A Study of Excimer Emission in Solutions of Poly(9,9-dioctylfluorene) Using Electrogenerated Chemiluminescence

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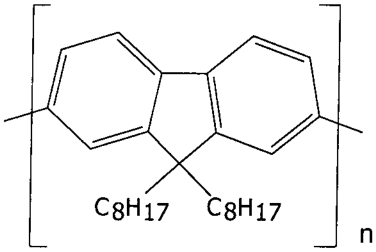
We report electrochemical studies and the observation of excimer emission from the conjugated polymer poly(9,9-dioctylfluorene) (PDOF) in benzene−MeCN solutions during electrogenerated chemiluminescence (ECL). The ECL emission spectrum resulting from the annihilation reaction between PDOF radical ions is characterized by two bands, one at 438 nm and a broad band centered at 610 nm. The ECL emission at shorter wavelengths is assigned to intrapolymer emission of PDOF, while the emission at longer wavelengths arises from the excited-state complex of the polymer formed in the radical annihilation reaction. The relative excimer emission from PDOF (the ratio of excimer ECL emission to intrapolymer emission) depends on polymer concentration.

Introduction

In this work we report an electrogenerated chemiluminescence (ECL) study of dissolved polymeric species that are also of interest in solid electroluminescent (EL) devices. We describe electrogeneration of radical ions and demonstrate that the observed emission is consistent with excimer formation via the reaction of polymer radical cation with the corresponding polymer radical anion in the benzene−MeCN solution. The conjugated polymer poly(9,9-dioctylfluorene) (PDOF) is of particular interest because films of this polymer show high EL quantum yields along with blue light emission and superior chemical stability, making it an excellent candidate for a wide variety of electrooptic devices.[1−4] In addition, one can synthetically alter the substituent at the 9-position to change the fluorescence properties as a result of substituent-induced interpolymer effects.[5] Polyfluorene belongs to the family of “stiff-chain” polymers,[6] and in combination with its flexible alkyl substituents, its stiff polymer backbone affords well-characterized nematic liquid crystalline behavior.[7] A recently demonstrated processing advantage of stiff-chain liquid crystalline polymers is that they can be ordered over large areas for use in polarizing light-emitting devices.[8,9] The ability to obtain highly polarizing polymer films depends on the nature of interpolymer interactions, both physical and photophysical. Interpolymer complexes can dramatically alter device performance through changes in fluorescence quantum yield and spectral distribution, but the mechanism of their formation is poorly understood.[10−13]



Greater ordering as a result of stiff chain interpolymer interactions such as aggregation and excimer formation can lead to a decrease in fluorescence quantum yield that is disadvantageous in EL devices. In conjugated polymers, excimers form by a reaction between two similar chromophores (eq 1), one in the excited state and one in the ground state where the energy of the resulting interpolymer complex is lower than that of the individual chromophores:

$$P + P^{*} \rightarrow P_2^{*} \qquad (1)$$

Excimer formation decreases the polymer fluorescence quantum yield because of a slower radiative rate and a greater number of nonradiative decay pathways, and it increases the contribution of lower energy fluorescence as compared to the isolated polymer or intramolecular fluorescence.[14] Therefore, there have been a number of investigations to characterize excimers in polyfluorene and to minimize their formation in solid-state devices.[15−17]

Another form of interpolymer interaction takes place in the ground state via aggregate formation in which aggregates can be directly excited. Excitation of these aggregates can also contribute to fluorescence which is red-shifted from the intrapolymer emission (eq 2):

$$P + P \rightarrow P_2 \xrightarrow{h\nu} P_2^{*} \qquad (2)$$

In contrast to the excimer, the aggregate involves a ground-state association and is characterized by broadening of the absorption spectrum and by distinct absorption bands. Previous studies of alkyl-substituted polyfluorene solutions and films have shown both aggregate[16] and excimer[2,15,17] formation, where the relative contribution depends on the choice of substituent,[5] film spinning and annealing conditions,[16] and polymer defects (oxidation sites that enhance excimer formation).[17] Due to the complexity of polymer films with a wide variety of intra- and interpolymer conformations and both ground- and excited-state

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associations, an absolute distinction between aggregate and excimer fluorescence cannot be presumed.

