Directing Energy Transfer within Conjugated Polymer Thin Films

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Received July 24, 2001

Light-harvesting organisms employ photosystems to collect and harness light energy. Photosystems use hundreds of chromophores arranged in an energy gradient to move absorbed energy unidirectionally toward the reaction center[1] and the efficiency provided by this directional energy transfer has inspired intensive investigation.[2] Our group has utilized energy transport within conjugated polymer (CP) films to create highly sensitive chemosensors.[3] Initially, we investigated the signal enhancement observed when multiple binding sites are linked together via a conjugated backbone.[4] This first-generation system featured a dilute solution of CP and relied on energy migrating along a single polymer chain. Within thin films, the polymers electronically couple, encouraging interpolymer energy transfer. The movement of energy between the CPs in three dimensions allows the film's luminescence to be more strongly quenched by energy traps such as TNT.[5] Further investigation of the energy movement within CP thin films revealed that transfer of energy was distance-dependent and was limited to films 16 polymer layers thick ($\sim$18 nm).[6]

The *z*-directional (film thickness) limitation observed in our previous work was confined to a film composed of 16 layers of **2**. Herein, we present a striated multipolymer system, which utilizes directional energy transfer to overcome the *z*-direction limitation. This system is analogous to the antenna complex in that it encourages maximum Förster energy transfer in one direction (Figure 1).[7] Three poly(*p*-phenylene ethynylene)s with tailored absorption and emission λ_{max} were synthesized. Polymers
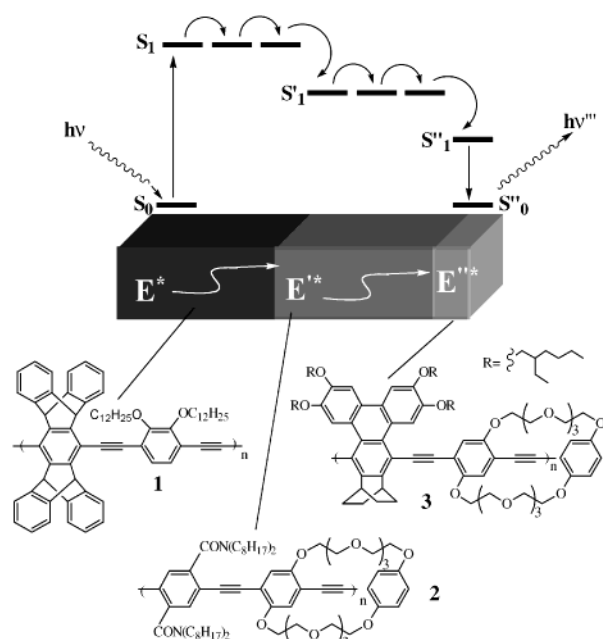

Figure 1. Energy is preferentially focused to the surface of a three-layer conjugated polymer film where the films have decreasing band gaps moving from the bottom to the top. Polymer **1** (abs./em. max 390/424 nm) overlaps with **2** (abs./em. max 430/465 nm) which overlaps with **3** (abs./em. max. 495/514 nm).

1−**3**[8] (Figure 1) were designed to have large spectral overlap between a donor emission and an acceptor absorption ranging from the blue (**1**) to the red (**3**).[9] The excellent spectral overlap encourages energy transfer from **1** to **2** and from **2** to **3**. Polymers **2** and **3** were also designed to be nonaggregating[10] and amphiphilic, thus allowing manipulation at the air−water interface.[11]

Multilayer films of **2** (4-, 8-, 16-, 24-, and 32-layers) were fabricated by the Langmuir−Blodgett (LB) method.[12] An LB monolayer of **3** was deposited on top of each multilayer film. As can be seen in Figure 2 efficient energy transfer occurs between **2** and **3**. The emission intensity of **3** (ex. 420 nm) gradually increases up to 16 layers of **2**. Above 16 layers the increase in fluorescence intensity levels off, clearly demonstrating the 16-layer limitation previously observed.[6] The acceptor-independent behavior suggests that the saturation observed above 16 layers is a property of thin films of **2** and is most likely due to the finite diffusion length of an exciton.

