to be 200 and 185 kg cm^{-2} with elongation at the break of about 5.0%, respectively. This was due to the synthesized monomer containing two carbazole units, with alkyl spacers linked to one fluorene unit. This reticular structure and long alkyl spacers between carbazole and fluorene units led to the formation of high quality free-standing polymer films. For comparison, polymers electrosynthesized by direct anodic oxidation of fluorene [61] or carbazole [16] are not very satisfactory.

Conclusions

In summary, homogeneous and free-standing poly(9,9-bis(6-carbazolylhexyl)fluorene) (P2Cz-H-F) and poly(9,9-bis(12-carbazolyldodecyl)fluorene) (P2Cz-D-F) films with relatively high conductivity and good tensile strength were electrochemically synthesized in mixed electrolyte of 30% CH_2Cl_2 + 70% BFEE. The internal structure among the carbazole units was the main reason for the formation of high quality polymer films. Fluorescence studies revealed

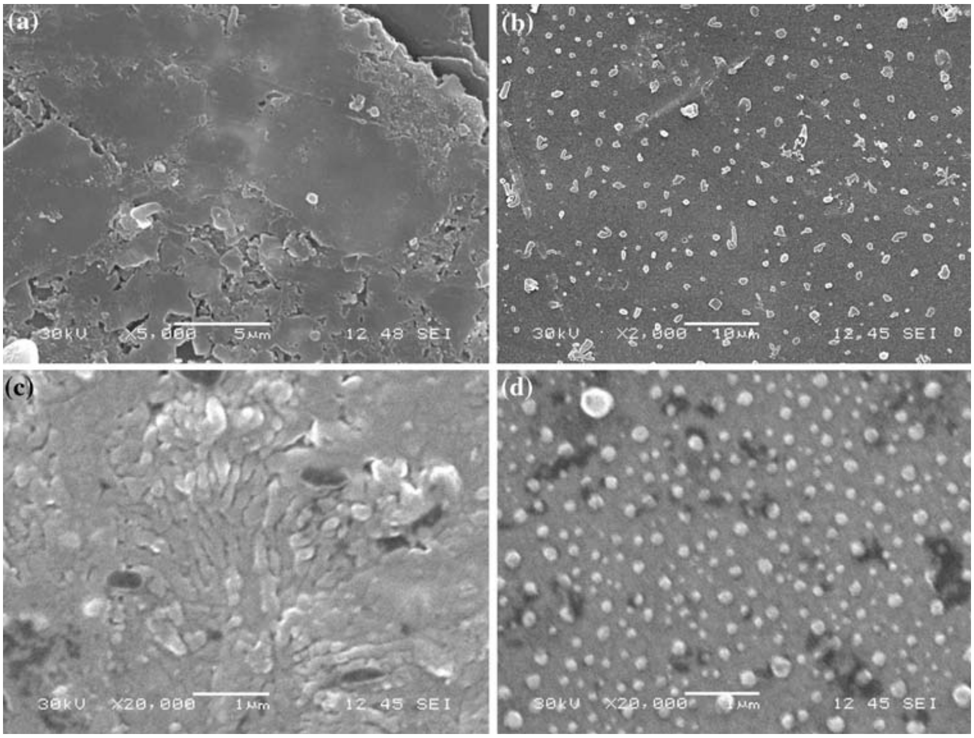


Fig. 9 Scanning electron micrographs of polymer films electrodeposited on ITO glasses from 70% BFEE + 30% CH_2Cl_2 (by volume) solutions: doped P2Cz-H-F (**a**), dedoped P2Cz-H-F (**b**), doped P2Cz-D-F (**c**), and dedoped P2Cz-D-F (**d**). P2Cz-H-F and P2Cz-D-F were synthesized electrochemically at a constant applied potential of 1.15 and 1.08 V vs. SCE, respectively

that as-formed polymer films were blue-light emitters. To the best of our knowledge, this is the first report showing that free-standing P2Cz-A-F films can be easily electrodeposited. The good mechanical properties, high conductivity, fine thermal stability, and blue-light emitting properties make this kind of polymer film a good candidate for applications in polymer light-emitting diodes.

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