In this study, we look at the electrogenerated chemiluminiscence (ECL) of PDOF in solution and report enhanced interpolymer emission of this polymer produced via ECL for the first time under these conditions as compared to photoexcitation. The study of excimer in polyfluorene has been limited to that occurring in thin films via photoexcitation where there is inherently greater interpolymer interaction. Interpolymer emission is not readily observed in polyfluorene solutions. ECL is a useful tool for the study of excited-state complexes because they are generated in solution by an annihilation electron-transfer reaction between oxidized and reduced species produced by pulsing an electrode potential:

$$P^{\bullet +} + P^{\bullet -} \rightarrow P_2^{*} \qquad (3)$$

$$P^{\bullet +} + P^{\bullet -} \rightarrow P^{*} + P \qquad (4)$$

Therefore, the two species are in close proximity in the vicinity of the electrode which facilitates excimer formation. Previous studies performed using ECL have demonstrated excimer formation of some aromatic hydrocarbons in solution even with higher dielectric constant solvents in which photogeneration of excimers is not observed.[18−21]

Because the energy of the excimer complex depends on the polymer's ability to adopt a conformation favorable for interpolymer interaction, the energy of the excimer can be used as a gauge of effective $\pi-\pi$ interactions between polymers. The use of ECL to study excimers in solution provides essential information on the difference between excimer emission in solution versus that in the solid state.

Experimental Section

PDOF was synthesized by a Ni(0) mediated aryl halide coupling reaction.[22] Degree of polymerization ($N = 14$), molecular weight (5800), and polydispersity (1.6) were determined using GPC with Water's Styragell columns and polystyrene standards.

Absorption and fluorescence spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer and a Photon Technology Instruments fluorimeter (Quantum Master C-60/2000), respectively. All fluorescence measurements were recorded in a 1 mm path length cell to obtain spectra free from self-absorption effects in the concentration range of 5×10^{-7} to 6×10^{-5} M.

Tetra-*n*-butylammonium hexafluorophosphate (SACHEM, Inc.; Austin, TX), $TBAPF_6$, was recrystallized from $EtOH/H_2O$ 4:1 three times and dried at 100 °C before use. Benzene (Aldrich, ACS grade) and MeCN (Burdick and Jackson, UV grade) were used as received after being transported unopened into an inert atmosphere drybox (Vacuum Atmospheres Corp.). The electrochemical and ECL solutions were prepared in a drybox and were sealed in airtight vessels (diameter, 1.5 cm) and removed from the box for measurements.

Cyclic voltammograms were recorded on a computer-controlled CH Instruments potentiostat (Model 600A). A platinum electrode disk (diameter, 2 mm) was used as working electrode, a platinum wire as counter electrode, and a silver wire as quasi-reference electrode (QRE). All potentials are reported versus a saturated calomel electrode (SCE) with the QRE calibrated by addition of ferrocene as standard ($E°_{Fc/Fc^+} = 0.424$ V vs SCE).

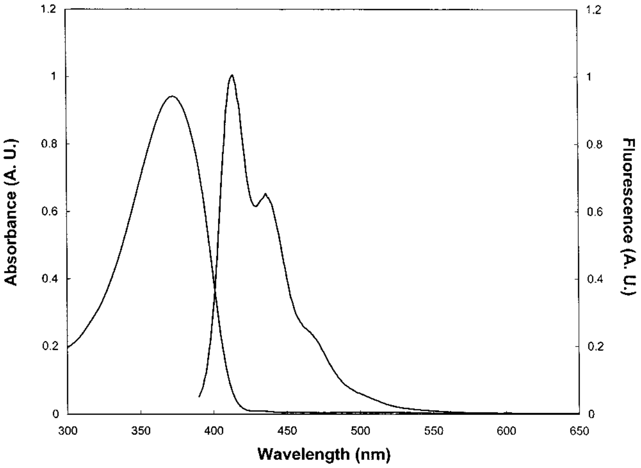


Figure 1. Absorption and fluorescence spectra of 3.3×10^{-5} M PDOF solution in benzene:MeCN 9:1 taken with a 1 mm cuvette under atmospheric conditions. $\lambda_{exc} = 380$ nm.

