

Long-Lived Exciplex Formation and Delayed Exciton Emission in Bulk Heterojunction Blends of Silole Derivative and Polyfluorene Copolymer: The Role of Morphology on Exciplex Formation and Charge Separation

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Long-lived exciplex emission is observed in blend films of poly[9,9-dioctylfluorene-*co*-*N*-(4-methoxyphenyl)diphenylamine] (TFMO) and the soluble silole derivative 2,5-bis-(2,2-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene (PyPySPyPy). The exciplex is characterized by a long-lived (~40–90 ns) component in both the photoluminescence and electroluminescence spectra, which is red-shifted relative to the emission of the pristine materials. In addition to exciplex emission, delayed fluorescence from the TFMO singlet state is observed and is attributed to exciton regeneration through the interfacial exciplex state. Comparing blend films made using chlorobenzene and *p*-xylene solvents, we find that exciplex lifetime and exciton regeneration in the blend film are sensitive to the choice of solvent and the resulting morphology of the blend film. The exciplex emissive lifetime can be correlated to changes in photoluminescence quenching and efficiency of light-emitting diodes.

Introduction

An exciplex is defined as an excited-state complex formed between two chemically dissimilar molecules involving a neutral acceptor and excited donor, or vice versa.¹ Exciplex formation has been observed in several polymer–polymer and polymer–small molecule blend films.^{2–5} It is most clearly indicated by a broad, long-lived, temperature-dependent emission feature in the blend film electroluminescence and photoluminescence spectra that is red-shifted with respect to the emission of the individual components^{3,6,7} and by delayed excitonic emission resulting from the regeneration of singlet excitons by the exciplex state.

Exciplex states have stimulated much recent interest, both at a fundamental level for their role in the key processes of interfacial charge recombination and charge separation and for their potential use in optoelectronic applications. Efficient exciplex emission has been obtained in polymer:small molecule organic light-emitting diode (OLED) structures and polymer:polymer OLED structures, resulting in luminous efficacies of up to 7⁵ and 19 lm/W,² respectively. The broad, red-shifted nature of exciplex emission, together with the capability to tune the emission wavelength by varying the energy levels of the donor and acceptor molecules,⁸ means that exciplex emission can be exploited to make efficient white light-emitting devices.⁹ When coupled with strong emission from the donor and acceptor components of the blend, exciplex emission can result in broader emissive coverage of the visible spectrum than available from the component materials alone, and so improve the efficiency of white OLEDs. In organic solar cells, the role of the exciplex

is not yet clear, but several studies suggest that the exciplex acts as a loss pathway, reducing the efficiency of charge separation.^{2,10,11} Other studies^{12,13} have reported evidence of an exciplex-like state that they refer to as a charge transfer (CT) exciton but which differs from an exciplex in that it possesses a ground-state counterpart. The different roles of charge transfer excited states, such as exciplexes and charge transfer excitons in charge separation are attracting a considerable amount of interest currently.

Recently, quantum chemical modeling has been used to explain exciplex formation between two dissimilar oligomers in terms of the relative position and orientation of specific moieties on the two molecules.¹⁴ That study shows that the likelihood of exciplex formation relative to singlet exciton or polaron pair formation depends on several factors, such as ionization potential of the polymers and the orientation and position of the chains with respect to each other.¹⁴ The important influence on exciplex formation of the relative position and orientation of the participating molecules indicates that modifications in the nanoscale morphology of the donor–acceptor interface, resulting, for example, from variations in thin film processing, may influence the characteristics of the exciplex state. In this context, many studies have shown that the performance of organic solar cells and OLEDs is critically influenced by the choice of solvent for film fabrication^{15–17} as well as by other film-processing parameters such as annealing time and annealing temperature, all of which influence the morphology of the donor:acceptor blend film. Some recent studies of light emission from polymer–polymer blends^{10,11} have shown that processing conditions do have an effect on exciplex formation and the resulting photovoltaic performance of devices made using these blends. However, to the authors' knowledge, the effect of blend film morphology on exciplex formation in polymer–small molecule blends has not yet been studied in

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detail, and the influence of solvent choice on exciplex emission and dynamics has yet to be explored.

