Conjugated Polymers

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Single-Molecule Studies of Electronic Energy Transfer in a Diblock Conjugated Polymer**

*John K. Grey, Doo Young Kim, Young Jong Lee, Jose J. Gutierrez, Nam Luong, John P. Ferraris, and Paul F. Barbara**

Electronic energy transfer across a molecular interface between two dissimilar conjugated polymers in a blend is a critical process for many promising optoelectronic device strategies.[1–9] Owing to the short range of electronic energy transfer, this process should in principle be strongly modulated by molecular-scale morphology in the interfacial regions of polymer blends. The most common approach for characterizing energy transfer in polymer blends, namely, ensemble fluorescence measurements, is obscured by morphological and kinetic heterogeneity of these materials and thus has done little to unravel the role of morphology in the energy-transfer process. Even nearfield scanning optical microscopy, which has been used to study polymer blends at the sub-100-nm scale,[10,11] lacks the spatial resolution in most cases to study individual morphological regions that can be as small as a few nanometers.

Herein, we take an alternative approach by using single-molecule spectroscopy (SMS) to study energy transfer across a molecular interface in isolated, single diblock polymer DMOS-co-MEH chains (DMOS = 2-dimethyloctylsilyl-1,4-phenylenevinylene; MEH = 2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) comprised of an energy-donor block (DMOS, $\lambda_{\max}^{\text{em}} = 490$ nm) and an energy-acceptor block (MEH, $\lambda_{\max}^{\text{abs}} = 500$ nm). The sizes of these molecules (≈ 10 nm) make them excellent models for developing a detailed understanding at the molecular level of energy transfer between a molecular interface of two dissimilar polymers. SMS has been used effectively to study intramolecular energy transfer in bi- and multichromophoric dendrimers,[12–15] end-capped polymers,[16,17] and conjugated homopolymers.[18,19] The SMS approach reported here provides detailed information at the molecular level on how energy transfer is influenced by polymer morphology within a single diblock polymer chain.

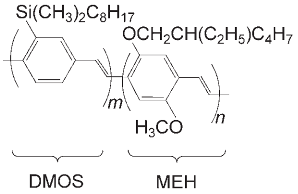

Figure 1 shows ensemble fluorescence spectra (solid lines) for DMOS (a) and MEH (b) homopolymers at $T = 298$ K dissolved at high dilution in a polymethyl methacrylate (PMMA) polymer host. These spectra were obtained by summing single-molecule spectra for isolated polymer chains. For comparison we also show absorption spectra (dotted lines) for the homopolymers which were acquired in dilute liquid solutions (solvent) rather than in polymer thin films because of the weak absorption of the latter. These data indicate that excitation wavelengths of 415 nm and 488 nm selectively excite DMOS and MEH, respectively, and also demonstrate a good spectral overlap of the emission bands of DMOS and the absorption bands of MEH which is important for promoting energy transfer by the Förster mechanism (the dominant mechanism for conjugated polymers).[20,21]

Analogous ensemble spectra for the DMOS-co-MEH diblock polymer are shown in Figure 1c. The emission spectra of DMOS-co-MEH (single molecules and ensembles) are well-modeled by a sum of MEH- and DMOS-like spectral components and do not show evidence of excimer emission between the two blocks. It is apparent from the spectrum of the diblock polymer in Figure 1c (solid line, $\lambda_{\text{ex}} = 415$ nm) that energy transfer occurs from the DMOS block to the MEH block with an overall efficiency of approximately 75%. The spectrum obtained upon excitation at 488 nm (dashed line) in Figure 1c demonstrates, as expected, that direct

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[*] Dr. J. K. Grey, D. Y. Kim, Dr. Y. J. Lee, Prof. Dr. P. F. Barbara
Center for Nano- and Molecular Science and Technology and
Department of Chemistry and Biochemistry
University of Texas at Austin
Austin TX 78712 (USA)
Fax: (+1) 512-471-3389
E-mail: p.barbara@mail.utexas.edu

Prof. Dr. J. J. Gutierrez, N. Luong, Prof. Dr. J. P. Ferraris
Department of Chemistry
University of Texas at Dallas
Richardson TX 75083 (USA)

