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Efficient Light Harvesting in Dye-Endcapped Conjugated Polymers Probed by Single Molecule Spectroscopy

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Abstract: The development of sophisticated microscopic models of energy transfer in linear multichromophoric systems such as conjugated polymers is rarely matched by suitable experimental studies on the microscopic level. To assess the roles of structural, temporal, and energetic disorder in energy transfer, single molecule spectroscopic investigations of the elementary processes leading to energetic relaxation in conjugated polymers are desirable. We present a detailed study of energy transfer processes occurring in dye-endcapped conjugated polymer molecules on the single molecule level. These processes are mostly masked in ensemble investigations. Highly efficient intramolecular energy transfer along a single polyindenofluorene chain to a perylene endcap occurs in many instances and is resolved in real time. We further consider the spectral emission characteristics of the single molecule, the polarization anisotropy which reveals the chain conformation, the fluorescence intermittency, and the temperature dependence and conclude that the efficiency of energy transfer in the ensemble is controlled by the statistics of the individual molecules. The weak thermal activation of energy transfer indicates the involvement of vibrational modes in interchromophoric coupling. Whereas backbone−endcap coupling is strong, the rate-limiting step for intramolecular energy transfer is the migration along the backbone. The results are particularly relevant to understanding undesired exciton trapping on fluorenone defects in polyfluorenes.

I. Introduction

Over the past decades, the exceptional interest in the photophysical properties of luminescent conjugated polymers has been stimulated by the simplicity of constructing bright and efficient light-emitting diodes.[1] A promising class of materials for such devices are polymer-based guest−host systems, in which a low concentration of a guest (a dye or a polymer) can lead to a strong enhancement of photoluminescence (PL) and electroluminescence quantum efficiencies.[2] Also, color-tunability across the visible spectrum through changes of either the type or the concentration of the guest has been demonstrated and permits a simplified design of full-color displays based on a common host polymer.[3−5] For these composite materials, energy transfer from the polymer host to the guest is the key process in light generation,[5−12] which has been found to occur in two steps: (1) the diffusion of the excitation within the host polymer matrix and (2) energy transfer from the host to the guest.[9,11,12] As vital as the intentional energy transfer in guest−host systems is, it can also be detrimental to device operation as the excitation energy can be funneled to defect sites or traps. This process effectively lowers the efficiency. Prominent examples of such a quenching mechanism are exciton funneling to nonemissive trap states observed in multichromophoric complexes[13−17] as well as inter- and intrachain exciton funneling to emissive on-chain keto defects in polyfluorenes, which vastly impedes color

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(1) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121−128.

(2) Wang, H.-L.; McBranch, D. W.; Klimov, V. I.; Helgeson, R.; Wudl, F. *Chem. Phys. Lett.* **1999**, *315*, 173−180.

(3) McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. *Adv. Mater.* **1999**, *11*, 1349−1354.

(4) Tasch, S.; List, E. J. W.; Ekström, O.; Graupner, W.; Leising, G.; Schlichting, P.; Rohr, U.; Geerts, Y.; Scherf, U.; Müllen, K. *Appl. Phys. Lett.* **1997**, *71*, 2883−2885.

(5) (a) Ego, C.; Marsitzky, D.; Becker, S.; Zhang, J.; Grimsdale, A.; Müllen, K.; MacKenzie, J. D.; Silva, C.; Friend, R. H. *J. Am. Chem. Soc.* **2002**, *125*, 437−443. (b) Becker, S.; Ego, C.; Grimsdale, A. C.; List, E. J. W.; Marsitzky, D.; Pogantsch, A.; Setayesh, S.; Leising, G.; Müllen, K. *Synth. Met.* **2002**, *125*, 73−80.

(6) Virgili, T.; Lidzey, D. G.; Bradley, D. D. C. *Adv. Mater.* **2000**, *12*, 58−62.

(7) Tasch, S.; List, E. J. W.; Hochfilzer, C.; Leising, G.; Schlichting, P.; Rohr, U.; Geerts, Y.; Scherf, U.; Müllen, K. *Phys. Rev. B* **1997**, *56*, 4479−4483.

(8) Cerullo, G.; Nisoli, M.; Stagira, S.; De Silvestri, S.; Lanzani, G.; Graupner, W.; List, E. J. W.; Leising, G. *Chem. Phys. Lett.* **1998**, *288*, 561−566.

(9) (a) List, E. J. W.; Creely, C.; Leising, G.; Schulte, N.; Schlüter, A. D.; Scherf, U.; Müllen, K.; Graupner, W. *Chem. Phys. Lett.* **2000**, *325*, 132−138. (b) Wiesenhofer, H.; Zojer, E.; List, E. J. W.; Scherf, U.; Brédas, J.-L.; Beljonne, D. *Adv. Mat.* **2006**, *18*, 310−314.

(10) Gupta, R.; Stevenson, M.; McGehee, M. D.; Dogariu, A.; Srdanov, V.; Park, J. Y.; Heeger, A. J. *Synth. Met.* **1999**, *102*, 875−876.

(11) Buckley, A. R.; Rahn, M. D.; Hill, J.; Cabanillas-Gonzalez, J.; Fox, A. M.; Bradley, D. D. C. *Chem. Phys. Lett.* **2001**, *339*, 331−336.