In this paper, we investigate how the photophysical properties of exciplex states depend upon morphological changes brought about by variation of the solvent used in blend film fabrication. We focus on blend films of a fluorene-triarylamine polymer, poly[9,9-dioctylfluorene-*co*-*N*-(4-methoxy-phenyl)diphenylamine] (TFMO), and a soluble silole derivative, 2,5-bis-(2,2-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene (PyPySPyPy). We show that exciplex formation occurs in this system, and by using different solvents, chlorobenzene and *p*-xylene, we find that exciplex lifetime and exciton regeneration are solvent dependent and are correlated to the morphology of the blend films. We propose that variations in film morphology play an important role in interfacial processes and electroluminescence properties in polymer:small molecule blend films and may have significant implications for the design of bulk heterojunction organic electronic devices.

Experimental Section

Equal weights of 2,5-bis-(2,2-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene (silole) (PyPySPyPy) and poly[9,9-dioctylfluorene-*co*-*N*-(4-methoxy-phenyl)diphenylamine] (TFMO) (Sumitomo Chemical) were blended in solution and spin-coated to form blend films containing 50% PyPySPyPy by weight. The silole derivative (PyPySPyPy) was synthesized according to previous reports.^{18,19} All films used for this experiment were cast from 20 mg/mL solutions using chlorobenzene (CB) or *p*-xylene (PX) in air in a clean room environment. For photoluminescence (PL) and atomic force microscopy (AFM) measurements, the films were spin-coated on Spectrosil B quartz substrates (Kaypul Optics Ltd.) which were cleaned in an ultrasonic bath of acetone for 10 min followed by a bath of isopropanol for 10 min and then were dried in a flow of air. Spin speeds of 1500 rpm (30 s) resulted in blend films with thicknesses of approximately 90 nm. Steady state photoluminescence measurements were carried out using a Fluoromax-3 spectrometer (Jobin-Yvon). Time-resolved PL experiments were carried out using excitation from a 409 nm, 70 ps pulse width, 1 MHz repetition rate pulsed laser (Hamamatsu stabilized picosecond light pulser model number C4725) and detection with a streak scope setup (Hamamatsu Streak Scope model number C4334), in order to measure the lifetime of emissive species.

Light-emitting diodes (LEDs) were fabricated using indium tin oxide (ITO) (25 Ω/cm^2) coated glass substrates that were cleaned in an ultrasonic bath of acetone and isopropanol and dried as above. Layers of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) aqueous dispersion (PEDOT:PSS) (Baytron P VP CH 8000 grade, HC Stark) were spin-coated at 2000 rpm for 60 s onto the ITO substrates and were soft-baked in air at 140 $^{\circ}\text{C}$ for 15 min resulting in films with thicknesses of 140 nm. The active layers of the LEDs were deposited via spin-coating at 1500 rpm for 30 s on top of the PEDOT:PSS layer, and the structure was subsequently soft-baked at 50 $^{\circ}\text{C}$ for 30 min resulting in films that were approximately 90 nm. Finally, calcium/aluminum electrodes were deposited via thermal evaporation at 3×10^{-6} mbar to a thickness of ~ 20 and ~ 100 nm for calcium and aluminum, respectively, defining six devices with areas of 4.2 mm². The current, voltage, and luminance values were measured using a Keithley (2410 1100 V) source-measure unit and a luminance meter (Topcon BM-9).