ECL measurements were performed as previously reported using a charge-coupled device (CCD) camera (Photometrics, Tucson, AZ) cooled to −115 °C.[23] ECL solutions were similar in composition to those used for cyclic voltammetry as described in the following results.

Results and Discussion

Photophysical Characterization. The photophysical characteristics of PDOF solutions are reported in a mixed solvent system (benzene:MeCN in a volume ratio 9:1). The absorption spectrum of PDOF in dilute solution shows a maximum at 373 nm, with an onset of absorption at approximately 420 nm (Figure 1, left side). The shape and width of this band remain constant over a wide range of concentrations (from 5×10^{-7} to 6×10^{-5} M). The absence of broadening at higher concentrations suggests a minimal contribution from ground-state aggregates that have been reported as the cause of broadening in absorption spectra of similar stiff-chain polymers in films.[13] However, we did observe a very small absorption band centered at 437 nm (barely perceptible in Figure 1) which increased slightly in going from 1.5×10^{-5} to 6×10^{-5} M solutions. This 437 nm band has been reported as indicating aggregate formation in polyfluorene in poorly solvating solutions and in the solid state.[16] If the extinction coefficient of the aggregate is equal to or greater than that of the isolated polymer species, the aggregate makes only a small contribution (<1%) to the overall absorption of PDOF. Thus, we should have a similar, minor contribution from any aggregate at similar solution concentrations in experiments on the electrochemistry and ECL of PDOF.

A typical fluorescence spectrum of a polyfluorene solution is shown in Figure 1 (right side). The emission spectrum shows well-resolved vibronic structure, with peaks at 418 and 438 nm and a shoulder around 460 nm. The shape of the fluorescence spectra remained constant over a range of concentrations (from 5×10^{-7} to 6×10^{-5} M) with no increase in low energy emission. We can therefore assign the fluorescence spectrum of the dilute solution of PDOF to that of the isolated polymer, which we will refer to as intrapolymer emission.

The photophysical characteristics of the monomer unit, 9,9-dioctylfluorene (DOF), have been studied under the same experimental conditions as PDOF. The absorption spectrum of DOF in dilute solution shows a broad band with maximum at 260 nm and two sharp bands at 292 and 304 nm, with the onset of absorption at approximately 315 nm. The fluorescence

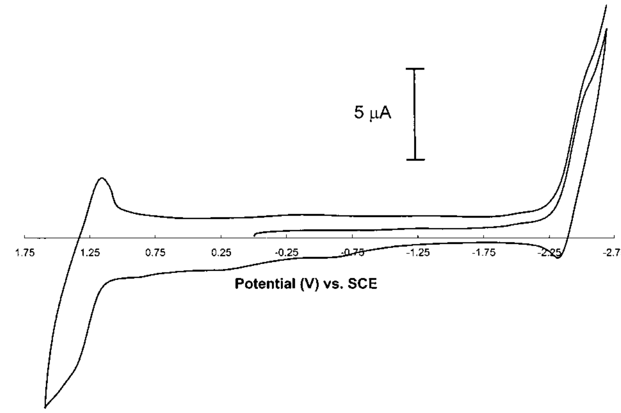


Figure 2. Cyclic voltammogram of 6 × 10^{-5} M polyfluorene in 9:1 benzene:CH_3CN 9:1 containing 0.1 M $TBAPF_6$ as an electrolyte with a scan rate of 0.5 V/s.

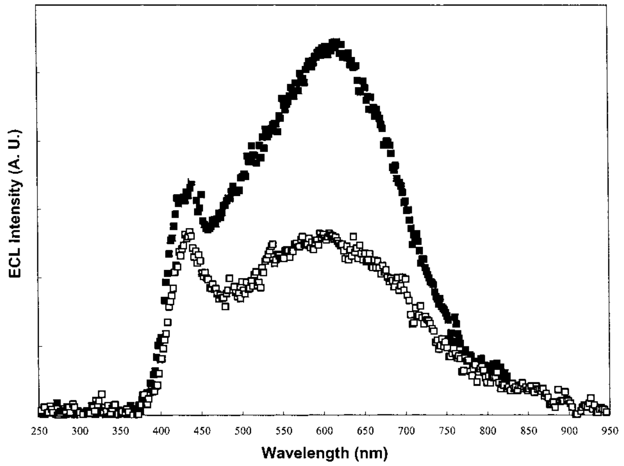


Figure 3. Electrogenerated chemiluminescence emission spectra of 3.3 × 10^{-5} M (open squares) and 6 × 10^{-5} M (filled squares) PDOF solutions in benzene:acetonitrile 9:1 containing 0.1 M $TBAPF_6$ as an electrolyte. All spectra were obtained with an integration time of 10 min.