(12) Lemmer, U.; Ochse, A.; Deussen, M.; Mahrt, R. F.; Göbel, E. O.; Bässler, H.; Bolivar, P. H.; Wegmann, G.; Kurz, H. *Synth. Met.* **1996**, *78*, 289−293.

(13) VandenBout, D. A.; Yip, W. T.; Hu, D. H.; Fu, D. K.; Swager, T. M.; Barbara, P. F. *Science* **1997**, *277*, 1074−1077.

(14) Yu, J.; Hu, D.; Barbara, P. F. *Science* **2000**, *289*, 1327−1330.

(15) Hofkens, J.; Maus, M.; Gensch, T.; Vosch, T.; Cotlet, M.; Köhn, F.; Herrmann, A.; Müllen, K.; De Schryver, F. *J. Am. Chem. Soc.* **2000**, *122*, 9278−9288.

(16) Hofkens, J.; Schroeyers, W.; Loos, D.; Cotlet, M.; Kohn, F.; Vosch, T.; Maus, M.; Herrmann, A.; Müllen, K.; Gensch, T.; De Schryver, F. C. *Spectrochim. Acta, Part A* **2001**, *57*, 2093−2107.

(17) Müller, J. G.; Lemmer, U.; Raschke, G.; Anni, M.; Scherf, U.; Lupton, J. M.; Feldmann, J. *Phys. Rev. Lett.* **2003**, *91*, 267403.

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purity.[18,19] In contrast, a striking application making use of intramolecular energy transfer in conjugated polymers is ultrasensitive chemical and biochemical sensing based on reversible fluorescence quenching in a polyanionic poly(*para*-phenylenevinylene).[20] Likewise, for solar cells the migration of optically generated electronic excitations to dissociation centers is required for charge generation.[21] In this case, an analogy to natural[22−25] or synthetic[26,27] light-harvesting complexes can be drawn, where the efficiency of exciton funneling to the reaction center approaches unity.[22] Recent publications have stressed the necessity to differentiate between intermolecular energy transfer between adjacent polymer chains, and intramolecular energy transfer, that is, a hopping of the excitation along the polymer chain in the absence of any chain−chain contact.[28−31]

In this contribution, the nature of intramolecular energy transfer in a dye-endcapped conjugated polymer,[32,33] which has perylene derivatives covalently bound to both ends (perylene endcap, or PEC) of a polyindenofluorene (PIFTEH) chain with tetraethylhexyl substitutents (PEC-PIFTEH,[34] see Figure 1), is discussed in the light of single molecule spectroscopy. The PEC-PIFTEH copolymer is an appealing conjugated polymer for the production of efficient light-emitting diodes as covalent attaching of dyes to the polymer has the advantage of allowing the use of high acceptor concentrations without facing the problem of phase segregation, which may reduce the overall PL quantum yield.[5] Moreover, PEC-PIFTEH is also an ideal model system for studying energy transfer processes in conjugated polymers as both steps, the excitation diffusion along the host polymer chain and the energy transfer onto the perylene endcaps, can be investigated simultaneously. The studied polymer−endcap system in effect resembles a nanoscale photonic wire, where both the individual chromophores with respect to each other and the chromophore−endcap group act as model donor−acceptor systems. In contrast to previously studied supramolecular model systems,[35−37] the conjugated polymer constitutes a purely covalently bound conjugated structure with potentially strong interactions between the individual units. As single molecule spectroscopy eliminates the otherwise inherent averaging over a large ensemble of individual molecules, it is excellently suited for the direct investigation of the dynamics of the excitation within the molecule.[38,39]

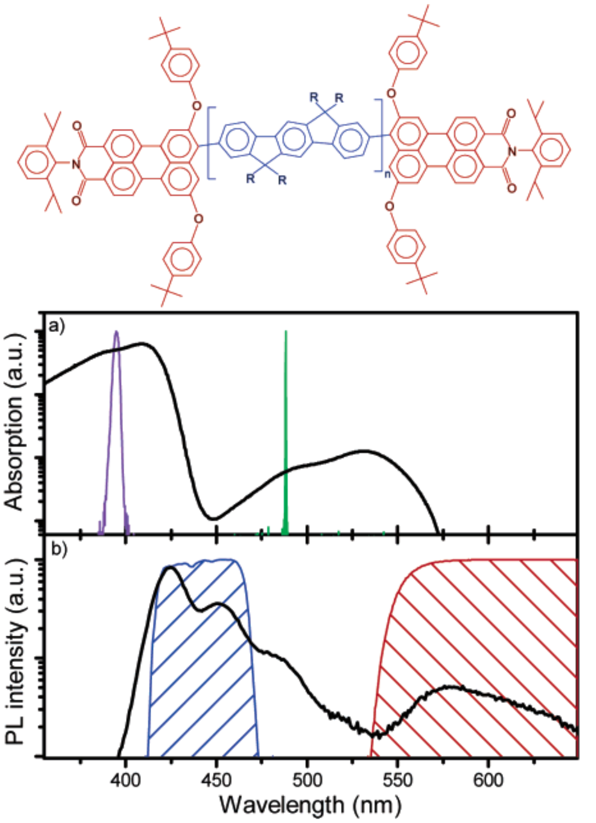

Figure 1. Absorption and emission spectra of the perylene-endcapped polyindenofluorene (PEC-PIFTEH) (R = ethylhexyl) polymer at 300 K shown on a logarithmic scale. (a) Absorption of PEC-PIFTEH dissolved in toluene (10 mg/L). The spectra of the laser excitation sources are indicated by the purple and green lines. (b) PL spectrum of PEC-PIFTEH dissolved in toluene (10^{-1} mg/L). The hatched areas indicate the transmission of the optical filters used for spectrally separating the polymer backbone emission (blue) from the endcap emission (red).