Electrochemical measurements of PyPySPyPy (2 mM) were performed using 0.1 M tetrabutylammonium perchlorate (TBAP)

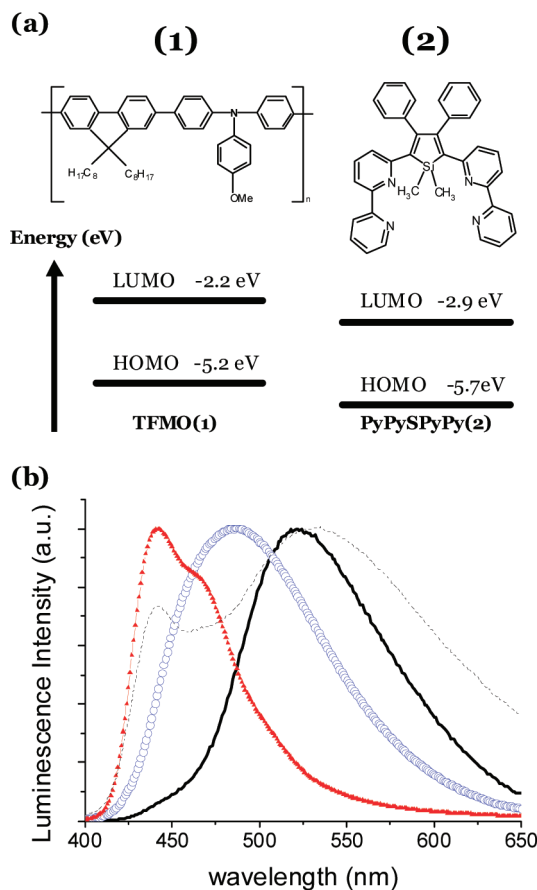


Figure 1. (a) Chemical structures and HOMO and LUMO energies of TFMO (1) and PyPySPyPy (2). (b) Normalized, steady state photoluminescence spectra of pristine TFMO (triangles), pristine PyPySPyPy (open circles), and TFMO:PyPySPyPy (50 wt % PyPySPyPy) films (dashed line) cast from chlorobenzene solutions compared with the normalized electroluminescence (EL) spectrum of a TFMO:PyPySPyPy (50 wt % PyPySPyPy) light-emitting diode cast from chlorobenzene (solid line). The peak of the EL spectrum is red-shifted by 90 and 50 nm from the peaks of the TFMO and PyPySPyPy emission, respectively.

as the supporting electrolyte in a 1:1 by volume dichloromethane/acetonitrile solution. The oxidation potential of PyPySPyPy was referenced to an Ag/AgNO₃ electrode using a potentiostat at a scan speed of 100 mV/s. It is well documented that the highest occupied molecular orbital (HOMO) of ferrocene is -4.8 eV below vacuum level,²⁰ and therefore, the HOMO of the PyPySPyPy is calculated using the relationship $E_{\text{HOMO,PyPySPyPy}} = -e(E_{\text{ox,PyPySPyPy}} - E_{\text{ox,Fc/Fc}^+}) - 4.8$ eV, where $E_{\text{HOMO,PyPySPyPy}}$ is the HOMO energy of the PyPySPyPy in electron volts, $E_{\text{ox,PyPySPyPy}}$ is the onset of oxidation of the PyPySPyPy versus an Ag/AgNO₃ electrode, and $E_{\text{ox,Fc/Fc}^+}$ is the onset of oxidation of ferrocene versus an Ag/AgNO₃ electrode.

Results and Discussion

The chemical structures of the materials used in this study are shown in Figure 1a. Normalized photoluminescence (PL) spectra of the pristine materials and the TFMO:PyPySPyPy (50 wt % PyPySPyPy) blend film are shown in Figure 1b along with the normalized electroluminescence (EL) of TFMO:PyPySPyPy (50 wt % PyPySPyPy) light-emitting diodes. Henceforth TFMO:PyPySPyPy refers to blends containing 50% of each component by weight.

