

## Efficient Intramolecular Energy Transfer in Single Endcapped Conjugated Polymer Molecules in the Absence of Appreciable Spectral Overlap

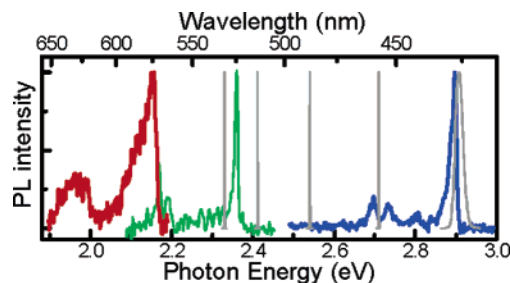
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Excitation energy transfer (EET) is central to understanding the photophysics of molecular aggregates.<sup>1–3</sup> Conjugated polymers (CPs) constitute a particularly interesting subset of such materials as multiple chromophoric units arise naturally on their strongly bound linear chains. Furthermore, CPs form an important class of organic semiconductors with a range of technological applications, making a detailed understanding of EET processes in them particularly timely.<sup>3</sup> Both inter- and intramolecular EET are relevant in the solid state. Whereas intermolecular relaxation channels have been studied in detail and are well-characterized,<sup>2</sup> intramolecular energy migration along the one-dimensional chain has recently shifted to the focus of attention.<sup>3</sup> Both experiments on ensembles of isolated chains as well as detailed quantum chemical calculations have illustrated that EET in one dimension is generally inefficient.<sup>3</sup> Such models effectively provide a microscopic picture, parametrized to match the ensemble experiment by suitable choice of bulk characteristics such as the spectral overlap between a donor and acceptor unit.<sup>3c</sup> Single molecule (SM) spectroscopy (SMS) provides facile access to the microscopic parameters governing EET by overcoming ensemble averaging.<sup>4</sup> Although this approach has proved successful in studying EET at room temperature,<sup>5</sup> only a few low temperature investigations have been reported.<sup>6,7</sup> We show here that SMS provides insight into EET in polymeric donor systems bound covalently to acceptor dye endcaps and demonstrate that such complexes can exhibit an extremely high efficiency in intramolecular EET unexpected from the ensemble.<sup>3c</sup> Bonding the dye to the polymer modifies its spectral properties and increases the spectral separation between donor and acceptor emission maxima to almost 150 nm ( $\sim 6000\text{ cm}^{-1}$ ). While we cannot measure the acceptor absorption spectrum directly, we can assess the degree of spectral overlap between donor emission and acceptor absorption by selectively exciting the endcap at different wavelengths. This shows that the spectral overlap between the two is negligible. Our results offer a direct visualization of the recently stated paradigm<sup>1a–e</sup> that, in contrast to common practice,<sup>3c</sup> far-field linear spectroscopy provides insufficient information to determine fluorescence resonant ET rates.

We recently demonstrated the feasibility of SMS in the near-UV on wide-gap CPs such as polyfluorenes.<sup>7d</sup> As a model system to study intramolecular EET in one dimension, we chose a previously described polyindeno[1,2-b]fluorene (PIF) endcapped with perylene acceptors.<sup>3c</sup> Figure 1 shows low temperature (5 K) photoluminescence (PL) spectra of single PIF and dye molecules dispersed in a zeonex film. Whereas the polymer was pumped using the broad band ( $\sim 200\text{ cm}^{-1}$ ) of a femtosecond laser pulse centered at 395 nm, the free perylene was excited at 488 nm by an Ar<sup>+</sup> laser. Both the PIF and the perylene exhibit narrow zero-phonon lines of less than 1 nm width ( $\sim 40\text{ cm}^{-1}$ ) followed by a distinct vibronic progression, which in both cases is particularly dominant

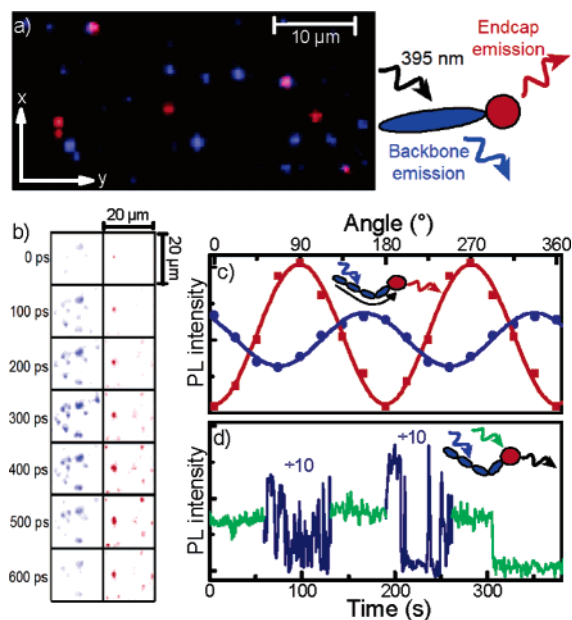


**Figure 1.** Single molecule PL of the PIF backbone (blue), a free perylene dye (green), and a perylene endcap (red). The spectra of the laser lines used to probe direct excitation of the endcap are marked in gray.

in the region of the C=C stretching modes ( $\sim 1500\text{ cm}^{-1}$ ). The perylene endcap, on the other hand, was excited indirectly by absorption on the polymer backbone and EET to the endcap. The spectrum is an order of magnitude broader ( $\sim 400\text{ cm}^{-1}$ ) than the free dye and is shifted by almost 150 nm from the PIF emission. In contrast to the ensemble spectra,<sup>3c</sup> assumption of a simple mirror relation between absorption and emission suggests spectral overlap between donor and acceptor to be near negligible. To assess the acceptor absorption, we used different laser lines shown in Figure 1 to probe direct excitation of the endcap. These correspond approximately to the vibronic progression of PIF (i.e., the wavelengths for which appreciable donor–acceptor spectral overlap would be most probable). We only succeed in exciting the endcap at 532 nm. While the absorption of the PIF endcap acceptor is negligible below 500 nm, the backbone does not show any detectable emission on the SM level above 500 nm.

