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Spectroscopic and Electrochemical Study of a Novel Blue Electroluminescent *p-n* Diblock Conjugated Copolymer

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A novel *p*−*n* diblock copolymer, poly[*N*-(2′-ethylhexyl)-carbazole-3,6-diyl-1″,3″,4″-oxadiazole-2″,5″-diyl-2‴,5‴-dioctyloxy-1‴,4‴-phenylene-1⁗,3⁗,4⁗-oxadiazole-2⁗,5⁗-diyl] (PCOPO**)** composed of an electron-rich moiety carbazole and an electron-deficient unit aromatic oxadiazole was synthesized aiming at balancing the abilities of conducting holes and electrons. Electrochemical analyses by cyclic voltammetry indicate that PCOPO can be reversibly *n*-doped and irreversibly *p*-doped. The cathodic sweep reveals that the reduction involves two-electron process with respect to the successive reduction of oxadiazole rings and carbazole moieties in the polymer chain. The highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) energy levels of the polymer are estimated to be 5.60 and 2.66 eV from the onset of oxidation and reduction potentials, respectively. The band gap energy of the polymer estimated by the electrochemical measurement (2.94 eV) is in good agreement with that from the optical method (2.82 eV). The photoluminescence (PL) of film samples shows that the polymer emits greenish-blue light (475 nm). The PL of solutions is concentration-dependent. In dilute solutions, the PL emission is from the singlet exciton transition, whereas in the concentrated solutions, it is mainly originated from excimers. The excimer formation is related to the incorporation of oxadiazole rings into the polymer backbone, which can enhance the interchain interactions. Both photophysical and electronic properties demonstrate that the polymer may be a promising candidate material for the fabrication of an efficient blue light-emitting device.

Introduction

The discovery of electroluminescence (EL) from poly(*p*-phenylenevinylene) (PPV)[1] has triggered enormous research interest in the field of electroluminescent conjugated polymers. On one hand, this encourages material chemists to synthesize a variety of novel conjugated polymers with exciting and diverse physicochemical properties. On the other hand, this gives physicists opportunities to achieve a better understanding of photophysics, charge transport, and optoelectronic properties of various conjugated polymers.

From the viewpoint of material synthesis, many efforts have been devoted to developing blue light-emitting polymers with high efficiencies in the past several years. This is because blue light emission is the most difficult to be realized of the three primary colors.[2,3] Blue light generation from emissive polymers is much more attractive compared to the inorganic semiconductor counterparts for applications in display technology because of the solution processability, flexibility of the synthetic strategies, and facile ways of tuning the chemical structures of conjugated polymers to adjust the energy levels of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) to achieve highly efficient emission. Polyfluorenes (PFs),[4] polycarbazoles (PCs),[5] and polythiophenes (PTs),[6] as well as polyoxadiazoles (POs),[7] are some examples of blue light-emitting polymers.

Reportedly, the obstacle for improving the EL efficiency of light-emitting diode (LED) devices is mainly due to the imbalance of the charge injection rates from opposite contacts into the emission layer. For most of the electroluminescent polymers investigated so far, the barrier for the electron injection from metal contact is much larger than that for the hole injection, which leads to the charge capture near the metal contact. This results in poor quantum efficiency. To overcome this problem, two approaches were developed. One approach is to use low work function metals such as Ca or Mg as the cathode so as to improve the ability of electron injection. The other approach is to introduce an electron transporting and hole blocking layer to lower the energy barrier for electron injection and also to provide an intermediate area for charges to capture each other. However, there are some technical problems for the practical device fabrication utilizing the above two approaches. Alternatively, conjugated polymers with well-matched HOMO and LUMO energy levels with respect to the electrode energy barrier heights will lead to high efficiency for light-emitting device application.