We recently demonstrated that this fascinating material system provides a graphical visualization of the failing of simple Förster theory in covalently bound molecular aggregates by showing that efficient energy transfer can occur from the backbone to the endcap in the absence of an appreciable spectral overlap between absorption and emission of the two at low temperatures.[40] Here, we demonstrate that this surprising efficiency in energy transfer also holds at room temperature. The weak temperature dependence observed further underlines that intramolecular energy transfer from the backbone to the endcap is mainly governed by temperature independent electronic couplings, whereas a clear thermal activation of the fluorescence depolarization of the backbone, and hence of the on-chain exciton mobility, is observed. By resolving the energy transfer

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(18) Lupton, J. M.; Craig, M. R.; Meijer, E. W. *Appl. Phys. Lett.* **2002**, *80*, 4489−4491.
(19) List, E. J. W.; Guentner, R.; de Freitas, P. S.; Scherf, U. *Adv. Mater.* **2002**, *14*, 374−378.
(20) Chen, L.; McBranch, D. W.; Wang, H.; Helgeson, R.; Wudl, F.; Whitten, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 12287−12292.
(21) Müller, J. G.; Anni, M.; Scherf, U.; Lupton, J. M.; Feldmann, J. *Phys. Rev. B* **2004**, *70*, 035205.
(22) Kühlbrandt, W. *Nature* **1995**, *374*, 497.
(23) Hofmann, C.; Ketelaars, M.; Matsushita, M.; Michel, H.; Aartsma, T. J.; Kohler, J. *Phys. Rev. Lett.* **2003**, *90*, 013004.
(24) Scholes, G. D. *Annu. Rev. Phys. Chem.* **2003**, *54*, 57−87.
(25) Fleming, G. R.; Scholes, G. D. *Nature* **2004**, *431*, 256−257.
(26) Adronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 1175−1185.
(27) De Schryver, F. C.; Vosch, T.; Cotlet, M.; Van der Auweraer, M.; Müllen, K.; Hofkens, J. *Acc. Chem. Res.* **2005**, *38*, 514−522.
(28) (a) Beljonne, D.; Pourtois, G.; Silva, C.; Hennebicq, E.; Herz, L. M.; Friend, R. H.; Scholes, G. D.; Setayesh, S.; Müllen, K.; Brédas, J. L. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 10982−10987. (b) Hennebicq, E.; Pourtois, G.; Scholes, G. D.; Herz, L. M.; Russel, D. M.; Silva, C.; Setayesh, S.; Grimsdale, A.; Müllen, K.; Brédas, J.-L.; Beljonne, D. *J. Am. Chem. Soc.* **2005**, *127*, 4744−4762.
(29) Nguyen, T. Q.; Wu, J. J.; Doan, V.; Schwartz, B. J.; Tolbert, S. H. *Science* **2000**, *288*, 652−656.
(30) Nguyen, T. Q.; Wu, J.; Tolbert, S. H.; Schwartz, B. J. *Adv. Mater.* **2001**, *13*, 609−611.
(31) Beljonne, D.; Pourtois, G.; Shuai, Z.; Hennebicq, E.; Scholes, G. D.; Brédas, J. L. *Synth. Met.* **2003**, *137*, 1369−1371.
(32) Rose, A.; Lugmair, C. G.; Swager, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 11298−11299.
(33) Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886−4893.
(34) Setayesh, S.; Marsitzky, D.; Müllen, K. *Macromolecules* **2000**, *33*, 2016−2020.
(35) Hernando, J.; de Witte, P. A. J.; van Dijk, E.; Korterik, J.; Nolte, R. J. M.; Rowan, A. E.; Garcia-Parajo, M. F.; van Hulst, N. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4045−4049.
(36) Heilemann, M.; Tinnefeld, P.; Mosteiro, G. S.; Parajo, M. G.; van Hulst, N. F.; Sauer, M. *J. Am. Chem. Soc.* **2004**, *126*, 6514−6515.
(37) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491−1546.
(38) Moerner, W. E.; Orrit, M. *Science* **1999**, *283*, 1670−1676.
(39) Moerner, W. E. *J. Phys. Chem. B* **2002**, *106*, 910−927.
(40) Becker, K.; Lupton, J. M.; Feldmann, J.; Setayesh, S.; Grimsdale, A. C.; Müllen, K. *J. Am. Chem. Soc.* **2006**, *128*, 680−681.