The broad, red-shifted emission in the photoluminescence (PL) and electroluminescence (EL) spectra of the TFMO:

PyPySPyPy samples relative to the component materials indicates the formation of an exciplex state at the interface between the donor and acceptor components. In order to eliminate silole excimer emission as the origin of the red-shifted emission, absorption, PL, and time-resolved PL measurements were performed on polystyrene:silole blend films containing 5, 50, and 100% silole by weight. The measurements showed that while increasing silole concentration in the blend films led to a small red shift in the emission, neither the red shift nor the lifetime of the silole emission could explain the emission in the polyfluorene:silole blend films. (See the Supporting Information section for details.) Exciplex formation has previously been recognized from red-shifted emission in polymer:polymer blend films^{3,6} and small molecule bilayer films.⁷

The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energies of TFMO are reported as -2.2 and -5.2 eV, respectively, from cyclic voltammetry measurements.²¹ In this work, we find using cyclic voltammetry measurements that the HOMO energy of PyPySPyPy is -5.7 eV. The optical gap of PyPySPyPy is 2.8 eV, as measured from the onset wavelength of the optical absorption (and in agreement with literature values)⁵ and sets a lower limit to the LUMO energy of PyPySPyPy at -2.9 eV. Incorporating the exciton binding energy in this calculation would result in a less negative estimate of the LUMO level. As seen in Figure 1b, the EL spectrum of the TFMO:PyPySPyPy LED (solid line) and the PL spectrum of the TFMO:PyPySPyPy blend film (dashed line) are red-shifted by approximately 50 nm from the pristine silole emission (open circles) and 90 nm from the pristine TFMO emission (triangles). The red-shifted EL emission at 530 nm (2.34 eV) is attributed to emission from an exciplex in the device. The energy of exciplex emission is approximately the same for devices made from chlorobenzene (CB) and *p*-xylene (PX) solutions. It should be noted that the boiling points of these solvents are 132 and 138 °C, respectively. From previous studies which investigated the dependence of exciplex emission energy on the HOMO and LUMO levels of the component materials, it was shown empirically that the energy of exciplex emission ($h\nu_{\text{exciplex}}$) can be described using the following relation⁸

$$h\nu_{\text{exciplex}} \sim |\text{HOMO}_D| - |\text{LUMO}_A| - 0.15 \text{ eV} \quad (1)$$

where HOMO_D is the magnitude of the donor HOMO energy and LUMO_A is the magnitude of the acceptor LUMO energy. From this relationship, the expected energy of the exciplex emission for TFMO:PyPySPyPy films would be 2.15 eV (577 nm) given the measured values of the HOMO and LUMO energies stated above and summarized in Figure 1. This is approximately 0.2 eV less than the experimentally observed exciplex emission energy. This difference can readily be attributed to the exciton binding energy in the silole component which was not incorporated into the determination of the LUMO level of the silole. Therefore, the LUMO of the silole is concluded to lie above -2.9 eV, and the observed exciplex emission energy is in good agreement with the energy level values calculated from eq 1.

The wavelength of exciplex emission is almost identical for blend films made from CB and PX solvents (see inset to Figure 2), and, thus, the main radiative decay pathway in these devices is assigned solely to exciplex decay. However, the amount of photoluminescence quenching in blend films cast from different solvents and the performance of LEDs made from films cast from different solvents is different. PL quenching measurements show that the emission from films spin-coated from CB is

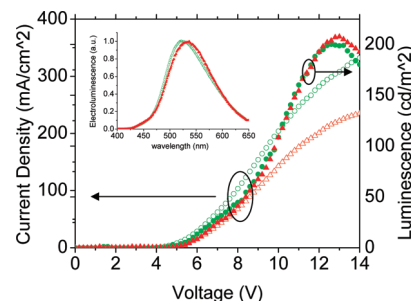


Figure 2. Current density and luminescence intensity for TFMO:PyPySPyPy (50 wt % PyPySPyPy) light-emitting diodes cast from chlorobenzene (circles) and *p*-xylene (triangles) as a function of applied voltage. While the maximum luminescence intensity is the same for both devices, the current density required to achieve the same brightness in devices made using chlorobenzene is significantly larger than that required for devices made using *p*-xylene.

quenched by 98% in TFMO:PyPySPyPy blends compared to pristine TFMO emission, while the PL from blend films spin-coated from PX is quenched by only 90%.