Carbazole-based conjugated polymers have demonstrated strong hole-transporting ability in optoelectronic devices,[8,9] whereas oxadiazole-based polymers have played an important role in the fabrication of multilayer LED devices as good electron transport materials.[10,11] Both carbazole- and oxadiazole-based electroluminescent polymers demonstrate quite different charge injection and transporting abilities for holes and electrons in polymer light-emitting diode (PLED) devices. High quantum efficiencies are difficult to achieve using either carbazole- or oxadiazole-based polymers alone. Combining carbazole moiety (a typical hole injection unit) and oxadiazole segment (an electron injection unit) into the same polymer backbone might meet this requirement. Our previous work that was based on

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combined oligothiophene and oxadiazole units as functional materials for blue light-emission LED devices demonstrated good results,[12−14] which motivates our continuous efforts in this regard.

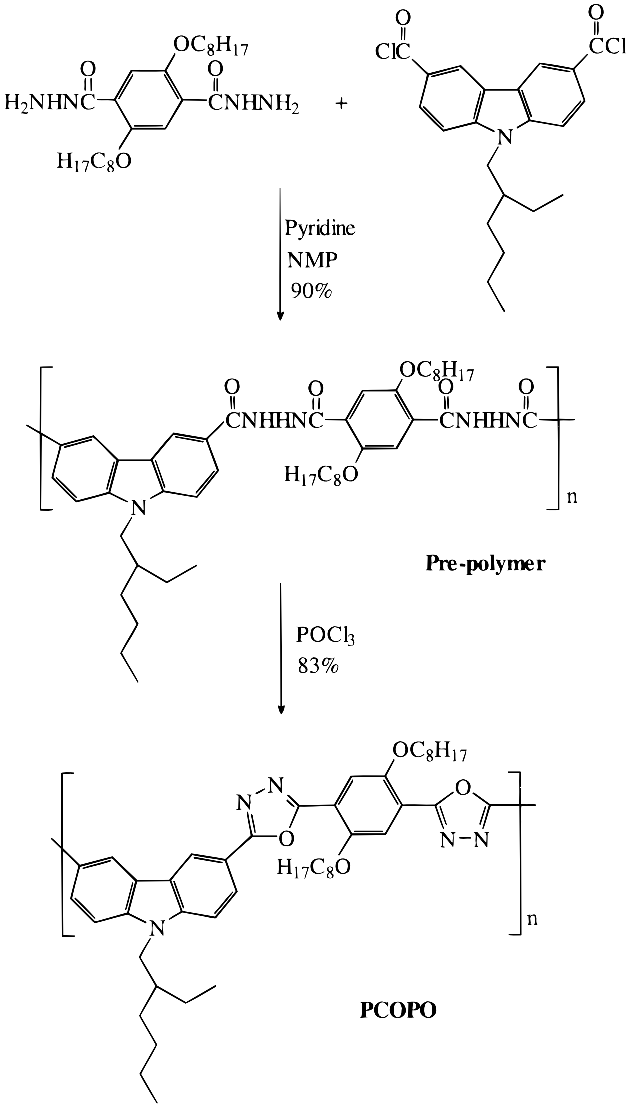
Note that many efforts have focused on the photophysics of electroluminescent polymers aimed at understanding the excited states and emission characteristics of conjugated polymers. Recent studies on the supramolecular structures and morphologies of the conjugated polymers indicate that the electroluminescent properties of conjugated polymers are also affected by the molecular interaction pattern in addition to the intrinsic optoelectronic nature of the isolated polymer chains in the film state as well as in solutions. In the excited state, conjugated polymer chains may exist in the forms of several charged or neutral species, such as polarons, bipolarons, excitons, excimers, or aggregates. As films or in concentrated solutions, the interchain/intrachain interactions of the excited species in one polymer chain with one or more adjacent polymer chains lead to the formation of excimers and/or aggregates with new optical properties by delocalization of the species over the polymer chains.[15,16] It is well known that the formation of excited-state complexes can lower the luminescent efficiencies because nonradiative decays compete with radiative routes.[17] However, in the absence of significant interchain interactions, for example, by dispersing the luminescent polymers into nonconjugated matrixes, relatively high luminescent efficiency can be achieved.[18] In addition, the formation of excited-state complexes provides another opportunity to tune the light-emitting color.[19] Apart from luminescence, other photophysical processes such as photoconductivity and charge photogeneration of conjugated polymers are also involved with the excimer mechanism. Consequently, a better understanding of the photophysics of the luminescent polymers can provide guidelines on the development of various applications in optoelectronics.