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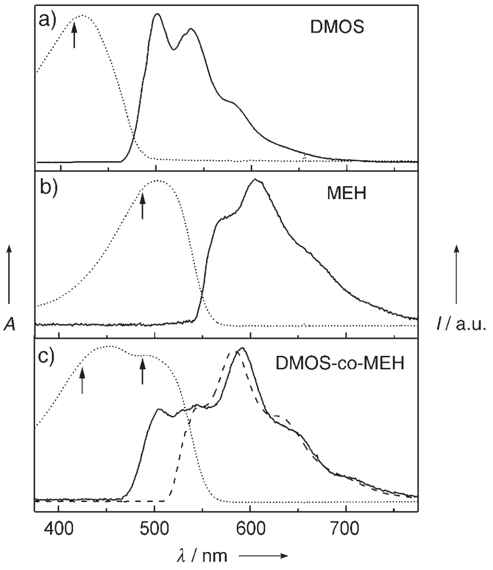

Figure 1. Absorption spectra recorded on dilute solutions (•••••) and emission spectra from dilute thin-film ensembles (——) of a) DMOS, b) MEH, and c) DMOS-co-MEH. Ensemble spectra were obtained by summing single-molecule spectra for each polymer. Excitation wavelengths are indicated by arrows on the respective absorption bands (DMOS $\lambda_{\text{ex}}=415$ nm; MEH $\lambda_{\text{ex}}=488$ nm). Part (c) shows the dependence of the emission spectra from the DMOS-co-MEH ensemble at 298 K on the excitation wavelength: $\lambda_{\text{ex}}=415$ nm (——); $\lambda_{\text{ex}}=488$ nm (-----).

excitation of the MEH block does not lead to uphill energy transfer from the MEH block to the DMOS block.

Further insight into the energy-transfer process was gained in a molecule-by-molecule analysis of the spectroscopy of DMOS-co-MEH. Typical spectra for single isolated DMOS-co-MEH molecules excited in the donor DMOS block at 415 nm are shown in Figure 2a. Single-molecule spectra were acquired individually over approximately 3-minute periods, during which time the spectra did not vary, which indicates that spectral diffusion and photochemistry are not complicating factors for these measurements. A histogram (Figure 2b) of the peak wavelength for the DMOS-co-MEH molecules reveals three distinct classes: 1) 490–530 nm, 2) 535–560 nm, and 3) 570–605 nm. Sub-ensemble spectra (Figure 2c) for the different classes were generated by sorting the spectra according to the peak wavelength. Class 1 corresponds to almost pure DMOS-like emission ($\lambda_{\max}^{\text{em}} = 505$ nm). Class 2 ($\lambda_{\max}^{\text{em}} = 550$ nm) and 3 ($\lambda_{\max}^{\text{em}} = 590$ nm), in contrast, closely correspond to the previously reported blue- and red-light-emitting morphological forms of the MEH homopolymer[19,22] and thus imply efficient DMOS-to-MEH energy transfer.

It is informative to directly calculate the distribution of apparent energy-transfer efficiencies for the diblock single molecules. This has been determined by fitting the blue edge of each spectrum to a model DMOS spectrum and then using the amplitude of the donor spectrum to determine the fraction (f_{D}) of the donor intensity for each spectrum. Figure 3a shows a histogram of apparent energy-transfer efficiencies $(1-f_{\text{D}})$[23] for all DMOS-co-MEH single molecules excited at 415 nm. The results clearly demonstrate that

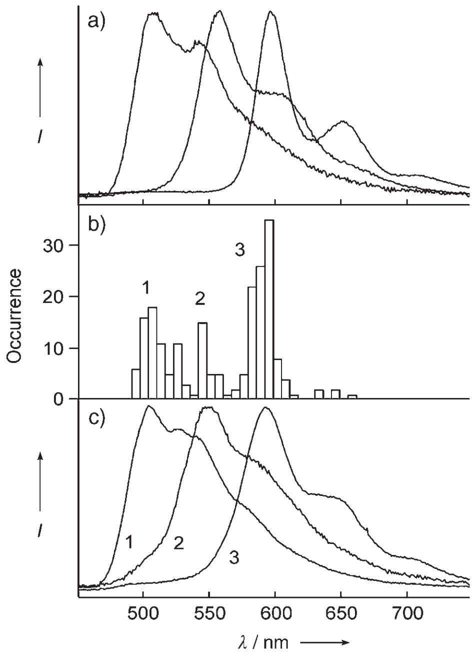

Figure 2. a) Typical single-molecule spectra for DMOS-co-MEH excited at 415 nm, b) histogram of peak wavelengths of 210 single DMOS-co-MEH molecules, and c) sub-ensemble spectra excited at 415 nm. Sub-ensemble spectra were sorted according to their wavelength distribution ranges (labeled 1, 2, and 3), which correspond to 1) DMOS (500–530 nm), 2) blue MEH (540–560 nm), and 3) red MEH (570–600 nm).