along the polymer backbone toward the perylene endcap in real-time, we demonstrate that intramolecular energy transfer along the polymer backbone, being slow and inefficient in the ensemble,[28] can actually be quite efficient in individual molecules. This constitutes a manifestation of the importance of nondipolar relaxation processes of the overall donor−acceptor excited-state complex.[24,25,41−46] Polarization sensitive single molecule spectroscopy reveals conformational aspects of the single polyindenofluorene chains, which are masked in the ensemble, and allows us to assess the degree of chain extension as well as the efficiency of interchromophoric excitation transfer. The investigation of single molecule PL spectra unveils a substantial degree of inhomogeneous broadening of the emission. As energy transfer along the polymer backbone in the dipole coupling limit depends on the spectral overlap of the transitions of adjacent donor and acceptor chromophores and therefore on the homogeneous and inhomogeneous line width,[17] the inefficiency of intramolecular energy transfer along the backbone is primarily a consequence of disorder broadening. This simple paradigm clearly breaks down when considering energy transfer over a large energy gap from the backbone to the endcap. Microscopic measurements of intramolecular energy transfer on the single molecule level are therefore crucial for establishing complete theoretical models of exciton migration in conjugated polymers,[28] as ensemble measurements cannot unveil all of the possible individual energy transfer processes in covalently bound systems.

II. Experimental Section

Sample Preparation. Two different samples for single molecule spectroscopy were prepared by spin-coating highly diluted solutions of either PEC-PIFTEH or of pure perylene dye molecules from toluene or chloroform solution containing 5 mg/mL Zeonex onto thoroughly cleaned suprasil substrates. Spinning at 5000 rpm yielded thin (approximately 20 nm) films. For the polymer sample, a concentration of PEC-PIFTEH of 10^{-7} w/w in Zeonex/toluene resulted in an average distance of approximately 5 μm between the fluorescent molecules within the film. A similar intermolecular spacing was achieved for the pure perylene dye sample at a concentration of 10^{-9} w/w in Zeonex/chloroform. For ensemble measurements, a higher concentration of the polyindenofluorene was chosen. Further details of the polymer system (full name: α,ω-bis(*N*-(2,6-diisopropylphenyl)-1,6-bis(4-*tert*-butylphenoxy)-3,4-dicarbonicaci dimide-9-perylene-poly-2,8-(6,6,12,12-tetraethylhexyl)indenofluorene) and of similar materials have been reported elsewhere.[5,28,34] Note that the synthesis of PEC-PIFTEH is similar to that of dye-endcapped polyfluorenes, described in detail previously.[5] The PEC fraction by molecular weight amounts to approximately 5%, corresponding to an average chain length of roughly 50 units.[28] As some polymer chains (∼60%[28,47]) only indicate the presence of a single endcap, one may conclude that the average chain length is somewhat shorter.[28] In contrast to this, consideration of the absorption strength together with the calculated oscillator strength has suggested an average chain length of 50−100 units, whereas the molecular weight M_n points toward approx. 30 units.[28] The samples have been found to be rather polydisperse (GPC against a polystyrene standard gave $M_w = 11\,000-40\,000$ g/mol at a polydispersity >3.6), corresponding to chain lengths of 15−55 units.[28] Because of the lack of suitable standards for GPC and light-scattering, it is hard to determine the persistence length of such a stiff rigid-rod polymer accurately. While a comparison of theoretical and experimental spectra of oligomers with the polymers has previously indicated an effective conjugation length of 4−6 units in absorption and of 6−7 units in emission,[28] we note that our recent detailed analysis of the conjugation length on rigid single polymer molecules suggested that a mere direct comparison of polymer and oligomer electronic spectra underestimates the true conjugation length.[48] Because of the structural similarity of PIFTEH and the ladder-type poly(para-phenylene),[48] we propose that the conjugation length could substantially exceed the previously suggested upper limit of 7 units.[28]

Ensemble Spectroscopy. Room-temperature absorption and PL spectra were recorded using a Varian Cary 50 UV−vis spectrophotometer and a Varian Cary Eclipse fluorescence spectrophotometer, respectively.

Time-Resolved Ensemble Spectroscopy. For temporally and spectrally resolved ensemble measurements, a Hamamatsu streak camera combined with a spectrometer (Cromex, 40 grooves/mm, resolution 4.2 nm) was used. The streak camera was operated in a mode providing 18 ps time resolution. The frequency-doubled output (395 nm) of a Kerr-lens mode-locked titanium-sapphire laser (120 fs pulses, 76 MHz repetition rate) was used for excitation of the polymer backbone. All time-resolved measurements were performed at room temperature, and the samples were placed in a vacuum chamber at a pressure below 10^{-6} mbar to prevent photooxidation.

Single Molecule Spectroscopy. The samples were mounted in a continuous flow cold finger helium cryostat under a vacuum of 10^{-6} mbar, providing temperatures ranging from 5 to 300 K. The polymer backbone could be 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. Typical intensities were 50 W/cm^2. The laser pulse was centered at 395 nm with a spectral width of 2.8 nm (180 cm^{-1}), thereby allowing the simultaneous excitation of different polymer chains or different chromophores on the chain. An Ar$^+$-laser operating at 488 nm was used for the direct excitation of the perylene dyes. Optical filters allowed a spectral separation of the blue polymer backbone emission from the red perylene endcap emission. Both the laser spectra and the transmission characteristics of the filters are given in Figure 1. The PL was collected in an imaging microscope using an objective with a numerical aperture of 0.55, dispersed in a monochromator (300 grooves/mm) and imaged onto a cooled, front-illuminated charge-coupled device camera (Sensicam QE, PCO AG, Kelheim, Germany). The intensity transients of single molecules were obtained from fluorescence microscope images. For time-resolved PL experiments, a LaVision Picostar intensified gated charge-coupled device camera was used, providing a temporal resolution of 200 ps with a timing accuracy of 50 ps. For polarization-sensitive single molecule spectroscopy, a half-wave plate in the excitation beam was used to set the polarization of the laser. An analyzer in the PL pathway allowed the determination of the plane of polarization of the emission. Both were cycled consecutively in steps of 22.5° for at least two full cycles. Polarization angle-dependent PL intensities were obtained from the fluorescence microscope images and corrected for the slight polarization dependence of the sensitivity of the detection system.