Additionally, LED performance is different for devices made from films cast from different solvents, as shown in Figure 2. While devices made from both solvents achieve a similar maximum brightness (cd/m^2) at a given applied voltage, the device made using CB requires a significantly larger current to achieve the same amount of light emission as that made using PX. This trend was repeated in several device sets. Thus, more charges must be injected into the blend films made using CB to achieve a given amount of light emission than into the PX-based device. Either the probability of exciplex formation in the blend films or the charge injection efficiency in the devices must be different to cause such a difference in LED performance. Although efforts were made to keep the injection conditions the same for the LEDs made using the different solvents, by using identical blend ratios and identical electrodes (Ca/Al and ITO/PEDOT:PSS), it is still possible that an effect of solvent on the direction or degree of phase segregation in the blend film could have altered the composition close to the electrodes and thereby altered the injection efficiency. An alternative explanation is that differences in morphology lead to differences in exciplex formation yield in the blend films. Therefore, in order to compare potential differences in exciplex characteristics in films which were prepared using different solvents, time-resolved PL measurements were conducted.

Two observables are of importance for PL lifetime studies of organic blends which form exciplex states. First, the lifetime of the exciplex state itself must be determined for the blend materials studied. Second, the photoluminescence spectrum of the blend film must be averaged over times long after the singlet emission of both component materials is finished in order to determine whether any delayed singlet emission occurs in the blend film.³ From our measurements, TFMO singlet excitons have a radiative lifetime of 0.6 ns (± 0.02 ns), and PyPySPyPy singlet excitons have a lifetime of 2.7 ns (± 0.2 ns). (The PyPySPyPy emission was measured from a polystyrene:PyPySPyPy (5 wt % PyPySPyPy) blend film which was cast from chlorobenzene solution.) Emission from blend films of TFMO:PyPySPyPy (50 wt % PyPySPyPy) shows multiphasic decays with a pronounced slow phase on the 10 – 100 ns time scale. When integrated only over exciplex emission wavelengths (500 – 570 nm) the slow phase lifetimes were found to be 65 ns (± 5 ns) and 95 ns (± 5 ns) for films cast from PX and CB, respectively. The lifetime of the red-shifted part of the emission is thus very much longer than the singlet emission lifetime for

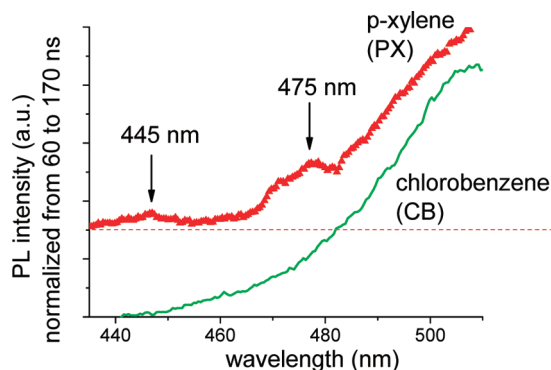


Figure 3. Spectrum of delayed photoluminescence intensity from TFMO:PyPySPyPy (50 wt % PyPySPyPy) blend films integrated over the period from 60 to 170 ns. Emission peaks of the TFMO can be distinguished in the PX film spectrum (triangles) at 445 and 475 nm. This emission is absent in the film made from CB (solid line). The spectra are offset for clarity.

either component and is similar to exciplex emission lifetimes reported for other systems.^{2,11}

The time-resolved photoluminescence spectra averaged over the period from 60 to 170 ns of the TFMO:PyPySPyPy blend films cast from different solvents are compared in Figure 3. The spectrum of TFMO:PyPySPyPy film cast from PX shows emission features at energies characteristic of the singlet state of TFMO at 445 and 475 nm. These are assigned to delayed emission from the TFMO singlet. No such delayed TFMO singlet emission is visible in spectra from films of the same composition cast from CB solutions. Since this delayed emission of the TFMO singlet state occurs long after direct TFMO emission is expected (~ 0.6 ns), this suggests that recycling of the TFMO singlet exciton occurs through the interfacial exciplex state in films made using PX.