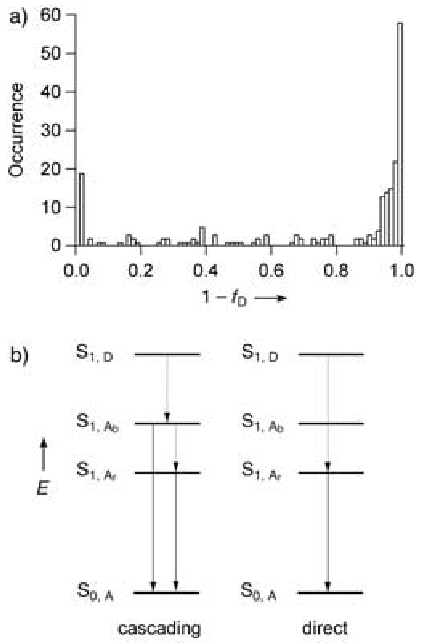

Figure 3. a) Apparent energy-transfer efficiencies $(1-f_{\text{D}})$ for single DMOS-co-MEH molecules excited at 415 nm. b) Schematic diagrams illustrating energy transfer to red-light-emitting MEH sites in the diblock polymer: left) cascading energy transfer to blue-light-emitting MEH followed by emission and intrachain energy funneling to red—light-emitting MEH sites; right) direct energy transfer to red MEH. Spectroscopic states are represented by solid horizontal lines, and energy-transfer and emission transitions are shown as vertical dotted and solid lines with arrows, respectively.

the energy-transfer process in the diblock conjugated polymer sample is highly heterogeneous. The molecules that show a low energy-transfer efficiency (< 0.1) in the histogram consist mostly of diblocks that exhibit DMOS-only emission and closely correspond to class 1 in Figure 2c. Successive SMS scans of the same region of the sample using excitation alternatively at 415 and 488 nm demonstrated that these molecules contain extremely short MEH blocks, which lead to the lower efficiency of energy transfer. Thus, the major factor responsible for the low efficiency of energy transfer for a diblock molecule is a short MEH (acceptor) block. Presumably, energy transfer is slower for the shorter MEH block molecules owing to a smaller number of effective acceptor chromophores.

Two-color (415 nm/488 nm) excitation experiments were also carried out on the individual homopolymers to measure the contribution of "cross-talk" to the observed energy-transfer efficiencies by exciting MEH at 415 nm. The relative excitation efficiency of DMOS and MEH blocks excited at 415 nm was found to be greater than 9:1, which demonstrates that energy transfer rather than direct excitation is the dominant mechanism for the excitation of MEH. The data were not corrected for the small contribution from direct excitation.

It has recently been shown that MEH homopolymer chains can be roughly classified into blue- and red-light-emitting chains. The red-light-emitting single molecules have been shown to comprise a small number of low-energy "red" chromophores, due to chain–chain contacts, which act as acceptors of electronic energy from the much greater number of blue chromophores.[19,24] In contrast, the blue-light-emitting morphological forms of MEH lack red chromophores and thus directly emit from the blue chromophores. One of the main results of this study is that the presence of the DMOS block induces folding of the MEH block which leads to a larger fraction of red-light-emitting MEH sites in the diblock polymer, as compared to the MEH homopolymer. Over 70% of all single diblock polymer molecules studied exhibit high apparent efficiencies of energy transfer (> 0.8), with the MEH red-light-emitting form (class 3 in Figure 2c) being the dominant emitting species. It should be emphasized that the efficiency of energy transfer from DMOS to MEH is close to unity for a majority of both red- and blue-light-emitting molecules. The red and blue forms differ, however, in the ultimate sink for excitation energy, that is, the red or blue MEH chromophores. The reason for a larger fraction of red sites in the diblock case has not been established, but we speculate that it may be due to a co-collapse of both blocks to favor a more collapsed chain conformation, and hence a larger number of chain–chain contacts.