III. Results

(a) Energy Transfer Imaging in Single Polymer Molecules. We begin by discussing the optical properties of the material system and demonstrating energy transfer on the single molecule level at room temperature. The absorption and PL spectra of

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(41) Tretiak, S.; Mukamel, S. *Chem. Rev.* **2002**, *102*, 3171−3212.
(42) Grage, M. M. L.; Zaushitsyn, Y.; Yartsev, A.; Chachisvilis, M.; Sundström, V.; Pullerits, T. *Phys. Rev. B* **2003**, *67*, 205207.
(43) Jang, S.; Newton, M. D.; Silbey, R. *Phys. Rev. Lett.* **2004**, *92*, 218301.
(44) Sumi, H. *J. Phys. Chem. B* **1999**, *103*, 252−260.
(45) Scholes, G. D.; Fleming, G. R. *J. Phys. Chem. B* **2000**, *104*, 1854−1868.
(46) Lin, S. H.; Xiao, W. Z.; Dietz, W. *Phys. Rev. E* **1993**, *47*, 3698−3706.
(47) Muls, B.; Uji-I, H.; Melnikov, S.; Moussa, A.; Verheijen, W.; Soumillion, J.-P.; Josemon, J.; Müllen, K.; Hofkens, J. *ChemPhysChem* **2005**, *6*, 2286−2294.
(48) Schindler, F.; Jacob, J.; Grimsdale, A. C.; Scherf, U.; Müllen, K.; Lupton, J. M.; Feldmann, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 1520−1525.

PEC-PIFTEH measured from toluene solution with concentrations of 10 and 10^{-1} mg/L, respectively, are depicted in Figure 1a and Figure 1b on a logarithmic scale. The absorption shows two broad features originating from the dominant polymer backbone absorption at 410 nm and the weaker perylene absorption at 530 nm. Because of the large offset in the absorption energy of the two constituents, it is possible to exclusively excite the two molecular components individually with the laser sources at 395 nm and at 488 nm. The PL of PEC-PIFTEH (Figure 1b) excited at 395 nm (the $\pi-\pi^*$ transition of the polymer backbone) corresponds to a superposition of the polymer emission peaking at 424 nm and the perylene endcap emission centered at 580 nm. The small spectral overlap of the polymer emission and the endcap absorption should in principle enable energy transfer from the polymer backbone to the perylene endcap.[49] Accordingly, emission from the perylene endcap is observed, providing direct evidence for energy transfer as the perylene is not excited directly at 395 nm. There are two steps necessary for energy transfer from the polymer backbone to the perylene endcaps: (1) the diffusion of the excitation along the polymer backbone and (2) the final energy transfer step from the polymer to the endcap.[9] Intramolecular energy transfer, which is the only way of transferring the excitation energy to the perylene either in dilute films containing isolated molecules or in solutions, has previously been shown to be inefficient as compared to the highly efficient intermolecular energy transfer occurring in bulk films of PEC-PIFTEH.[28,31] To account for this high efficiency in bulk films,[28] step (2) should quite generally be efficient. Under this assumption, exciton diffusion along the polymer backbone appears to be the limiting process for light harvesting in this material system. This process will be investigated in the course of the present contribution.

Intramolecular energy transfer is directly visualized in the fluorescence microscope images[50] of isolated PEC-PIFTEH chains dispersed in a Zeonex matrix. Here, PL from the polymer and the perylene dye is spectrally separated with optical filters, the transmission properties of which are given in Figure 1b. Figure 2a shows the superposition of the spatial emission distribution of single polymer chains excited at 395 nm (blue) and the perylene endcap excited via energy transfer from the polymer (red). The different situations observed range from very efficient energy transfer, corresponding to exclusive perylene emission (red), over moderately efficient energy transfer with both backbone and dye emission (marked violet as the combination color of red and blue), to no energy transfer, resulting in emission purely from the polymer backbone (blue).

