

Linewidth-Limited Energy Transfer in Single Conjugated Polymer Molecules

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Using low temperature single molecule spectroscopy on rigid-rod conjugated polymers we are able to identify homogeneously broadened, strongly polarized emission from individual chromophore units on a single chain. Gated fluorescence spectroscopy allows real time imaging of intramolecular energy transfer as the chain behaves as a series of weakly interacting chromophores. Energy transfer is controlled by the chromophoric spectral linewidth, which depends on temperature. Linewidths exceeding intramolecular disorder lead to incoherent chromophore coupling and collective fluorescence phenomena.

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Conjugated polymers are an exciting class of organic semiconductors used in devices such as organic light-emitting diodes, lasers, solar cells, and field-effect transistors [1,2]. One of the major problems in applications is material stability, which requires expensive shielding of the organic compounds from the environment. A severe loss mechanism limiting the luminescence yield of devices is efficient excitation energy transfer (EET) towards quenching centers [3–5]. In contrast, EET is a prerequisite for efficient light harvesting in organic solar cells and is important in polymer-based sensing applications [6]. EET is therefore a crucial parameter determining device efficiency and operational lifetime. Improving the performance of polymer devices requires a microscopic understanding of EET processes in conjugated polymers. We report here on the first temperature-dependent measurements on single rigid-rod conjugated polymer chains, which allow us to resolve the energetic level distribution of interacting chromophores present in a single molecule (SM). We demonstrate a control of EET on a single chain by tuning the temperature-dependent chromophoric spectral linewidth. Our results suggest design strategies for controlling EET in polymeric semiconductors and provide new directions towards SM optoelectronic devices. We identify general features of EET in disordered assemblies of localized two level systems, which are also of relevance to EET in, for example, biological systems [7] and colloidal quantum dot solids [8].

Comparisons of inter- and intramolecular EET in conjugated polymer ensembles suggest that for both poly(phenylene-vinylenes) (PPVs) and polyfluorenes intramolecular exciton migration is substantially slower than intermolecular diffusion [9–11]. In puzzling contrast to this, ultrafast depolarization has been observed in isolated polymer chains [12], indicating that the primary step in exciton relaxation may be intramolecular. Moreover, the demonstration that polymers may be used as efficient chemical sensors by exploiting a huge amplification of fluorescence quenching at localized defects

provides strong evidence for ultrafast intramolecular EET [6]. Intra- and intermolecular EET in conjugated systems is generally modeled within the framework of incoherent dipole-dipole coupling according to Förster theory, where the rate of EET depends on the spectral overlap between chromophores. In polymers, which are often thought of as chains of weakly interacting chromophore units, the spectral linewidth of the individual chromophores is usually hidden by large inhomogeneous broadening and is thus unknown, as is the energetic spacing between chromophores. Photon echo measurements on aggregated PPV molecules in toluene solution have suggested that homogeneous broadening can be the main source of spectral broadening [13]. Because of the complicated structure-property relationships in PPVs [14], however, it is unlikely that this is due to intrinsic chromophore properties, but rather due to intramolecular aggregates. Studying the photoluminescence (PL) of single polymer chains allows us to overcome limitations of ensemble averaging and inhomogeneous broadening and to determine the true spectral properties of individual chromophores on a chain. Previously, studies have been carried out at room temperature on SMs of high molecular weight, which typically contain thousands of monomer units per chain, exhibit spectral properties similar to the bulk [14–16] and tend to form aggregated nanoparticles rather than extended linear π -systems [17]. We chose to investigate a model-type polymer based on ladder-type poly(*p*-phenylene) (MeLPPP), which has been extensively studied [18] and has wide application potential. This polymer is subject to a particularly low degree of disorder induced inhomogeneous broadening, as the full ladder structure along the backbone blocks chain coiling and bending, enforcing a rigid-rod type geometry.

MeLPPP molecules ($M_w = 50\,000$, corresponding to an average of 70 repeat units per chain) were dispersed in polystyrene (glass transition at $T_g = 365$ K) at 10^{-7} molar concentration and spin coated from toluene

solution in a nitrogen atmosphere. The samples were mounted in a He flow cryostat under vacuum. The molecules were excited by linearly polarized laser light from a pulsed frequency-doubled Ti:sapphire laser operating at 80 MHz repetition rate, supplying pulses centered at 2.9 eV with a linewidth of 50 meV and a pulse length of 100 fs. PL was collected by a microscope objective (NA:0.55) and passed through a grating spectrometer with 2.5 meV resolution. The luminescence spectrum was detected by a LaVision Picostar gated intensified CCD with a temporal resolution of <200 ps. The polarization anisotropy in PL was measured by rotating a polarizer in the emission path of the setup and averaging over all excitation polarizations, which were set using a $\lambda/2$ plate.