In this paper we present the work of characterization of a new polymer, poly[*N*-(2′-ethylhexyl)-carbazole-3,6-diyl-1″,3″,4″-oxadiazole-2″,5″-diyl-2‴,5‴-dioctyloxy-1‴,4‴-phenylene-1⁗,3⁗,4⁗-oxadiazole-2⁗,5⁗-diyl] (PCOPO) (Scheme 1), in which the oxadiazole moiety as the electron injection and transporting unit is incorporated into the carbazole main chain to form a *p*−*n* diblock structure.[12] On the basis of this concept, it is expected that the designed polymer will possess good charge injection and transporting properties for both holes and electrons. This property will be investigated by electrochemical measurements to provide information about the redox properties and the HOMO and LUMO energy levels. The absorption and photoluminescence (PL) behavior of the films as well as in various concentrations of solutions will be studied to determine the photophysical process and emission characteristics.

Experimental Section

Measurements. FTIR spectra were recorded on a Bio-Rad FTS 165 spectrometer by dispersing samples in KBr disks. UV−vis and fluorescence spectra were obtained on a Shimadzu UV 3101PC UV−vis−NIR spectrophotometer and Perkin-Elmer LS 50B luminescence spectrometer with a xenon lamp as light source, respectively. Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer for C, H, N, and S determinations. Cyclic voltammograms were performed using an EG&G model 273A potentiostat/galvanostat under argon atmosphere. All potentials were measured against a Ag/Ag$^+$ (0.1 M in acetonitrile) electrode (0.34 V vs saturated calomel electrode (SCE)) and all experimental values in this report were corrected with respect to SCE.

SCHEME 1. The Synthetic Route to PCOPO



Materials. A brief synthetic procedure for polymer PCOPO is depicted in Scheme 1. The final polymer was converted from its precursor by cyclization and dehydration in $POCl_3$ in a yield of 83%.[13,14] The light yellow precursor polymer, which was soluble in dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidinone (NMP), and dimethyl formamide (DMF), was facilely obtained by polycondensation of the di-alkoxy substituted phenylene dihydrazine with the bischlorocarbonyl of *N*-(2′-ethylhexyl)-carbazole using pyridine as the base to promote the reaction (yield 90%). The *N*-alkyl carbazole diacid chloride was prepared from its acid, which was obtained from 3,6-bis(*N*,*N*-dimethylcarbamoyl)-9-(2′-ethylhexyl)carbazole.[20] The *N*,*N*-dimethylcarbamoyl substituted carbazole was synthesized through Friedel−Crafts carbonylation reaction from *N*-(2′-ethylhexyl)-carbazole and *N*,*N*-dimethylcarbamoyl chloride catalyzed by aluminum chloride (yield 73%). The detailed synthetic procedure will be published elsewhere.