A film composed of a monolayer of **3** sandwiched between 16 layers of **2** on the bottom and eight layers of **2** on the top (16-1-8) showed higher fluorescence intensity emission from **3** (Figure 2) than that of the nonsandwiched films 16-1, 24-1, 32-1. The higher intensity observed for the 16-1-8 film further illustrates that the 16-layer limitation is due to the film thickness and not due to an intrinsic property of the acceptor. On the other hand, the observation that the fluorescence intensity of the 16-1-8 is not a linear combination of the fluorescence from films 16-1 and 8-1 may be due to acceptor limitations (e.g., poor orientation or longer lifetime of the excited-state residing on **3** that can lead to

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(7) Although not shown for clarity, within each polymer layer there are also small energy gradients due to disorder. Site-selective luminescence from energy transfer to low-energy traps in conjugated polymers has been previously shown. Bässler, H.; Deuben, M.; Huen, S.; Lemmer, U.; Mahrt, R. F. *Zeitsch. Phys. Chem.* **1994**, *184*, 233.
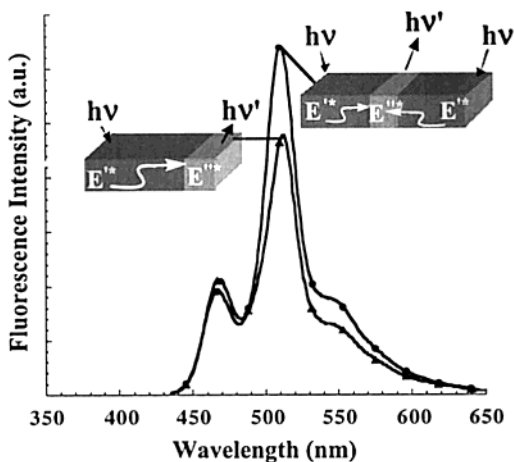
(8) Polymer **1** M_n = 73 000, PDI = 3.0; Polymer **2** M_n = 81 200 PDI = 3.4, Polymer **3** M_n = 103 000, PDI = 1.5.
(9) Polymer **2** was reported earlier (ref 4), and the synthesis of **1** and **3** will be reported in forthcoming manuscripts.
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(12) Polymers **2** and **3** were deposited at a surface pressure of 27 and 20 mN/m, respectively. Transfer ratios were greater than 95%.

Figure 2. Comparison of photoluminescence (ex. 420 nm) of two 24-layer films, in one case (▲) a monolayer of **3** is placed atop 24 layers of **2** and in the second case (●) a monolayer of **3** is sandwiched between 8 and 16 layers of **2**.

Figure 3. (A) Absorption and emission (ex. 390 nm; ◆ ex. 490 nm) spectra for a film of spin-coated **1**, 16 LB layers of **2**, and a LB monolayer of **3**. (B) Absorbance and emission spectra (ex. 390 nm) of spin-coated mixtures of **1** and **2** topped with a LB monolayer of **3** where the thickness of the spin-coated layer is varied. The emission represented by the middle spectra (●) emanates from a film of similar optical density as that shown in Figure 3A.

singlet−singlet annihilation), quenching sites created by the interfaces between the polymer layers, or the change in dielectric surrounding **3**.

