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Ultrafast intramolecular energy transfer in single conjugated polymer chains probed by polarized single chromophore spectroscopy

J. G. Müller, J. M. Lupton,[a] and J. Feldmann
Photonics and Optoelectronics Group, Physics Department and CeNS, Ludwig-Maximilians-Universität München, Amalienstrasse 54, 80799 Munich, Germany

U. Lemmer
Lichttechnisches Institut, Universität Karlsruhe, Kaiserstrasse 12, 76128 Karlsruhe, Germany

U. Scherf
FB Chemie, Universität Wuppertal, Gauss-Strasse 20, 42097 Wuppertal, Germany

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Single molecule spectroscopy of rigid-rod ladder-type conjugated polymers reveals individual chromophore units on a polymer chain, exhibiting fluorescence linewidths of less than 1 nm. Whereas the fluorescence from a single chromophore is fully linearly polarized at low temperatures, a number of excitation pathways and polarizations exist due to rapid intramolecular energy transfer to the emitting site. We propose that the slightly branched structure of the polymer results in neighboring molecular sites with orthogonal dipole orientations, enabling rapid polarization rotation. We demonstrate linearly polarized emission, which is independent of the excitation plane of polarization and may form the basis for molecular optical logic operations. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1647704]

Single molecule spectroscopy is a powerful analytical tool to study the intrinsic electronic properties of optically active materials in the absence of disorder induced inhomogeneous broadening.[1,2] In combination with polarization sensitive excitation and detection it can be used to derive information on molecular orientation, the conformation of macromolecular compounds,[3–5] or even supramolecular arrangements of natural photosynthetic pigments. Conjugated polymers form an exciting class of semiconducting materials and find wide applicability in numerous optoelectronic devices. These macromolecules are commonly thought of as long chains of weakly interacting chromophore units. Spectroscopy of isolated single chains of these molecules has thus far been limited to room temperature and predominantly high molecular weight materials with a low degree of order. In many cases, the spectroscopic signatures observed from single polymer chains are similar to those of the bulk, except for the tendency of isolated chains to exhibit strong fluorescence intermittency and a weak degree of polarization anisotropy under the condition of collapsed chain conformations.[3,4]

In this letter we discuss the polarization dependence of excitation and emission of highly emissive ladder-type rigid-rod conjugated polymers, which find applications in a range of devices such as light-emitting diodes and lasers. We observe fully polarized emission, as well as ultrafast rotation of the plane of polarization between absorption and emission. The present results complement our recent studies of temperature dependent energy transfer in conjugated polymers, which we found to be controlled by the average chromophore linewidth as well as the level of intramolecular disorder.[7] Here, we discuss a specific case of efficient intramolecular energy transfer occurring in branched structures.

Samples for single molecule spectroscopy were prepared by dispersing a methyl substituted ladder-type poly(para-phenylene) polymer (MeLPPP, see Fig. 1) in toluene solution in a polystyrene matrix at very low concentrations and subsequent spin-coating under inert conditions. The films were mounted in a continuous flow helium cryostat under a vacuum of 10^{-6} mbar. Fluorescence was excited using linearly polarized light from a pulsed Ti:sapphire laser operating at 80 MHz repetition rate and generating pulses of 100 fs duration, frequency doubled and focused to a spot approximately 100 μm in diameter. The laser pulse was centered at 426 nm (2.911 eV) (i.e., in the first vibronic of the polymer absorption band) and had a spectral width of approximately 8 nm (55 meV), thereby allowing the simultaneous excitation of many different molecules. The photoluminescence (PL) was collected in an imaging microscope through an objective with a numerical aperture of 0.55, dispersed in a monochromator and detected using a LaVision Picostar intensified gated charge coupled device (CCD) camera. Evidence for the detection of individual molecules comes both from the strong fluorescence intermittency observed as well as the scaling of the number of fluorescence centers with polymer concentration. From the density of the polymer matrix (1.05 $\mathrm{g\,cm^{-3}}$), the molecular weight of MeLPPP ($M_w = 50\,000$), the sample thickness of 50 nm as determined through interferometry, and the concentration of MeLPPP in the polystyrene matrix of 10^{-7} weight by weight we expect an average distance between MeLPPP molecules in the sample plane of approximately 4 μm. The experimental observations in the far field projection of the microscope image on the CCD detector coincide with this value within a factor of 2.