Results and Discussion

The final polymer PCOPO was obtained as a greenish-yellow solid. The polymer is partially soluble in common organic solvents such as chloroform, tetrahydrofuran, xylene, and DMSO. However, it is readily dissolved in chloroform with a small amount of trifluoroacetic acid (TFA). The complete conversion of prepolymer to final polyoxadiazole can be

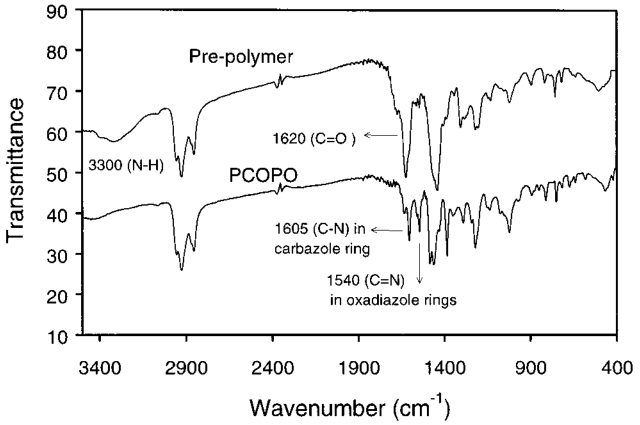


Figure 1. FT-IR spectra of PCOPO and its prepolymer.

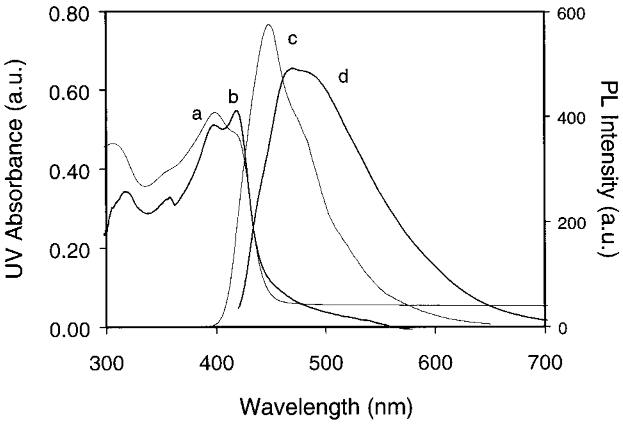


Figure 2. UV−vis spectra and fluorescence spectra of the polymer in solution and as films. (a) UV in solution; (b) UV in film; (c) PL in solution; (d) PL in film.

confirmed by FT-IR. The FT-IR spectra are shown in Figure 1. The absorption peak at 1620 cm^{-1} owing to the carbonyl group and the absorption broad peak in the range of 3300 cm^{-1} owing to the amide groups of the precursor polymer disappeared after the treatment with $POCl_3$. A new peak at 1540 cm^{-1} attributed to the C=N in oxadiazole ring clearly appeared in the spectrum of the final polymer. These results indicate that the cyclodehydration reaction was completed.[14] It is well known that high purity of the electroluminescent materials is a crucial factor for good performance in a PLED device. Impurities existing in the emission layer will quench the excitons, which will lower the electroluminescent quantum efficiency. During the conversion of the prepolymer to the final polymer, a complete cyclization ensures the required purity for PLED application and also clears quench sites of the carbonyl groups in the final polymer.

The UV−vis absorption and photoluminescence spectra of the polymer, both in a dilute solution (ca. 1×10^{-5} M) of chloroform with a small amount of TFA and as thin films which were prepared by spin-coating the solution on quartz plates, were measured at room temperature. The spectra are displayed in Figure 2. The solution sample gives a main absorption peak at 398 nm and a shoulder at 418 nm, whereas the maximum absorption peak of the solid films of the polymer appears at 418 nm with a shoulder at 398 nm. The relatively identical absorption spectra of the polymer in solution and as solid films indicates that there is little difference in the conformation of polymer in the two states.[21] When the absorption spectra of the film samples were compared to that of a copolymer composed of thiophene unit and oxadiazole−benzene−oxadiazole block, a hypsochromic effect of the absorption bands was observed.[13,14] The blue shift can be attributed to the linkage through 3,6 position of the carbazole group incorporated in the polymer. The conjugation of the π electrons along the polymer chain will be partially interrupted in such a linkage. A similar phenomenon was found in poly(*N*-alkylcarbazole)(s), in which the delocalization of π electrons is limited to a dimer.[21b]

