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13. ABSTRACT *(Maximum 200 words)*

Electronic energy transfer plays a critical role in biological photosynthesis, artificial photosynthesis, photovoltaic devices, photocatalysis, and other multichromophore systems and photoinduced processes. Our studies of electronic energy transfer in novel thin film light-harvesting nanocomposite polymer assemblies consisting of a rod-coil copolymer "antenna" and a conjugated polymer energy trap are presented. Total singlet electronic energy transfer efficiencies as high as 93% were observed at energy trap concentrations as low as 9 mol %. It will be shown that the efficiency of energy transfer can be regulated by the supramolecular structure of the rod-coil copolymer (antenna component). The nanoscale morphology of the nanocomposite polymer systems was characterized by the technique of nonradiative energy transfer, revealing interchromophore distances of 1.0-2.5 nm in the series of materials investigated.

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Efficient Electronic Energy Transfer in Polymer Nanocomposite Assemblies

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Samson A. Jenekhe and Chen -Jen Yang

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Efficient Electronic Energy Transfer In Polymer Nanocomposite Assemblies

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1. Introduction

Electronic energy transfer (EET), a process in which light energy absorbed by one chromophore is transferred over long spatial distance to another chromophore of different excitation energy, plays a critical role in biological photosynthesis, artificial photosynthesis, photovoltaic and other photoelectronic devices, photocatalysts, and other *multichromophore systems* [1-4]. Subsequent to energy transfer from a donor (or "antenna") chromophore to an acceptor (or "trap") chromophore, the electronic energy can result in charge generation and separation or chemical reactions at the trap chromophore [1-4]. Efficient EET is essential to efficient photoinduced processes in these systems. In the special case of *nonradiative energy transfer* (NRET), electronic energy transfer represents an extremely high spatial resolution technique for the characterization of nanostructure (distances as small as ~0.4 nm and as large as 10 nm can be measured) [1,2]. EET and NRET have been widely studied in biological and synthetic polymers [1-3, 5-8]. However, electronic energy transfer has not previously been investigated in nanocomposite polymer systems or in polymer blends containing a conjugated polymer component.

Recently, our group reported the use of a "supramolecular engineering" approach to prepare novel electroactive and photoactive rod-coil copolymers whose solid state morphology and photophysical properties can be regulated by the copolymer composition [9]. For example, it was demonstrated that at rod mole fraction below 0.5 the rod-coil copolymers formed *nanocomposites* in which the luminescence was enhanced by up to an order of magnitude compared to the pure rodlike conjugated polymer [9]. Here, we report studies of electronic energy transfer in thin film nanocomposite polymer assemblies **3** composed of a photoactive rod-coil copolymer **1** which is used as the energy donor or "antenna" component and a conjugated rigid-rod polymer **2** which functions as the energy acceptor or "trap". The novel multichromophore nanocomposite **3** represents a synthetic light-harvesting system which can be used to investigate the role of molecular and supramolecular structures on EET as well as the applicability of the NRET technique as a high spatial resolution optical probe of nanostructured polymeric materials. These studies will be reported in detail elsewhere [10].

2. Experiments

The synthesis and characterization of the rod-coil copolymers **1a** (x = 7), **1b** (x = 10), and **1c** (x = 12) are similar to methods used for the related homopolymers [10,11]. The synthesis and characterization of the dithienylvinylene-linked conjugated polyanthrazoline **2** (PBTVDA) have previously been reported [12].

Blends of the rod-coil copolymes **1** with the rodlike conjugated polymer **2** were prepared from solutions of their diphenylphosphate (DPP) complexes in 1:1 formic acid/ trifluoroacetic acid. Solutions with total polymer concentration of 0.1-0.5 wt.% were spin coated onto glass or fused silica substrates at speeds between 1800 and 3200 rpm. After drying the DPP/polymer complexes in vacuum oven at 60°C overnight, the thin films were immersed in triethylamine/methanol to coagulate thin films of the blends (or pure polymers) which were dried in a vacuum oven overnight at 50°C. The resulting thin films have a thickness that was varied between 20-100 nm, as measured by an Alpha Step profilometer and the absorbance of the optical absorption spectra.

Steady-state photoluminescence studies were done on a Spex Fluorolog-2 fluorometer equipped with a computer-driven DM3000F program. All fluorescence measurements were done at room temperature. The polymer films on glass slides were positioned such that the emission was detected at 22.5^0 from the incident beam. The relative fluororescence quantum efficiencies of the thin films of the three rod-coil copolymers were determined from the integrated emission intensity of fluororescence spectra, corrected for absorbance at the excitation wavelength that was kept at ~0.1 for all three copolymer films. To estimate the absolute quantum efficiency, we used ~10^{-3} M 9,10-diphenylanthracene in poly(methyl methacrylate) as a standard (ϕ = 83%) [13].