For polarized fluorescence measurements the half-wave plate used to set the polarization of the laser and the analyzer

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[a] Author to whom correspondence should be addressed; electronic mail: john.lupton@physik.uni-muenchen.de

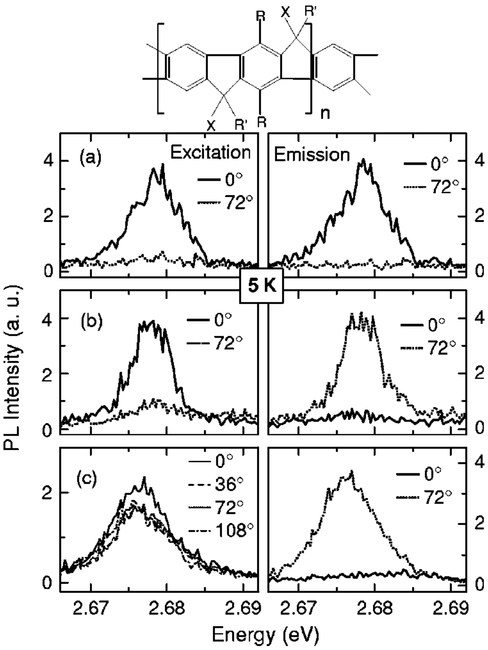

FIG. 1. PL spectra of single MeLPPP molecules at 5 K in dependence of the plane of polarization of the exciting laser beam (left panel) and the emitted light (right panel). The relative polarization angles are given in the graphs. (a) Polarization of excitation and emission in phase. (b) Polarization of excitation and emission out of phase. (c) No polarization dependence of excitation with fully polarized emission. The chemical structure of MeLPPP is shown at the top (X:methyl, R:*n*-hexyl, R′:1,4-decylphenyl).

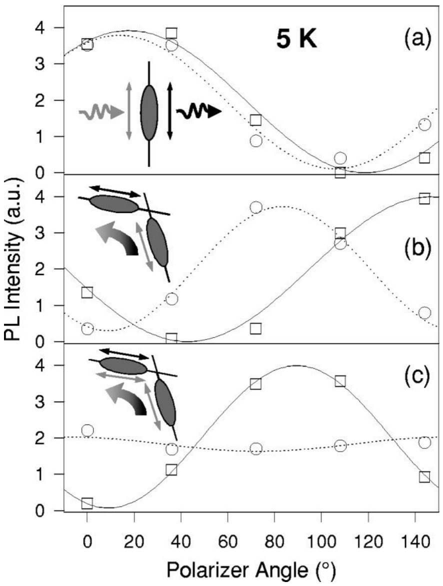

FIG. 2. Polarization angle dependent intensities in emission (□) and excitation (○) for the spectra shown in Fig. 1 with $\cos^2(\theta)$ fits as a guide to the eye (solid line: emission, dashed line: excitation). (a) Linear polarization in excitation and emission from a single dipole. (b) Rotation of the plane of polarization between excitation and emission due to energy transfer between at least two chromophores. (c) Excitation of multiple chromophores at different angles with rapid energy transfer to a single chromophore exhibiting linearly polarized PL. The sketches show the interaction between different chromophore units on the polymer chain. Gray arrows indicate the polarization of excitation, black arrows of emission.

in the fluorescence pathway were consecutively cycled in steps of 36°, so that at least ten spectra were measured for each combination of polarizations.

Figure 1 shows typical PL spectra of single MeLPPP molecules at 5 K in dependence of the plane of polarization of the incident laser (left panel) and the emission (right panel). The emission band shown corresponds to the strong 0–0 line of MeLPPP at 2.676 eV (463 nm). The spectral width of the single molecule is in the range of 5 meV (1 nm), which is almost two orders of magnitude less than what has previously been reported in single molecule studies of conjugated polymers at room temperature.[3,6] The PL spectra for two different planes of polarization of the laser are shown in the left panel of Fig. 1(a), demonstrating that the absorption depends strongly on the polarization of the incident light. An analogous change in intensity is observed if the excitation polarization is set to maximum absorption and an analyzer is rotated in the path of the collected fluorescence, as shown in the right panel of Fig. 1(a). This indicates that both emission and absorption occur from the same species, which has a linear dipole moment. A similar effect is shown in Fig. 1(b), however in this case the polarization angles of excitation and PL are not in phase, indicating that absorption occurs from one linear segment and emission from a second linear segment with a different orientation. The case is very different in Fig. 1(c), where virtually no effect of polarization is observed in excitation, but the emission remains fully polarized. This suggests that a number of units with different dipole orientations may absorb, but emission may only occur from one single unit.

The results are summarized in Fig. 2, where the polarization angle dependent fluorescence intensities from Fig. 1 are plotted together with $\cos^2\theta$ fits. In Fig. 2(a) both excitation and emission are in phase, suggesting that the molecule consists of a linear arrangement of chromophores. We recently argued that the PL observed in Figs. 1(a) and 2(a) may correspond to the emission from a single chromophore unit.[7] In contrast, in Fig. 2(b) at least two chromophore units are involved in absorption and emission, giving rise to the phase shift in polarization. As the emission is again fully polarized we conclude that ultrafast intramolecular energy transfer occurs from one chromophore to the other, and that the absorbing chromophore emits at most 10% of the total fluorescence. This result is rather surprising, as intramolecular energy transfer along the backbone of conjugated polymers is generally considered to be rather slow and inefficient.[8] Our results, however, indicate that on-chain energy transfer is so efficient that most of the excitation energy is channeled from one chromophore to the other before it decays radiatively. This observation is even more pronounced in Fig. 2(c), where the excitation exhibits virtually no polarization dependence, but the emission is again fully polarized. We propose that this case originates due to at least two optically active chromophore units on the polymer chain, which have dipole orientations almost orthogonal to one another. Whereas both units absorb radiation of different polarization, only one unit may emit. In this case ultrafast energy transfer on time scales much shorter than the exciton lifetime of approximately 300 ps gives rise to a conversion of unpolarized excitation light to fully linearly polarized emission. Although we are not able to provide a definitive quantitative estimate for the number of species responsible for the polarization effects observed, we can make a lower estimate. Whereas only one species is required to achieve case (a), at least two are necessary to arrive at an effect as seen in (b) or (c). Most probably even more units are involved in case (c).