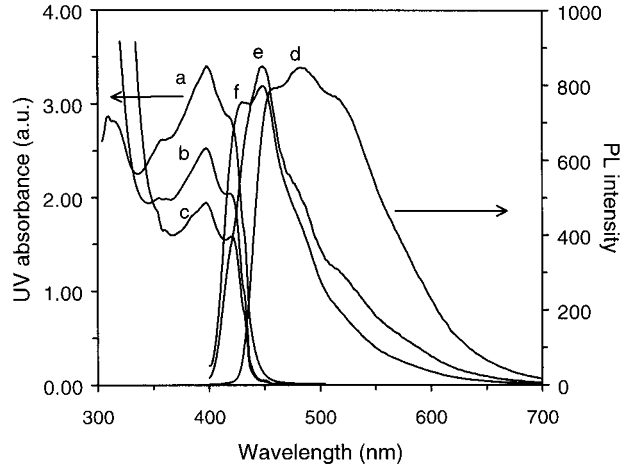


Figure 3. The dependence of the absorption and PL spectra of PCOPO in chloroform on the concentration of the polymer: (a) 1×10^{-4} M; (b) 1×10^{-5} M (UV absorbance × 5); (c) 1×10^{-6} M (UV absorbance × 30); (d) 1×10^{-4} M; (e) 1×10^{-5} M; (f) 1×10^{-6} M. Curves d, e, and f are normalized for clarity.

The emission spectra of the polymer in solution and as solid films are quite different. In comparison with its solution emission peak at 448 nm, the main emission peak in the solid films shifted about 25 nm toward longer wavelength. Note that the emission peak is more broadened in the film state than that in the solution state. The red-shift of the emission band of the film samples compared to the polymer in solution may be due to the intrachain and/or interchain excimers generated in the polymer. The possible formation of excimer was investigated in a concentration−dependent PL measurement.

Figure 3 shows the dependence of the absorption and PL spectra of the polymer solution on the concentration of the polymer. The absorption spectra of the samples in three concentrations from 1×10^{-6} to 1×10^{-4} M resemble each other in shape; they all center at 398 nm with two shoulders at 358 and 418 nm, respectively. The absorption edges are all about 445 nm for the three concentrations. However, the shoulders become clear as the polymer solution is diluted. The resolved absorption spectrum results from the excitonic transition coupling to vibrations. The energy space is 150 meV, which is a typical vibrational energy of carbon−carbon or carbon−nitrogen bond stretching.[22] Because of the intense absorption, we cannot obtain the UV−vis spectra of those solutions with concentration higher than 1×10^{-4} M. Unlike the absorption spectra, the PL spectra clearly demonstrate a concentration-dependent feature. At 1×10^{-6} M, the emission band is composed of two peaks at 430 and 449 nm, respectively, which can be ascribed to a vibronic progression with respect to the absorption spectrum. The red shift of the emission spectrum of the dilute solution compared to its absorption spectrum originated from the Stokes shift, which is in agreement with the typical 0.2−0.3 eV of energy difference.[23] The Stokes shift can come from two sources: emission either from the excited segments of conjugated polymer undergoing a deformation into more planar conformation along the chain or from the migrated excitons in other segments where ring rotations are not hindered.[22]