In the bulk, MeLPPP displays a well-resolved emission spectrum with a narrow 0-0 band at 2.68 eV and a vibronic side band at 2.50 eV [18]. Figure 1(a) shows spectra of single MeLPPP molecules measured at three different temperatures under polarized broad-band excitation. At 5 K two distinct peaks are clearly visible at 2.70 and 2.73 eV with a third weak feature at 2.71 eV. As the temperature is raised to 80 K, the two main peaks broaden substantially and start to overlap (light gray or orange curve). At 160 K (gray or red curve) one broad featureless peak is observed, which engulfs the spectroscopic structure observed at lower temperatures. The structure in the emission at low temperatures arises from contributions from distinct chromophore units on the polymer chain, which is seen by studying the polarization of the spectra emitted. Figure 1(b) shows PL spectra from a further chain at 20 K detected through a polarization filter at orthogonal orientations. Three independent chromophore units with slightly different conjugation lengths and transition energies are identified by their distinct polarization, which results from the molecular dipole orientation. The case is very different at 250 K in Fig. 1(c), where the three peaks are broadened to one featureless band and the emission spectrum is only weakly polarized.

Using a gated CCD camera, we directly time resolve slow transfer of excitation energy from higher to lower energy chromophores on a single chain. Figure 2 shows emission spectra recorded at four different delay times after excitation at 5 K. At short times only one prominent Lorentzian peak is observed at 2.69 eV. As the delay time is increased, a further peak appears, which can be approximated by a second, redshifted Lorentzian at 2.67 eV. The fluorescence kinetics arising from EET between the two chromophores can be modeled quantitatively. Assuming identical intrinsic lifetimes of both chromophores an EET rate of 2 ns^{-1} is extracted, which agrees well with calculations of the Förster rate from the measured spectral overlap assuming a chromophore separation of 5.6 nm corresponding to the average conjugation length [19]. Note that the rate for EET in this case is very small and less than the rate of spontaneous emission of 3 ns^{-1} .

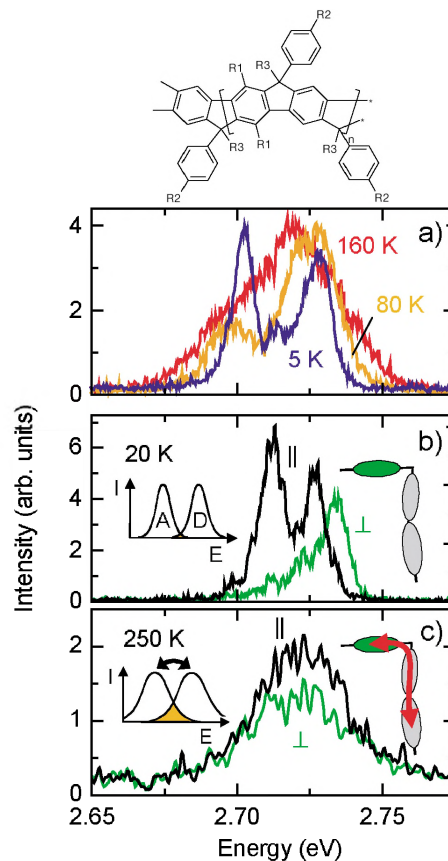


FIG. 1 (color online). (a) Single molecule PL spectra recorded at 5 K (black or blue), 80 K (light gray or orange), and 160 K (gray or red) of MeLPPP in a polystyrene matrix. The polymer chain consists of individual chromophore units of slightly different energies. At low temperatures the fine structure arising from emission from single chromophores on the chain becomes visible. (b) Single molecule PL spectra of a second molecule detected through a polarization filter at orthogonal polarizations at 20 and 250 K (c), showing the existence of a number of chromophore units with different orientations. The sketch indicates the spectral overlap between donor (D) and acceptor (A) chromophores required for intramolecular energy transfer. The structure of the polymer is given at the top (R1: *n*-hexyl, R2: *n*-decyl, R3: methyl).