Regeneration of the TFMO singlet exciton in the PX film was rather unexpected. TFMO is the electron-donating material in this organic blend film and has an optical gap that is 0.2 eV larger than the PyPySPyPy material. Thermodynamically, back transfer of the exciplex state would be expected to occur to the lower energy singlet exciton in the system, as has been seen in the literature.³ However, the emission from TFMO is clearly visible while regeneration of the silole exciton is not observed. (It should be noted that a weak emission from the silole exciton could be present but not visible on account of the overlap between the exciplex and silole exciton spectra.) The observation of the TFMO exciton suggests that the exciton regeneration process may not be governed purely by thermodynamics. Instead, the morphology of the film and of the molecular components may be involved in determining the exciton-recycling pathways in the film. For this reason, atomic force

TABLE 1: Summary of Observations for TFMO:PyPySPyPy (50 wt % PyPySPyPy) Blend Films Cast from *p*-Xylene (PX) and Chlorobenzene (CB) Solvents

film property	<i>p</i> -xylene (PX) film	chlorobenzene (CB) film
charge separation (PL quenching %)	90%	99%
LED performance	~ 200 cd/m ² , 250 mA/cm ²	~ 200 cd/m ² , 350 mA/cm ²
exciplex emission lifetime	65 ns \pm 5 ns	90 ns \pm 5 ns
TFMO regeneration	yes	no
morphology	aggregate formation	smooth films

microscopy (AFM) measurements were performed to compare the surface morphologies of the TFMO:PyPySPyPy blend films cast from CB and PX. The results are shown in Figure 4.

The surface morphologies of films cast from CB and PX are clearly different. The PX film, Figure 4b, shows circular aggregates on the surface of the film, suggesting phase separation of the components. The CB film, on the other hand, exhibits a more intimate mixing of the donor and acceptor materials.

Table 1 summarizes the results for TFMO:PyPySPyPy blend films cast from PX and CB. The data show that as PL quenching increases, so does the lifetime of the slow exciplex emission phase. Additionally, as PL quenching increases, LED efficiency is decreased. We now draw some conclusions about the function of the exciplex state and how it influences charge separation and recombination.

First, we note that exciton recycling is observed in blend films of TFMO:PyPySPyPy cast from PX but is not observed in TFMO:PyPySPyPy films cast from CB. This may be due to the different morphology of the blend films which is shown schematically in Figure 5a and b for PX and CB, respectively. An exciplex at the donor–acceptor interface may evolve in several ways: it may decay radiatively, dissociate and form separate charges, or regenerate an exciton in either phase. A singlet exciton regenerated in this way may itself decay radiatively, or it may diffuse to a neighboring interface and become “retrapped” to reform an exciplex. The absence of delayed singlet exciton emission from films cast from CB indicates that either excitons are not regenerated efficiently or that the regenerated excitons are efficiently retrapped. This is shown schematically in Figure 5b. The extended exciplex lifetime that is observed in CB films suggests that retrapping is part of the explanation: retrapping repopulates the exciplex state and leads to a longer apparent exciplex lifetime. The small domain size in CB cast films and correspondingly large interfacial area would encourage exciton retrapping. In contrast, the larger domain size in films cast from PX leads to a lower probability of regenerated excitons being retrapped before they decay radiatively. As a result, the exciplex lifetime appears