The possible photophysical processes pathways following excitation of the donor block at 415 nm which lead to the red-light-emitting forms are illustrated in Figure 3b. $S_{n,D}$ ($n = 0, 1$) represent the donor states and $S_{n,A}$ represent acceptor states, with the blue and red forms denoted with b and r subscripts, respectively. Interestingly, the fraction of red-light-emitting molecules is a factor of four greater than that observed for an MEH homopolymer of the same molecular weight as the MEH block in the DMOS-co-MEH diblock polymer (Figure 4). The origin of the greater number of red-light-emitting molecules for the diblock sample relative to the homopolymer samples is revealed in low-temperature SMS studies on diblock and homopolymer samples. Figure 4 shows the distributions of peak wavelengths and sorted sub-ensemble spectra of blue- and red-light-emitting species for MEH homopolymer samples ($M_W = 186$ kDa and 1000 kDa, panels a and b, respectively) and single DMOS-co-MEH molecules (MEH block $M_W = 186$ kDa, panel c) excited at 488 nm at around 20 K. Blue-to-red ratios for the 186-kDa MEH homopolymer and the DMOS-co-MEH diblock polymer are around 4:1 and 1:1, respectively, with the latter being similar to the high-molecular-weight MEH homopolymer sample ($M_W = 1000$ kDa, Figure 4b). This establishes that the MEH region of the diblock in fact contains higher number of red sites on average than an MEH homopolymer of the same length. The significantly better spectral resolution achieved at low temperature allowed for a precise, quantitative determination of the relative yields of the blue and red emission bands for MEH.

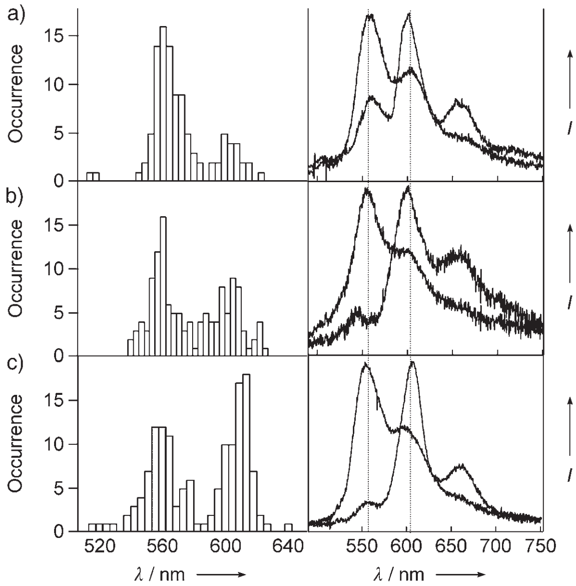

Figure 4. Histograms of peak wavelengths (left) and sorted sub-ensemble spectra (right) for a) MEH ($M_W = 186$ kDa), b) MEH ($M_W = 1000$ kDa), and c) DMOS-co-MEH (MEH block $M_W = 186$ kDa), excited at 488 nm at around 20 K. The dotted vertical lines show the peak wavelength positions of the red- and blue-light-emitting forms of MEH in the diblock polymer as well as the polymers of different molecular weights.

Unfortunately, the experimental data did not allow us to establish whether energy transfer from DMOS to red chromophores of MEH proceeds predominantly by a cascading or a direct mechanism (see Figure 3). If the MEH block has very few red chromophores per MEH block, as suggested by experiments on pure MEH,[19] the cascading mechanism would be expected to be more rapid as it involves energy transfer from DMOS to blue chromophores in the first step.

In this report, single-molecule spectroscopy on diblock donor/acceptor polymers has been used to show that energy transfer across a polymer–polymer interface can be highly heterogeneous as a result of morphological features at the interface. Furthermore, the results demonstrate that the morphology of the chains that comprise the diblock can differ substantially from the morphology of the separate homopolymers.

Experimental Section

Dilute thin-film samples of poly(2-methoxy,5-(2′-ethylhexyloxy)-*p*-phenylenevinylene)-co-poly(2-dimethyloctylsilyl-*p*-phenylenevinylene) (DMOS-co-MEH; $M_W = 312$ kDa, polydispersity inde*x*: 1.18) were prepared according to a reported procedure,[19] and the synthesis and characterization of DMOS/MEH are described in detail in the Supporting Information. Typically, samples were diluted in a solution of PMMA (3% w/w) in toluene and spin-cast onto glass substrates to yield films of approximately 100-nm thickness. Samples were then coated with either gold or aluminum (≈ 200 nm) to prevent oxygen and water from diffusing into the PMMA layer. Single molecules were excited with the doubled output (415 nm) of a Ti:sapphire laser centered at 830 nm, and the 457.9 nm and 488 nm lines of an argon-ion laser and images and spectra were obtained from a confocal scanning microscope apparatus described elsewhere.[19] Excitation intensities were approximately 200 W cm^{-2}.

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