Within Förster theory, energy transfer as observed in Fig. 2 depends on the spectral overlap of adjacent donor and acceptor chromophore units. In order to determine the general interchromophore spectral overlap directly, we measured the temperature dependence of the spectral line shape of individual chromophore units, i.e., for chains exhibiting only one fully polarized emission line. Figures 3(a) and 3(b) compare the temperature dependence of the purely electronic transition at 2.68 eV of a bulk MeLPPP film and an individual chromophore on a single chain. Whereas the SM spectra are similar in width to the bulk spectra at room temperature, they are over an order of magnitude narrower at 5 K. The SM spectrum can generally be described by a Lorentzian line, indicating homogeneous broadening of the emission spectrum

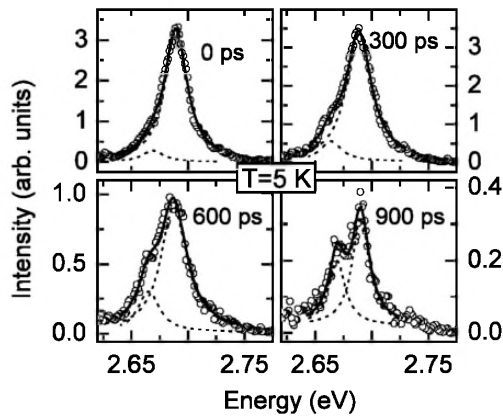


FIG. 2. Temporal evolution of single chain PL at 5 K showing intramolecular energy transfer from a higher energy to a lower energy chromophore unit. The dotted lines indicate Lorentzian fits to the spectrum, the full lines give the sum of the two peaks.

[20,21]. We imaged a total of over 150 molecules and observed linewidths at 5 K down to the resolution limit of 2.5 meV. Since lifetime broadening has a negligible contribution to the homogeneous linewidth Γ , this translates to a dephasing time $T_2 = 2\hbar/\Gamma > 520$ fs. This is in excellent agreement with recent measurements of coherence loss using resonant Rayleigh scattering in conjugated polymers [22].

The decrease in linewidth with decreasing temperature is summarized in Fig. 3(d), where the single chromophore linewidth is plotted as a function of temperature (black line). We note that the linewidth Γ changes virtually linearly with temperature, corresponding to a width of $\Gamma \propto T^{1.1}$. Linewidth studies of isolated dye molecules in polymeric matrices have shown a similar temperature

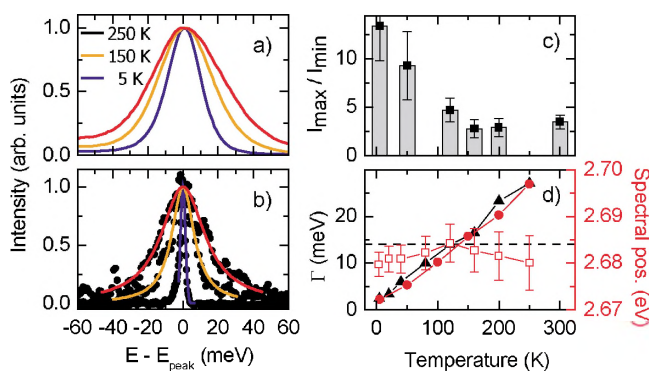


FIG. 3 (color online). Comparison of bulk film (a) and single chromophore (b) spectra at three different temperatures. (c) Average SM polarization ratios in emission as a function of temperature. (d) Spectral linewidth Γ of a single emitting chromophore as a function of temperature (black triangles). The dashed line gives the average level of intramolecular disorder ΔE . The right axis shows the spectral position determined for SMs (red squares) and a bulk film (dark gray or red circles).

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dependence [23,24], which can be well described theoretically in the framework of two level systems and soft potential models [25]. The second parameter determining the spectral overlap required for EET is the energetic spacing ΔE between chromophores. We find $\Delta E = 14$ meV by calculating the standard deviation of the energetic positions of the individual chromophores on a SM and subsequently averaging over many molecules. As Fig. 3(d) shows, Γ exceeds ΔE above 120 K, allowing full spectral overlap of chromophores on a chain.