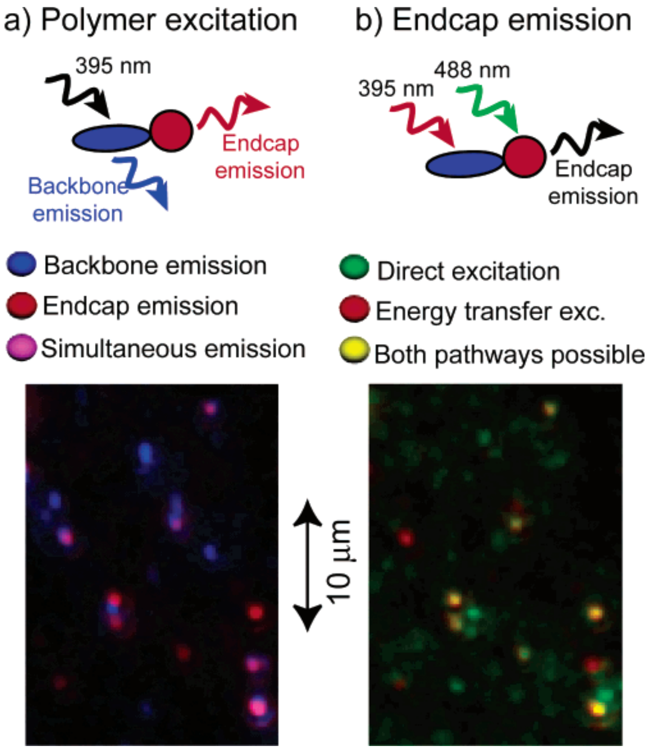

Figure 2. False-color fluorescence microscope images of isolated PEC-PIFTEH molecules dispersed in a Zeonex matrix at 300 K, illustrating the different excitation and emission pathways of the polymer. The two panels show the same sample position, which is visible in the arrangement of the molecules. (a) Excitation of the polymer backbone at 395 nm. Superimposed PL microscope images of the polymer backbone emission and the emission from the endcaps, which were recorded separately by using spectral filters. Blue spots indicate backbone emission, whereas red spots correspond to endcap emission. Simultaneous emission of both species appears purple. (b) Different excitation pathways of the endcaps. Superimposed PL microscope images of the endcap excited via energy transfer from the PIFTEH backbone (i.e., excitation at 395 nm, encoded in red) and excited directly at 488 nm, encoded in green. Endcaps that can be excited by both pathways are shown in yellow.

We next consider the actual excitation pathways of the same molecules. Figure 2b shows the superposition of the microscope image of the identical spatial position on the sample as in Figure 2a for different excitation pathways. The PL of the perylene endcap excited via energy transfer from the polymer (excitation at 395 nm) is marked red, and the emission of the perylene endcap excited directly without energy transfer at 488 nm is indicated by green spots. Perylenes excited by both pathways appear yellow. This proves directly that the observed emission in the spectral band of the perylene encoded in red in Figure 2a indeed stems from perylene dyes bound to the polymer, as they can be excited directly at 488 nm without pumping the polymer. The strength of single molecule spectroscopy comes into play to reveal the inhomogeneity and variety of the individual polymer chains due to their specific structural and conformational properties, which constitutes the focus of this work. Note that some endcaps can only be excited via energy transfer from the backbone, while a direct excitation is not efficient. This may be a consequence of either unfavorable orientation of the endcap with respect to the plane of polarization of the laser or result from better spectral overlap between the laser spectrum and the molecular absorption spectrum in the case of backbone excitation. In contrast, the fact that some perylene dyes are only visible when excited directly and cannot be excited by energy transfer may be explained by the presence of nonradiative defects on the polymer chain, inhibiting polymer backbone emission as well as efficient energy transfer to the perylene endcap.[13,14,17,51,52] The important point to note is that inefficient intramolecular energy transfer from the polymer to the endcap is not a universal property of the system, in contrast to the conclusions drawn from ensemble measurements and quantum chemical calcula-

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(49) Förster, T. *Ann. Phys.* **1948**, *2*, 55.

(50) Deniz, A. A.; Dahan, M.; Grunwell, J. R.; Ha, T.; Faulhaber, A. E.; Chemla, D. S.; Weiss, S.; Schultz, P. G. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 3670−3675.

(51) Hu, D. H.; Yu, J.; Padmanaban, G.; Ramakrishnan, S.; Barbara, P. F. *Nano Lett.* **2002**, *2*, 1121−1124.

(52) Mirzov, O.; Cichos, F.; von Borczyskowski, C.; Scheblykin, I. *Chem. Phys. Lett.* **2004**, *386*, 286−290.

tions:[28,31] for many individual molecules, highly efficient energy transfer from the polymer to the endcap occurs.

We estimate that around 25% of all single molecules show efficient energy transfer from the polymer to the endcap. This case appears as red spots in Figure 2a showing exclusive emission from the endcap upon backbone excitation. Such highly efficient energy transfer to the perylene endcap may be explained by a fast downhill cascade process in the inhomogeneously broadened energy distribution of sites of the polymer backbone, followed by a jump of the on-chain molecular exciton[48] to the perylene endcap. A high energy transfer efficiency along the backbone is maintained throughout the process by favorable spectral overlaps of the microscopic emitting and absorbing units, the polymer chromophores.[17] In contrast, inefficient energy transfer along the backbone arises due to energetic barriers in the energetic distribution of sites, slowing down the transfer process which in turn competes directly with spontaneous emission from the polymer. These interpretations will be justified by comparing estimates of the homogeneous and inhomogeneous line width of the polymer backbone with each other. Because of the large absorption cross-section of the polymer chain as compared to the perylene endcap, it is actually possible to excite the endcap more efficiently via energy transfer from the polymer than by direct absorption, demonstrating the light-harvesting properties of PEC-PIFTEH.