3. Results and Discussion

The preparation of the nanocomposite polymer assemblies **3** from blends of the rod-coil copolymers **1** and conjugated polymer **2** is shown in scheme 1. The maximum concentration of **2** in all the blends **3** investigated was 8.7 mol% (based on repeat unit). All the as-prepared blends were transparent orange/yellow in color, indicating a homogeneous blend. Extensive differential scanning calorimetry (DSC) and fluorescence spectroscopy studies established the single-phase nature of the blends below ~250° C. At higher temperatures (>250°C), blends with the highest concentration (8.7 mol%) of the conjugated polymer appear to undergo partial phase separation as revealed by DSC and other techniques [10].

The optical absorption spectrum of a 6.5 mol% PBTVDA (**2**) blend with **1c** was composed of the two component absorption bands with peaks at 370 and 530 nm, revealing no new absorption features. This indicates that there is no observable ground-state interaction between the two chromophores in the blend. The absorption spectra of all the blends were very similar. The absorption band with peak at 370 nm corresponds to the absorption of the rod-coil copolymer **1c** and the visible band with a peak at 530 nm corresponds to the absorption of the conjugated polymer PBTVDA. The absorption spectra of rod-coil copolymers **1a** and **1b** were identical to that of **1c**. The emission spectra of all three rod-coil copolymers (**1a, 1b, 1c**) were identical, having emission λ_{max} at 530 and 560 nm. Thus the energy donor emission band is extensively overlapped with the energy acceptor absorption band, as required for nonradiative energy transfer (NRET) via the Förster mechanism [1,2]. From the overlapped integral of the donor emission and acceptor absorption spectra, the Förster radius R_o for singlet electronic energy transfer was determined to be 19.1, 21.0, and 22.5 Å for **1a/2, 1b/2, and 1c/2** blends, respectively.

The donor/acceptor blends emit only one band with peak at 650 nm when excited at 530 nm, the acceptor absorption maximum. However when the same blends were excited at 420 nm, two emission bands with peaks at 530 nm and 650 nm were observed. Furthermore, the intensity of the 650 nm acceptor emission from the 420-nm (donor) excitation was almost twice the intensity of the acceptor emission from the direct acceptor excitation. The 650-nm emission intensity of the pure PBTVDA thin film when excited at 420 nm was only 14% of the similar emission intensity of the blends containing PBTVDA. These results suggest that ~86% of the emission of the antenna/trap assemblies originate from EET. The variation of the fluorescence spectra of the antenna (**1c**)/trap assemblies with the acceptor (trap) concentration for a ~100 nm thin film excited at 420 nm are shown in Figure 1. These emission spectra, which were normalized relative to the 530-nm donor emission intensity, clearly show the strong dependence of EET on acceptor concentration. The partial contribution of radiative transfer (trivial mechanism) to the observed EET was expected because of the extensive overlap of donor emission with acceptor absorption which could facilitate acceptor re-absorption of light emitted by the donor. The separate contributions of NRET and radiative transfer to EET were determined from the observed film thickness dependence of EET over the thickness range 20-100 nm [10].

EET efficiency χ in the nanocomposite donor (D)/acceptor (A) blends was determined from the integrated emission intensities I_A, I_D, and

corresponding fluorescence quantum efficiencies ϕ_A and ϕ_D. I_A was corrected for the 420-nm direct excitation of the acceptor. Spectra deconvolution of the blend emission spectra was used to resolve the partially overlapped donor and acceptor emission bands. EET efficiency was thus obtained as follows [1-3]: $\chi = (I_A/\phi_A)/[(I_A/\phi_A) + (I_D/\phi_D)]$. The acceptor concentration dependence of EET efficiency of **1c/2** blends is shown in Figure 2. The total efficiency increases from ~26% at 0.3 mol% PBTVDA to 93% at 8.7 mol% of the acceptor. However NRET contribution to the EET varies from ~100% at low acceptor concentration (<1 mol%) to only 51% at 8.7 mol%. Perhaps the most striking feature of the EET results is the large effect of the donor host (**1a, 1b, 1c**) on the efficiency. The maximum NRET efficiency drops dramatically from 48% and 42% in **1c** and **1b** respectively, to 14.4% in **1a**. This means that there is a factor of 3.3 increase in the NRET efficiency in going from the 7-methylene to the 12-methylene linked rod-coil copolymer (donor) host. Another interesting observation is the progressive shift of the critical acceptor concentration at which the NRET efficiency reaches asymptotic maximum, being about 1.0, 2.5, and 3.0 mol% PBTVDA for -C7, -C10, and -C12 rod-coil copolymers, respectively.