Although the relevant electronic and vibronic transitions are narrow and spectrally separated, efficient EET occurs from the backbone to the endcap. Figure 2 presents a range of experimental evidence illustrating the surprising efficiency of EET on the single molecule level. Panel a shows fluorescence microscope images of the polymer detected through either blue or red filters. Excitation in the maximum of the backbone absorption<sup>3c</sup> at 395 nm leads to emission from either the PIF (coded blue), the endcap (red), or both (purple). The density of blue (donor) spots in Figure 2a is approximately 5-fold the number of red spots (i.e.,  $\sim 20\%$  show efficient EET, roughly consistent with the blue/red intensity ratio we found in the ensemble). On average, therefore, intramolecular EET to the endcap remains inefficient, as expected from the ensemble.<sup>3c</sup> The probability for observing endcap emission increases slightly with increasing temperature and thus exciton mobility.<sup>7b</sup>

Time-resolved fluorescence microscope images of different sets of molecules recorded using a color-sensitive picosecond gated detection technique<sup>7b</sup> under femtosecond laser excitation at 395 nm are shown in panel b. The temporal resolution of the gate was 200 ps. Whereas blue emission appears instantaneously, there is a clear



**Figure 2.** Efficient intramolecular EET from the polymer backbone to the perylene endcap. (a) False color fluorescence microscope image of perylene endcapped PIF (backbone excitation at 395 nm; emission from the polymer (blue), endcap (red), or both (purple)). (b) Time-resolved fluorescence images (size: 20  $\mu\text{m}$ ) of single endcapped polymer chains excited at 395 nm. (c) Polarization anisotropy in excitation (blue) and endcap emission (red) under 395 nm excitation. (d) Fluorescence transient of the endcap under excitation of the polymer (blue) and the endcap (532 nm, green). Note the 10-fold intensity increase under backbone excitation.

rise time for most of the red molecules. In turn, the blue emission decays faster than the red emission. The apparent *average* temporal rise in the red, which was recently documented in the ensemble at room temperature,<sup>3c</sup> illustrates the feasibility of time-resolving EET on the SM level.

Further evidence for EET comes from a comparison of the polarization anisotropy in absorption and emission<sup>7c</sup> under endcap detection and PIF excitation. As the backbone is not fully extended and supports multiple chromophores of different orientation,<sup>3,7</sup> rotating the excitation plane of polarization will not yield a full modulation in emission intensity. This is because the different absorbing transition dipoles on the polymer chain have different orientations. In contrast, the single dye molecule at the end of the chain contains only one transition dipole and thus exhibits linearly polarized emission, as illustrated in Figure 2c. Most importantly, the planes of polarization in absorption and emission are out of phase by  $70^\circ$ . This phase shift is a result of EET occurring along the chain to the endcap. Direct excitation of the endcap on the other hand yields a full modulation in absorption and zero phase shift with respect to emission.

Finally, we also studied the time dependence of the endcap PL under excitation of either the backbone or the endcap. Figure 2d shows the evolution of the endcap PL intensity under alternating excitation at 395 nm (blue) and 532 nm (green). Whereas direct excitation (532 nm) leads to a comparatively smooth transient with little noise, the endcap intensity fluctuates much more strongly under indirect excitation (395 nm) while showing 10-fold intensities because of the efficient light harvesting. The strong fluctuation, which has also been observed at room temperature in dendritic donor–acceptor complexes,<sup>5c</sup> is a consequence of excitonic blockade in the one-dimensional energy cascade along the PIF backbone. This leads to a temporal variation in EET<sup>5c,7a</sup> efficiency modulated on top of the endcap intensity jitter.

Although the precise acceptor absorption is hard to quantify, a first approximation can be made by assuming that the mirror image relation between absorption and emission is upheld at low temperatures. Furthermore, we were unable to excite the endcap directly at the maxima of PIF emission. Efficient EET in polymeric photonic wires therefore occurs without spectral overlap between donor emission and acceptor absorption. Our results provide a graphic experimental illustration of the recent theoretical result stating that far-field spectroscopic information is insufficient for calculating EET rates.<sup>1a–e</sup> This insufficiency needs to be considered when developing microscopic models of EET in CPs.<sup>3</sup> While the precise nature of the efficient EET process remains to be clarified, a few speculative comments on processes involved lie on hand. We previously demonstrated that CPs exhibit a surprisingly strong and long-range intermolecular exchange coupling, which may be related to the strong polaronic nature of charge.<sup>8</sup> This coupling could assist intersegmental energy relaxation. Internal conversion via coupling to molecular vibrations can be very efficient in macromolecules (Kasha's rule) and thus enable rapid excited state relaxation (exciton trapping) to the global energetic minimum<sup>1f</sup> of the covalently bound donor–acceptor complex. This provides an effective means of dissipating energy, although the occurrence of a phonon bottleneck arising due to the creation of multiple vibrons may be an issue. In conclusion, we note that efficient EET does not occur in all molecules, as many SMs ( $\sim 80\%$ ) do not exhibit EET to the endcap (Figure 2a) and intrachain EET is inefficient on average.<sup>3</sup> This may be a subtlety of intramolecular disorder such as the difference in vibrational coupling strength<sup>7</sup> between SMs.

**Acknowledgment.** We thank W. Stadler and A. Helfrich for technical assistance. Generous support came from the VW Foundation and the DFG through the Gottfried Wilhelm Leibniz Prize.

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JA056469H