To overcome the distance limitation and still retain the red layer as the top layer, we created films starting with the shortest-wavelength polymer, **1**, spin-cast on a glass substrate.[13] On top of the spin-cast film of **1**, 16 LB layers of **2** were coated, and finally a monolayer of **3**, providing a film where the band gap decreases directionally from the substrate to the polymer−air interface. The UV−vis spectra of the three-component film and the emission spectra (ex. 390 and 490 nm) are presented in Figure 3A.[14]

Excitation of the three-component film at 390 nm (λ_{max} of **1**) results in an emission spectrum consisting of three peaks; the small peaks at 423 and 465 nm are attributed to emission from **1** and **2**, respectively. The third and most intense peak at 512 nm is a result of energy transfer from **1** and **2** to **3** and subsequent emission from **3**. The observation that most of the energy is transferred from **1** through 16 layers of **2** to **3** demonstrates that energy can be efficiently moved in the *z*-direction, thereby concentrating the energy at the film−air interface, which has significant implications for a turn-on sensor design.[15] Figure 3A also shows a spectrum from direct excitation of polymer **3** at 490 nm. This results in a peak at 512 nm of much lower fluorescence intensity than the peak resulting from excitation at 390 nm. The difference in fluorescence intensity is directly proportional to the difference in optical density at 390 nm versus 490 nm, again confirming the efficiency of energy transfer.

The importance of the layer structure was investigated by placing an LB monolayer of **3** atop spin-coated mixtures of **1** and **2** of varing thickness. The ratio of the emission from **2** (ex. 390 nm, em. 465 nm) to the emission from **3** (ex. 390 nm, em. 512 nm) was used to assess transfer efficiency. As illustrated in Figure 3B, the thickest film has a **3/2** emission ratio of 0.9, the
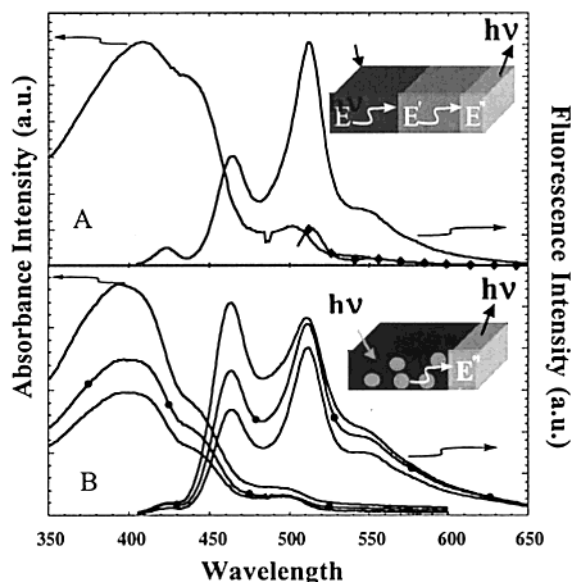
intermediate thickness has a ratio of 1.3, and the thinnest film has a ratio of 1.7. These ratios indicate that as the film thickness increases the bottom layers cannot effectively transfer energy to the uppermost layer. Films of mixed (Figure 3B) and striated (Figure 3A) were compared and striated films showed significantly higher emission from **3.** The **3/2** ratio for the striated and mixed films with identical optical densities at the excitation wavelength were 2.0 and 1.3, respectively. These data indicate that the multilayered structure provides much better directional energy transfer to the monolayer of **3**. The amount of **2** in the mixed film is less than in the striated film. However, the precentage of energy transfer from fewer than 16 layers of **2** to an emissive trap was found to be larger in our previous studies,[6] and striated films with smaller amounts of **2** would only lead to yet higher **3/2** emission ratios.

We have demonstrated that energy can be preferentially transferred to the surface of a thin film by utilizing CP layers of sequentially decreasing band gap. We have also provided two design manifolds to overcome the 16-layer energy transfer limitation. We are currently exploring the use of more than three layers; however, comparing the **3**/**2** emission ratios from Figure 2 and Figure 3A clearly illustrates that as the number of layers increases the ratio decreases. These data indicate that the interfaces created between layers introduce energy traps. We are currently investigating methods for blending the interfaces to decrease the traps as well as using the exceptional light-harvesting capabilities of our well-defined films in thin film sensors.

(13) Polymer **1** does not form a monolayer at the air−water interface.
(14) Spectra are corrected for lamp intensity variations at each excitation wavelength.
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