spectrum shows a peak at 309 nm and broad band around 460 nm. The absorption and emission spectrum of the PDOF shows a strong red shift as compared with the monomer spectra, as expected, because of the extended conjugation of the polymer.

Electrochemistry and ECL Measurements. Cyclic voltammograms of PDOF in a mixed solvent system (benzene:MeCN 9:1) with 0.1 M $TBAPF_6$ as the supporting electrolyte and at concentrations ranging from 2 × 10^{-5} to 6 × 10^{-5} M were recorded at different scan rates. At scan rates above 0.2 V/s, the polymer exhibited fairly well-defined waves with some chemical reversibility for reduction and oxidation, with E_p at −2.45 and 1.35 V vs SCE, respectively, as seen in Figure 2. At scan rates below 0.2 V/s, the anodic peak following scan reversal at the reduction wave became smaller, suggesting that the radical anion undergoes slow decomposition ($k \approx 5$ s^{-1}). Note that the proximity of the reduction wave to background reduction makes precise measurements difficult. Nevertheless, the radical anion was sufficiently stable for ECL generation. The radical cation was more stable than the radical anion and the reversibility of the PDOF oxidation wave varied little with scan rate. Extended electrochemical cycling caused deposition of insoluble products on the electrode surface.

The ECL spectra were obtained by the annihilation reaction of a radical anion and radical cation formed by first stepping to a potential corresponding to the reduction of PDOF, ca. −2.5 V vs SCE, followed by a step to a potential corresponding to the oxidation, ca. 1.4 V vs SCE with 100 ms steps. Radical anions and radical cations annihilate to form an excited state, reactions 3 and 4, whose subsequent emission signal was integrated for 10 min. The intensity was weak, much weaker than that seen with aromatic hydrocarbons, but the ECL spectra could be obtained using the CCD. Figure 3 shows ECL emission spectra obtained from 3 ×10^{-5} M (open squares) and 6 × 10^{-5} M (full squares) polyfluorene in a 9:1 benzene:MeCN solution containing 0.1 M $TBAPF_6$ as an electrolyte.

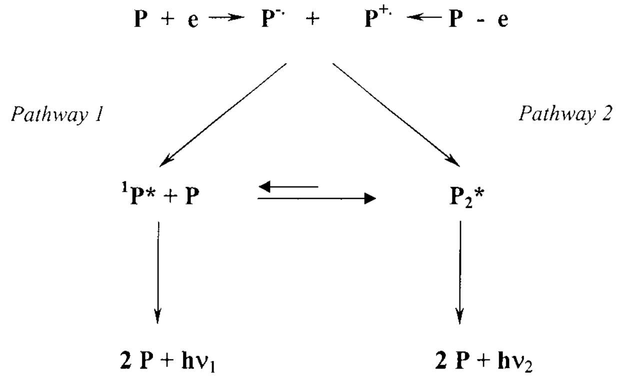
In all cases, the ECL emission spectra showed two maxima, one at 438 nm and a broad band centered at 610 nm (Figure 3). The ECL emission at shorter wavelengths is similar to the photoexcited fluorescence spectrum of the same PDOF solution (Figure 1). If self-absorption of the first vibronic peak is taken into account, the ECL emission at 438 nm directly corresponds to the second vibronic peak observed in the photoexcited fluorescence spectra of the PDOF solution. Therefore some ECL emission represents intrapolymer emission (reaction 4). However, in relation to the peak at 438 nm, the ECL spectra showed a much greater contribution from emission at 610 nm as compared to the photoexcited fluorescence spectra of the same solution which showed essentially no emission beyond 550 nm. This broad and featureless low energy band is characteristic of the excited-state excimer species, reaction 3, which is favored under the experimental conditions of ECL.