The measured NRET efficiency can provide high resolution spatial information about the nanoscale morphology of the nanocomposite donor/acceptor assemblies [1,2]. The average interchromophore distance between donor and acceptor chromophores was determined from the relation [10]: $1 + k_q/k_E + (r/R_o)^6 = 1/\chi$, where k_E is the rate constant for the reaction D* →A* (NRET) k_q is the rate constant for all the other nonradiative decay pathways, and R_o is the Förster radius. The average intersite distance between donor and acceptor chromophores, r, was in the range of 1.0-2.3, 1.1-2.3, and 1.2-2.5 nm for the **1a, 1b, and 1c** blends, respectively, depending on the acceptor concentration. It is remarkable that the donor/acceptor interchromophore distances are quite similar in the three series of blends (**1a, 1b, 1c**). This suggests that interchromore distance r is not the origin of the observed variation of NRET in the series of donor/acceptor assemblies. Instead, it is the ratio k_E/k_q which measures the "antenna power" of the light-absorbing donor rod-coil copolymer host that accounts for the variation of EET efficiency with donor host. The "antenna power" k_E/k_q varies from 0.17 to 0.71 and 0.91 in **1a, 1b, and 1c** respectively. The important conclusion is that the supramolecular structure of the light-absorbing donor host (antenna component) is very critical to the efficiency of energy transfer in multichromophore light-harvesting nanocomposite materials.

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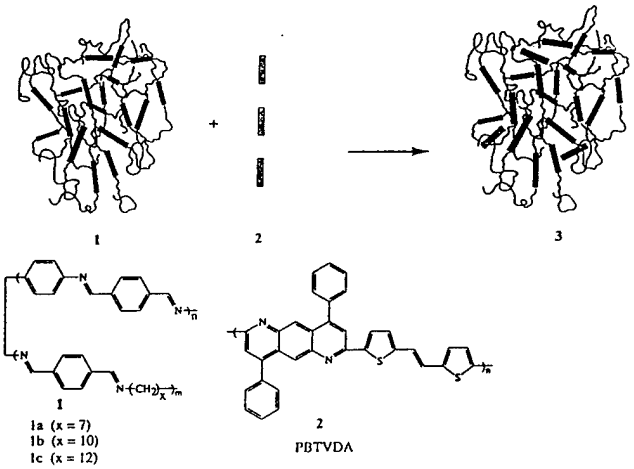
SCHEME 1



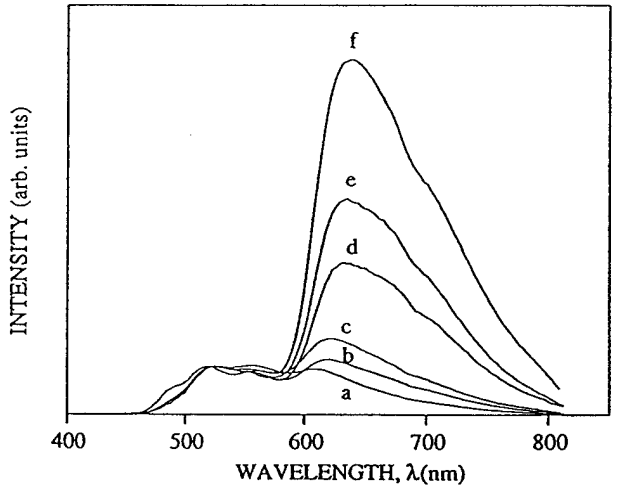


Figure 1. Acceptor concentration (mol% PBTVDA) dependence of normalized fluorescence spectra of thin films of **1c** donor/acceptor assemblies: 1.2 mol% (a), 2.4 mol% (b), 2.9 mol% (c), 4.2 mol% (d), 4.9 mol% (e), and 6.5 mol% (f). Excitation wavelength of all emission spectra was 420 nm.

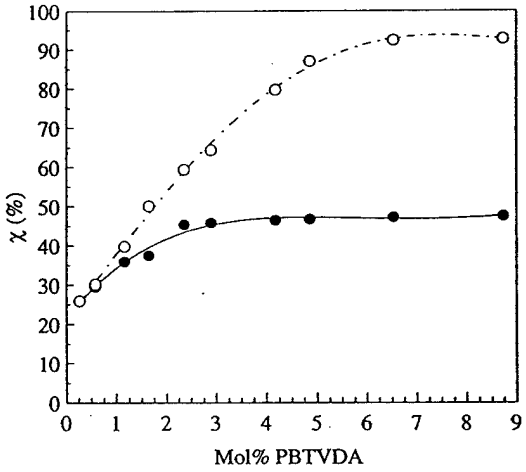


Figure 2. Acceptor (PBTVDA) concentration dependence of the total energy transfer efficiency (open circles) and the NRET (filled circles) in the **1c**-based donor/acceptor nanocomposite assemblies.