(b) Fluorescence Intensity Traces of Single Polymer Molecules. The temporal evolution of the emission of single molecules can provide detailed information on the photophysical processes in multichromophoric molecules.[13,15,27,53] A collection of four typical fluorescence intensity transients of single PEC-PIFTEH molecules are given in Figure 3. The transient in Figure 3a shows a two-step photobleaching of the perylene emission observed when exciting the perylene endcaps on the polymer chain directly with linearly polarized light at 488 nm. The emission is very stable with time and does not exhibit any blinking on the time scale of the measurement. In this case, the two independent emitters at the ends of the polymer chain are revealed by their uncorrelated emission. The comparable intensity drops following the two irreversible photobleaching events can be viewed as a signature of an almost elongated polymer chain with two emitting perylene endcaps with nearly parallel transition dipoles.[54] Such a situation of noninteracting fluorophore units was recently investigated using photon statistics, which could be directly related to photobleaching,[54] and has also been employed to assess the magnitude of chain extension.[47] Note that only about one-half of all molecules appear to contain two endcaps and exhibit a two-step photobleaching trace, in agreement with previous observations on single dye-endcapped polymers.[47]

In contrast, if the endcap is excited by energy transfer from the polymer backbone, strong fluorescence intermittency is observed. This intermittency is a characteristic of the backbone, not of the endcap, and is most likely due to fluctuations of the intrachain energy transfer efficiency, a process which was recently identified in single multichromophoric polymer chains.[55]

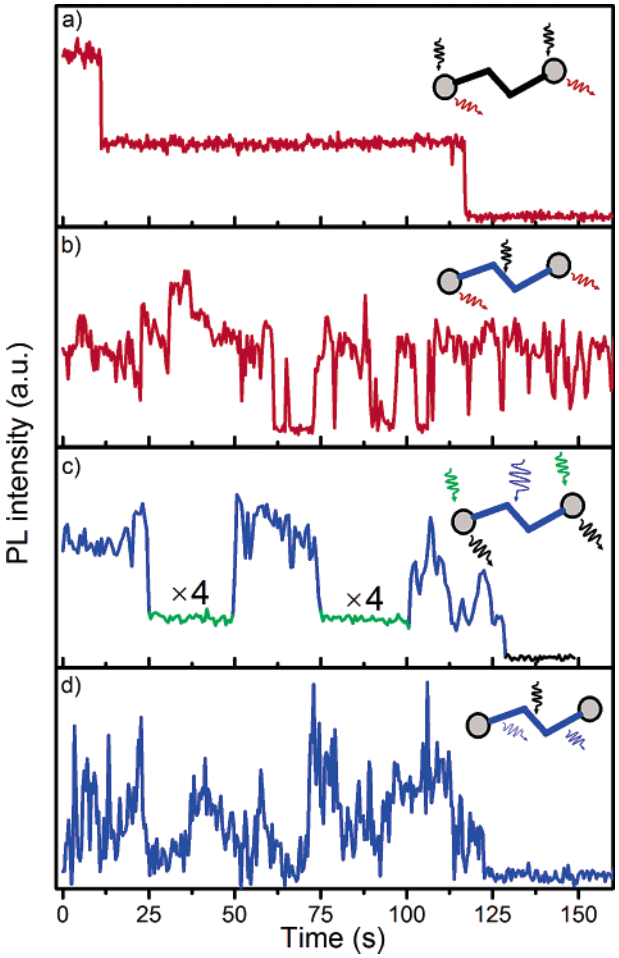

Figure 3. Fluorescence intensity traces of four characteristic single PEC-PIFTEH molecules dispersed in a Zeonex matrix at 300 K. The integration times were 0.25, 0.5, 0.6, and 0.4 s for panels a−d, respectively. (a) Typical two-step photobleaching transient of the polymer endcap emission following direct excitation at 488 nm. (b) Pumping of the dye endcap by energy transfer from the polymer backbone. In this case, strong intermittency of the endcap emission is observed due to reversible exciton quenching effects on the backbone. (c) Switching between energy transfer (395 nm, blue line) and direct (488 nm, green line) excitation of the endcap on one single molecule. Note that the green part of the trace is multiplied by a factor of 4. Indirect excitation of the endcap leads to stronger emission due to the efficient light-harvesting effect but also results in substantially more intensity fluctuations. This is not intrinsic to the endcap, but a consequence of energy transfer along the polymer chain. (d) Intensity fluctuations in the backbone emission under excitation at 395 nm. In contrast to the direct excitation of the (single chromophore) endcap, the multichromophoric backbone exhibits substantial intensity fluctuations.

"Off"-periods in the emission most likely stem from reversible nonradiative traps on the polymer inhibiting the transport of the excitation energy to the perylene endcaps,[13,14,17,27,51] but may also be related to the possibility of multiple excitations of the backbone occurring in the presence of long-lived meta-stable states. The mechanism underlying these fluctuations, which have also been observed in multichromophoric dendrimers, has been coined exciton blockade[56] due to the possibility of multiple excitation of chromophores involved in the cascade being blocked by long-lived intermediate states, such as charge separated states.