A similar fine structure was observed in the PL spectrum of the solution with concentration of 1×10^{-4} M, which is composed of a main peak at 482 nm accompanied by two shoulders at 459 and 509 nm, respectively. Compared to the 1×10^{-6} M solution sample, the emission band is broadened and the maximum emission peak is red-shifted by 33 nm. This spectrum is much like that of the film samples. The bathochromic shift in the PL spectra of concentrated solution and films indicates the formation of excimers. However, the spectrum of the middle concentration sample (1×10^{-5} M) is less structured, in which only one main peak at 448 nm is observed with the tailed emission at about 480 and 510 nm, respectively. The emission peak at about 450 nm, which corresponds to the absorption edge, is always observed in the three samples with different concentrations. This emission originates from the isolated exciton decay, which is a dominant emission in dilute solution, whereas in concentrated solutions or in films, the emission from excimers is observed and even becomes the main source of the PL. Excimer formation was found to be quite common in concentrated solution or films of some conjugated polymers such as PPV derivatives.[15,16,24] In dilute solutions, the polymer chains are well-separated from each other. While in concentrated solution or in films, a pair of chain segments with similar length can align parallel to each other and if they are close enough, the π wave functions on these segments will overlap sufficiently and the energies of the excited states will be lowered, which leads to the lower frequency emission. Excimer formation is sample-dependent and polymers or copolymers with electron withdrawing segments such as cyano,[25] pyridine,[26] benzobisoxazole, and benzobisthiazole[27] groups can enhance the interchain interactions by the greater electronegativity resulting from the incorporation of these groups, which may be due to the effect of reducing the distance between the polymer chains in the ground state. In each repeat unit of polymer PCOPO, the two oxadiazole groups incorporated into the polymer backbone, which have the same function as those of pyridinyl or cyano groups, may be one of the reasons for the observed excimer emission. Further work related to determining the emission lifetime is in progress.

The redox properties as well as the HOMO and LUMO energy levels of the polymers are crucial parameters for the device configuration consideration. Usually the ionization potential (IP, i.e., the HOMO of an organic molecule) is measured by ultraviolet photoelectron spectroscopy (UPS), while the electron affinity (EA, i.e., the LUMO of the organic molecule) is deduced from the IP value and the band gap obtained from optical absorption spectra, which is not a direct measurement. Cyclic voltammetry (CV) is an alternate approach to determine both the HOMO, LUMO energy levels and evaluate the redox reversibility, reproducibility, and stability of the polymer films on the electrode. The electrochemical processes are similar to the situation of charge injection and transport in LED devices. Therefore, CV is a simple and useful technique to measure the HOMO and LUMO energy levels of the polymer.[21]

Figure 4 depicts the CV curves of both the *p*-doping and *n*-doping processes. The polymer film on Pt electrode was scanned anodically and cathodically separately in an acetonitrile solution of n-Bu_4NClO_4. During cathodical scan, the polymer exhibits a reversible two-electron reduction process. The cathodical peaks occur at −1.90 and −2.25 V (vs SCE) with corresponding anodical peak at −1.78 V (vs SCE). The first redox peaks can be attributed to the reduction and oxidation of the oxadiazole rings and the second cathodical peak can be attributed to the reduction of the carbazole moiety in the polymer chain. The onset potential of the reduction is −1.74 V (vs SCE). The reduction potential is comparable with that of 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) (−1.95 to −1.94 V vs SCE),[14] which is one of the most widely used electron-transporting/hole-blocking materials. The onset potentials of *n*-doping and *p*-doping processes can be used to estimate the HOMO and LUMO energy levels of a conjugated polymer.[21,28] According to the equation reported by de Leeuw et al.,[28] $E_{\mathrm{LUMO}} = (E^{\mathrm{red}}_{(\mathrm{onset\ vs\ SCE})} + 4.4\ \mathrm{eV})$ and $E_{\mathrm{HOMO}} = (E^{\mathrm{ox}}_{(\mathrm{onset\ vs\ SCE})} + 4.4\ \mathrm{eV})$, where $E^{\mathrm{ox}}_{(\mathrm{onset\ vs\ SCE})}$ and $E^{\mathrm{red}}_{(\mathrm{onset\ vs\ SCE})}$ are the onset potentials for the oxidation and reduction processes of a polymer vs SCE. The onset potentials were determined from the intersection of the two tangents drawn at the rising current and baseline charging current of the CV curves. The LUMO energy of the polymer is thus determined to be 2.66 eV. This value is almost the same as that of poly[2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylenevinylene] (MEH-PPV) (2.6 eV) reported by Cervini et al.[29] It implies that the polymer may have similar electron-injection property to MEH−PPV when it is successfully used as the red-orange emitter in PLEDs. The LUMO energy level of 2.66 eV is smaller than that of CN−PPV (3.02 eV) and some poly(aromatic oxadiazoles) (2.8−2.9 eV),[29] which all exhibit good electron-injection properties. When we scanned the polymer films anodically, the polymer showed an anodic peak at 1.69 V with a cathodic peak at 1.56 V (vs SCE). The onset potential was determined to be 1.20 V, so that the HOMO energy level was estimated to be 5.60 eV. This value is almost the same as that of CN−PPV (5.55 eV), but is larger than that of MEH−PPV (4.87 eV).[29] This means that the polymer has similar hole-injection ability with CN−PPV as that of it is used in PLEDs, but the hole-injection ability is poorer than that of MEH−PPV. Note that both the *p*-doping and *n*-doping processes are reproducible up to being repeatedly swept for five times without any significant changes of the curves.