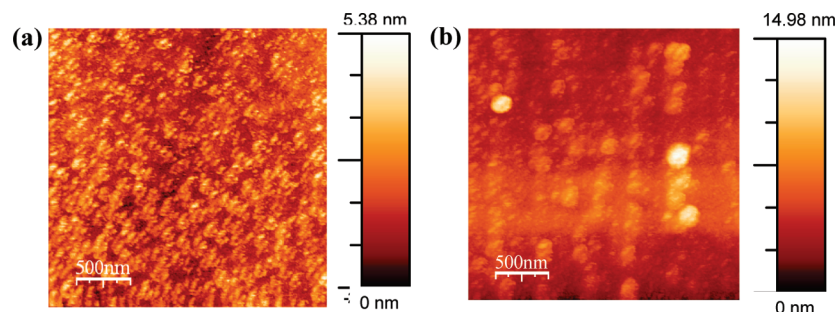


Figure 4. AFM images of TFMO:PyPySPyPy (50 wt % PyPySPyPy) films on quartz substrates cast from solutions of (a) chlorobenzene (CB) and (b) *p*-xylene (PX).

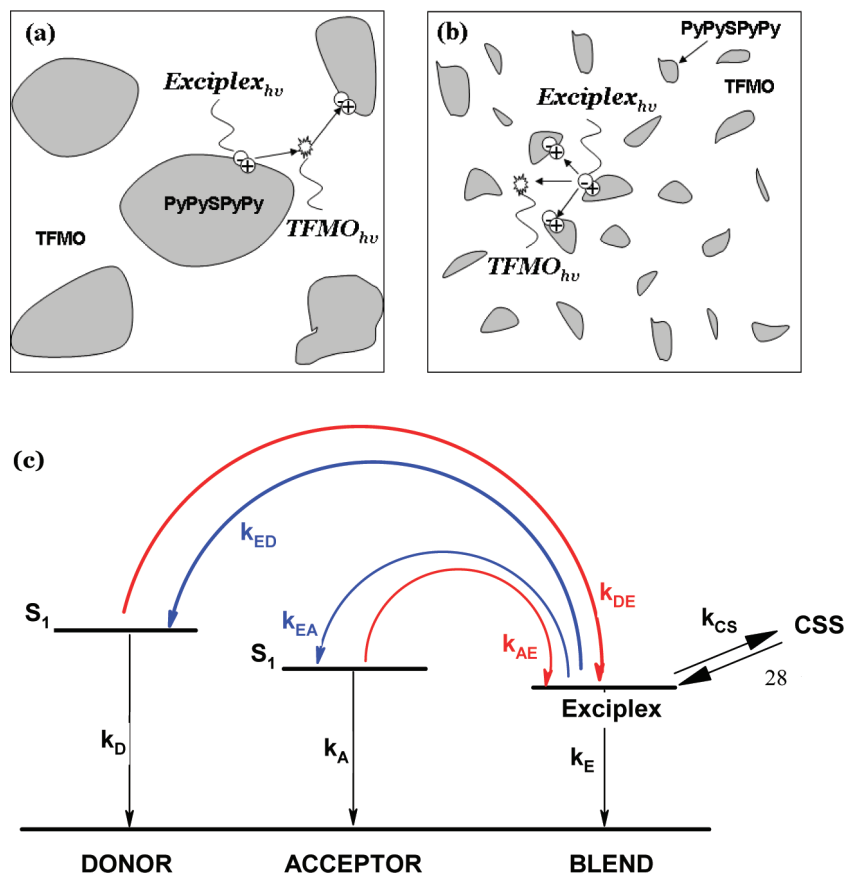


Figure 5. Diagram depicting the exciton-recycling process and the exciplex-retrapping process in TFMO:silole blend films. The figures on the right show schematic representations of the morphologies of (a) TFMO:PyPySPyPy cast from *p*-xylene (PX) and (b) TFMO:PyPySPyPy cast from chlorobenzene (CB).

shorter than in CB cast films, and the amount of exciton emission is larger (see Figure 5a). The reason why exciton recycling occurs primarily to TFMO, in spite of the larger thermodynamic barrier for exciton regeneration in the TFMO, is not clear. One possible explanation is that differences in the ease of exciton diffusion in the two materials may be responsible. An exciton regenerated in the polymer has the freedom to diffuse along the polymer chain and so escape the interface more easily while excitons regenerated in the amorphous silole domain may be quickly retrapped. Therefore, the net rate of exciton regeneration could be higher for TFMO excitons rather than silole excitons, despite the larger optical gap of TFMO.