As sketched in Fig. 2, polarized excitation and emission allows us to gain insight into the conformation of a single polymer chain. Hu *et al.* previously presented a study of polarization anisotropies of poly(phenylene-vinylene) polymers which led them to conclude that polarized emission occurs from aggregated chain segments of the flexible worm-like polymer.[3,4] In the present case of MeLPPP, the full ladder structure inhibits bending and coiling, and polarization rotation effects such as in Figs. 2(b) and 2(c) are not expected. We propose that rapid energy transfer and polarization rotation occur as a result of the slightly branched structure of MeLPPP which contains on average 2-3 linear, conjugated MeLPPP segments per molecule in a rigid, nonlinear arrangement. Measurements of the distinct increase of the molecular weight during the multistep synthesis of MeLPPP[9] suggest that a minor side reaction during the first step of the cyclization protocol of the single stranded precursor polymers into MeLPPP (i.e., single electron transfer followed by radical recombination under pinacol formation, which competes with the regular addition of methyl lithium to the diarylcarbonyl functions) creates such branching (or crossing) points. As a result, unlike for most other conjugated polymers, it is not possible to generate polarized PL through stretch-aligning MeLPPP. It is conceivable that chemical linking of molecular segments with different dipole orientations leads to rapid coherent intramolecular energy transfer by molecular relaxation (Kasha's rule), as, for example, in dendritic macromolecules.[10] In contrast, incoherent exciton hopping by resonant dipole–dipole coupling is usually invoked to describe intramolecular relaxation in conjugated polymers.[8]

We found that the degree of polarization of single polymer chain fluorescence is generally much stronger at low than at high temperatures.[7] However, a few molecules also exhibit strong polarization effects at room temperature, as shown in Fig. 3. At room temperature the single molecule emission spectrum is almost an order of magnitude broader. Figure 3(a) displays a weak polarization effect in excitation yet fully polarized emission. In this case the polarization of excitation and PL are out of phase by 90°: no light is emitted in the polarization plane which is most efficient for excitation (circles). In contrast, in Fig. 3(b) the excitation is completely independent of the plane of polarization, and the emission indicates components from different segments of slightly different orientation, as the PL intensity does not drop to zero for any analyzer angle. In both cases at least two nonparallel chromophore units can absorb, but whereas efficient energy transfer to one single unit occurs in the case of Fig. 3(a), bidirectional energy transfer gives rise to multiple chromophore emission in the case of Fig. 3(b).

The conversion of unpolarized light to fully polarized light as well as the controlled rotation of the plane of polarization between excitation and emission may be of interest for the design of novel optical molecular logic gates. The fully polarized emission from most likely a single chromophore also suggests that these molecules may be very appealing materials for developing spectrally narrow single photon sources with a high degree of control over photon polarization and efficient energy transfer from multiple absorbers to a single emitter.

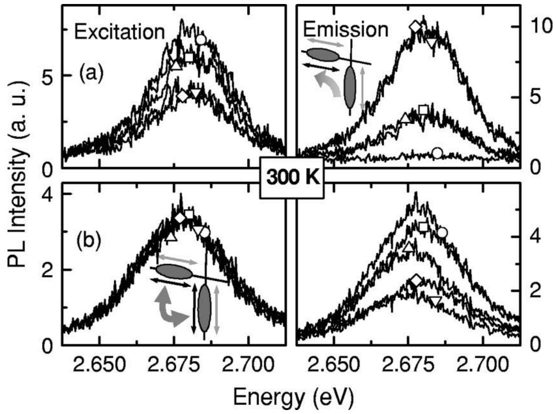

FIG. 3. PL spectra of single MeLPPP molecules at 300 K in dependence of the plane of polarization of the exciting laser beam (left panel) and the emitted light (right panel) for relative polarization angles of 0° (□), 36° (○), 72° (△), 108° (▽), 144° (◇). (a) Weakly polarized excitation and fully polarized emission. (b) Unpolarized excitation and partially polarized emission.

Furthermore, our results show that even in rigid molecules rapid depolarization may occur, suggesting that a number of rigid-rod defect conformations exist in the form of crossed chain segments. As the electrically active defect density in these polymers is very small (typically 10^{16} cm^{-3}),[11] but we are nevertheless able to identify single structural defects spectroscopically, we can conclude that the density of these structural defects is substantially higher and that they do not act as trapping sites in charge transport. The high degree of chemical and photochemical stability and purity of MeLPPP as well as narrow, well-defined electronic transitions suggest future application potential to single molecule optoelectronic devices.

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