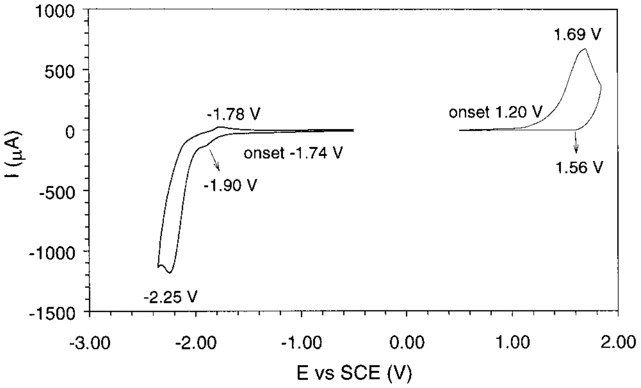


Figure 4. CV of PCOPO coated on Pt electrodes in acetonitrile containing 0.1 M n-Bu_4NClO_4 at a scan rate of 50 mV/s.

The electrochemical analysis results suggest that the hole injection ability of the polymer was lowered by incorporating the two oxadiazole rings into the polymer backbone, whereas the electron affinity was maintained at the level of MEH−PPV. To increase the quantum efficiency of PLEDs, it is necessary to balance the energy barriers of injection electrons and holes into the polymer layers from the opposite contacts. However, most of the current existing EL polymers, e.g., MEH−PPV, one of the best soluble EL polymers so far, are more favorable for hole injection when a stable metal, e.g., aluminum, is used as cathode. The new blue EL polymer can be expected to improve EL quantum efficiency when this polymer is used to fabricate single-layer PLEDs using stable metals as cathodes. These results reinforce our previous idea regarding the design of *p*−*n* diblock copolymers by tuning the intrinsic properties for possible applications as optoelectronic devices.

Conclusion

A new conjugated copolymer, PCOPO, which constituted alternating *N*-(2′-ethyl hexyl)carbazole and 1,4-bis(1,3,4-oxadiazole-2-yl)-2,5-dioctyloxybenzene segments, was synthesized and characterized. The UV−vis and PL spectra of the solution and film samples indicated that PCOPO is a blue light-emitting material. CV investigation revealed that the LUMO and HOMO energy levels of the polymer were adjusted by combining the electron-deficient oxadiazole moiety and the electron-rich carbazole segment into the polymer backbone together, which can improve the imbalanced hole-electron injection/transporting ability of most conjugated polymers encountered in PLED devices. The PL measurement of the solution samples demonstrated a concentration-dependent feature of the polymer. The emission in dilute solutions is the result of singlet exciton transition, whereas the bathochromic shift emission from concentrated solutions is attributed to the formation of excimers. The excited-state complexes formation can be related to the introduction of oxadiazole units, which can enhance the interchain interactions by reducing the distance of adjacent polymer chains in the ground state.

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