The relative amounts of PL quenching can also be explained by the morphology of the film, (Figure 5a and b). It is well established that more intimate blend mixing tends to lead to more efficient PL quenching in type II donor–acceptor bulk heterojunction films. Since the PX films show a more phase-segregated surface morphology, the distance between PyPySPyPy domains is larger relative to the exciton diffusion lengths of the component materials in PX than in CB cast films. This means that excitons (whether initially generated or recycled) will have a higher probability of recombining within the TFMO matrix in PX than in CB cast films, with the result that the amount of PL quenching appears to be less.

LED emission efficiency can also be understood in terms of this morphology schematic. If exciplex states in PX films either emit or are regenerated into excitonic species, they allow for injected charges to recombine in “vacated” exciplex states at donor–acceptor interfaces. The exciplex states in CB films are often refilled by previous exciplex species, and therefore, LEDs made from these films require a larger amount of injected

charges to achieve the same amount of light emission from the interfacial exciplex state.

While the above discussion provides a pictorial description of the physical mechanisms involved in exciton recycling and exciplex retrapping, our discussion is given more weight by examining a simple numerical rate model of donor–acceptor systems which exhibit exciplex formation. We define a set of rate equations based on the mechanisms illustrated in Figure 5. Details are given in the Supporting Information.

Using this model, we find that the rate at which the excited state on the donor or acceptor is trapped into an exciplex state has very little influence on the rate of exciplex decay. However, as the rate of exciton recycling to the donor (k_{ED}) or acceptor (k_{EA}) increases, the exciplex emissive decay becomes much faster. This indicates that the pathway for exciton recycling is critical in determining the emissive exciplex lifetime, as we justified earlier by discussing the morphological differences between PX and CB films.

Thus, we show from both a morphological discussion and a kinetic model that exciton recycling is a critical process which influences the exciplex PL lifetime and LED device performance. The amount of exciton recycling is determined by the morphology of the film and is enhanced when there is more significant phase segregation, as there is in PX films, and is reduced when films are smooth, such as those cast from CB. This finding is further evidence that the size and nature of the interface between the donor and acceptor in bulk heterojunction blend films influences interfacial charge transfer processes. Therefore, controlling blend film morphology on the nanoscale is critical to advance organic electronic technologies.

Conclusions

Exciplexes with long lifetimes are formed in polyfluorene:silole films and devices studied in this work. The choice of solvent influences the morphology of the blend film and thereby critically influences exciplex lifetime, PL quenching, LED efficiency, and exciton regeneration. Exciton recycling occurs through the exciplex state to the higher band gap, electron-donating material in this type II organic blend system. This indicates that another factor, possibly molecular packing, supersedes thermodynamic favorability for exciton-recycling processes. Since exciton regeneration has been shown to significantly influence the lifetime of exciplexes formed in this blend film, we conclude that a more comprehensive understanding of the factors that influence exciton recycling is critical for a complete understanding of charge separation in organic donor–acceptor blend films. The findings in this paper emphasize the importance of morphology for charge separation and recombination in organic electronic devices, specifically LEDs and solar cells. More control over morphology on the nanoscale is necessary to better understand and control charge separation events in donor–acceptor organic systems.

Supporting Information Available: Details of the emission from silole:polystyrene blend films, analysis of the time constants of the exciplex emission, and kinetic model of excited-state dynamics used to support the conclusions in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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