The ECL spectra in Figure 3 also depended strongly on the polymer concentration in solution. The relative excimer emission from PDOF (the ratio of the excimer ECL emission to the intrapolymer emission) strongly increased with concentration. This concentration dependence of the low energy emission suggests an interpolymer interaction. At 3.3 × 10^{-5} M, the ECL spectrum showed considerably more excimer than intrapolymer emission as compared with the photoluminescence spectrum, so we can infer that the rate of excimer formation must compete efficiently with the production of singlet excited state. When the concentration increased to 6 × 10^{-5} M, the extent of excimer formation was even larger and the ratio of excimer to intrapolymer emission went from close to unity at 3.3 × 10^{-5} M to 1.7 at this concentration.

Cyclic voltammetry and ECL experiments were also carried out with the monomer 9,9-dioctylfluorene (DOF) under the same experimental conditions. In the cyclic voltammetry experiments, a reduction peak was observed at −2.55 V in the cathodic scan. On the first anodic scan, no oxidation of DOF is observed before a large irreversible process at 1.6 V, similar to other 9,9-substituted fluorene compounds. However, the second cycle of CV showed two broad waves around 1.0 and 1.4 V after a cathodic scan. In this case, the peak potentials of DOF are similar to those observed for the polymer, showing that the anodic scan produces a polymeric film on the electrode. The ECL experiments showed no emission due to the formation of the polymer film on the electrode surface when the potential was pulsed between a potential corresponding to the reduction of DOF, followed by a potential corresponding to the oxidation of the monomer unit.

The ECL emission of PDOF under our experimental conditions can be described as the combination of different processes as shown in Scheme 1. The observed ECL emission spectrum implies that the cation−anion radical annihilation reaction undergoes two different reaction pathways. Pathway 1 produces the singlet excited state of the polymer during the annihilation reaction between the electrogenerated oxidized and reduced PDOF species. In this system, the enthalpy of the radical ion reaction calculated from the peak potentials, using eq 5,[24] is

SCHEME 1



3.7 eV, a value significantly greater than the singlet energies of PDOF, calculated from the maximum of the fluorescence spectrum (about 3.1 eV). Thus, the singlet excited state of PDOF can be reached in the electron-transfer reaction.

$$-\Delta H^\circ = E_{pa} - E_{pc} - 0.1\ \text{eV} \qquad (5)$$

where ΔH° is the annhilation reaction enthalpy and E_{pa} and E_{pc} are the peak potentials corresponding to oxidation and reduction processes. After its formation, the PDOF excited-state undergoes radiative decay to the ground state, which is responsible for the intrapolymer ECL signal at shorter wavelengths.

However, pathway 2 in Scheme 1 leads to direct formation of excimers by ionic recombination, since the radical ions must be in close proximity before the electron transfer reaction. Therefore, excimer formation, which is particularly favorable in stiff-chain polymers such as PDOF, is enhanced by the fact that when the excited state is formed, a second polyfluorene species is in the immediate vicinity. The radiative decay of the complex from the excited to the ground state produces the broad and featureless band at 610 nm. The occurrence of this reaction is supported by the very high intensity of the excimer band relative to that of intrapolymer emission, and the concentration dependence of the relative excimer emission which implies a bimolecular type reaction involved in the generation of the low energy emission. The lack of appreciable excimer emission during photoexcitation indicates that, at these bulk concentrations, the rate of reaction of the excited state during its lifetime (520 ps)[5] with ground state to produce excimers is negligible. Thus the large ECL excimer emission originates from a much higher "effective concentration" in the immediate vicinity of the excited state.

Conclusions

We have demonstrated that excimer emission can take place in PDOF solutions when generated via ECL, the ratio of which is dependent on the concentration of the polymer in solution. The excimer emission occurs at lower energy than the photogenerated excimer observed in films (data not shown), most likely because of reduced steric hindrance for planarization in solution.

In future studies we will compare solution and solid-state ECL spectra of dialkylpolyfluorenes of low versus high molecular weights. We also plan to examine the ECL behavior of a series of polyfluorenes with substituents of varying lengths in order to determine the effect of substituent length on the degree of interpolymer interaction.

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