The temperature dependence of the intramolecular chromophore spectral overlap results in a temperature-dependent EET rate along the polymer backbone, which is demonstrated by two independent means. As seen in Fig. 1, highly polarized emission is observed from a SM at low but not at high temperatures. To quantify this, we measured the temperature dependence of the average emission polarization ratio I_{\max}/I_{\min} for 91 molecules as shown in Fig. 3(c). At $T = 5$ K we find a high average degree of polarization of 13:1, which decreases strongly with increasing temperature. At low temperatures downhill energy transfer is inefficient and occurs only to local energetic minima of the SM, leading to strongly, and in many cases fully, polarized emission from individual chromophores. With sufficient thermal energy present, uphill exciton migration becomes possible [26]. This results in a randomization of the emission polarization, as excitation energy is statistically distributed over all chromophores. The critical temperature of ≈ 120 K for depolarization corresponds to the crossover from inhomogeneously to homogeneously limited SM spectral broadening for $\Gamma > \Delta E$.

A consequence of efficient energy transfer is strong fluorescence intermittency, which has previously been reported for organic nanoparticles [14–17,27]. Figure 4 shows a comparison of typical fluorescence intensity traces recorded over a duration of 6 min at 5 and at 300 K. The background level is given for reference.

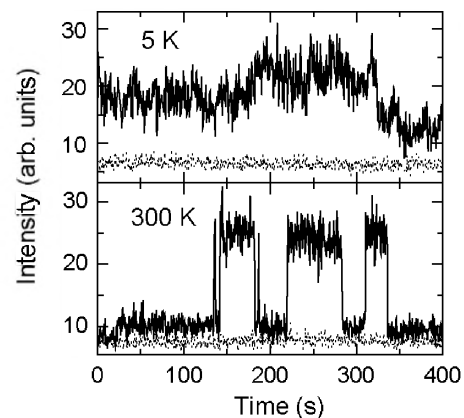


FIG. 4. Single chain fluorescence transients recorded at 5 and 295 K for 500 ms integration windows showing fluorescence intermittency at room temperature. The dotted curve indicates the background noise.

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Whereas the 5 K traces show no sudden jumps, but a constant noise approximately 5 times the background noise, at room temperature sudden jumps between different intensity levels are observed in combination with a reduction in overall noise. This collective fluorescence intermittency is a direct consequence of fast bidirectional EET, allowing efficient exciton quenching on reversibly formed quenching sites [16,17,27]. It has previously been observed that the strength of fluorescence intermittency depends on chain conformation, allowing a transition from strong to weak intermittency similar to that shown in Fig. 4 by varying the solvent polarity [15]. Whereas this transition is due to a variation of extrinsic chain properties (i.e., conformation), we demonstrate here that a similar changeover can be induced in a SM by varying intrinsic electronic properties, i.e., the chromophore spectral linewidth. Exciton quenching therefore depends on intrachain interchromophoric spectral overlap, which is controlled by temperature.

Important insight into the fate of primary photoexcitations is gained by a comparison of the spectral position of SMs and undiluted bulk films as a function of temperature. The spectral position was determined by integration over the emission spectrum weighted by photon energy. Whereas the averaged spectral position of 17 single molecules is temperature independent, a linear shift with temperature is observed for the bulk [Fig. 3(d)]. For single chains, unidirectional downhill energy transfer to the global minimum, i.e., the lowest energy chromophore, is usually absent at low temperatures due to the lack of spectral overlap between the few donor and acceptor chromophore units on a SM. As the chromophore spectra broaden with increasing temperature, thereby enabling downhill energy transfer, uphill energy migration also becomes possible due to thermally assisted exciton hopping. On average, the spectral position of the SM emission therefore does not change as all chromophores contribute to emission. The case is very different in the bulk film, where many more neighboring sites exist with suitable spectral overlap. Here, three-dimensional exciton diffusion is possible at all temperatures and many chromophore sites are visited during the excitonic random walk. In this case emission occurs from chromophores within approximately $k_B T$ of the global energetic minimum of the inhomogeneously broadened three-dimensional density of states [26,28].

Previous attempts to describe EET from polymeric hosts to guest dye molecules in photovoltaic and electroluminescence applications have invoked a thermally activated intramolecular diffusion process, although the origin of this has not been clear [29]. Our data show that the activation energy of 16 meV found in Ref. [29] arises due to thermal chromophore linewidth broadening and corresponds to the intramolecular disorder. Single polymer chains can behave as collective, incoherently coupled, emitters at room temperature, which can lead to efficient fluorescence quenching on defects. This form

of chromophore coupling is, however, no fundamental property of conjugated polymers, and can be fully dispersed by cooling. Chemical engineering should thus allow a control of the degree of intramolecular EET by controlling the level of intramolecular disorder as well as homogeneous line shapes.

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