To contrast these two excitation processes depicted in panels (a) and (b), we switch between direct endcap excitation and

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(53) Lippitz, M.; Kulzer, F.; Orrit, M. *ChemPhysChem* **2005**, *6*, 770−789.
(54) Hofkens, J.; Cotlet, M.; Vosch, T.; Tinnefeld, P.; Weston, K. D.; Ego, C.; Grimsdale, A.; Müllen, K.; Beljonne, D.; Bredas, J. L.; Jordens, S.; Schweitzer, G.; Sauer, M.; De Schryver, F. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 13146−13151.
(55) Schindler, F.; Lupton, J. M.; Feldmann, J.; Scherf, U. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 14695−14700.
(56) Cotlet, M.; Gronheid, R.; Habuchi, S.; Stefan, A.; Barbafina, A.; Müllen, K.; Hofkens, J.; De Schryver, F. *J. Am. Chem. Soc.* **2003**, *125*, 13609−13617.

backbone excitation on one and the same molecule as shown in Figure 3c. Note the strong increase in endcap emission intensity when excited via energy transfer, illustrating the excellent light-harvesting properties of the polymer. The temporal variability of the energy transfer efficiency will clearly also affect the emission intensity from the polymer backbone. This will be quenched when the transfer to the endcap is efficient. Figure 3d shows the emission intensity recorded in the blue spectral region, that is, the direct emission from the polymer backbone. It displays temporal fluctuations comparable to the fluctuations in endcap intensity under energy transfer excitation. Besides having to deal with a distribution between different molecules in terms of energy transfer efficiency as discussed in Figure 2, it is also extremely important to realize that the actual intramolecular energy transfer efficiency is a dynamic quantity and can fluctuate substantially. We also note that direct excitation of the endcap at 488 nm is more efficient at 300 K than at 5 K[40] due to the narrower transition lines at 5 K and the fact that spectral diffusion drives the PEC absorption in and out of resonance with the laser at 5 K.

(c) Time-Resolved Energy Transfer in Single Molecules. The relatively low average efficiency of intramolecular energy transfer is apparent from the ensemble PL spectrum of isolated molecules in Figure 1b. The energy transfer along the polymer backbone and the subsequent activation of the perylene endcap is thus rather slow as compared to the lifetime of the excitation on the backbone.[28] This is demonstrated in Figure 4a with the aid of time-resolved gated fluorescence microscope images of single PEC-PIFTEH molecules for the polymer emission (upper panel, blue) and the perylene endcap emission excited via energy transfer (lower panel, red). Note that the images show different patches on the sample. These images show the PL of single molecules as a function of time: after pulsed excitation the blue emission from the polymer appears instantly and decays rapidly within 500 ps, whereas the red endcap emission (i.e., the number of spots and their respective intensities) reaches its maximum later and decays much more slowly. In agreement with this, Figure 4b shows the rise and decay of the polymer and the perylene emission measured for a dilute ensemble of isolated PEC-PIFTEH molecules using a streak camera setup (solid line). The average single molecule emission is also superimposed (symbols). The delayed rise of the perylene emission as compared to the polymer emission is clearly visible and in agreement with recent reports,[28b] demonstrating that the energy transfer along the polymer chain to the perylene endcap occurs on the time scale of a few hundreds of picoseconds, much slower than the dominating intermolecular energy transfer in bulk films.[11,28,57,58] By comparing the time scales of this slow intramolecular energy transfer to intermolecular energy transfer in bulk films,[59] which can also be separated into excitation diffusion along the polymer chain and subsequent energy transfer to an acceptor dye,[9] it becomes apparent that the observed intramolecular energy transfer on the polymer backbone must undergo several steps before finally reaching the perylene endcap. We conclude this from the fact that the final step of energy transfer from the polymer chain to the acceptor dye molecule has to be fast and efficient to account for the bulk film measurements.[28]

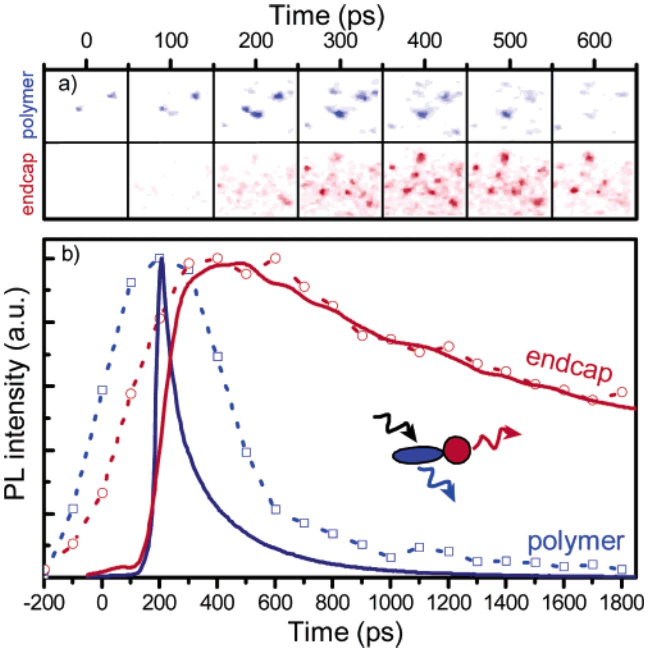

Figure 4. Time-resolved fluorescence measurements of PEC-PIFTEH dispersed in a Zeonex matrix at 300 K, excited at 395 nm. (a) Time-gated fluorescence microscopy images of the polymer backbone emission of single molecules (top, blue) and of the endcap emission (bottom, red). The images were obtained in gates of 200 ps and illustrate an area of 10 × 10 μm^2 on the sample. Note that the two panels correspond to different positions on the sample. (b) Temporal evolution of the fluorescence of the polymer backbone (thick blue line) and the endcaps (thick red line) obtained using a streak camera on an ensemble of PEC-PIFTEH molecules at a concentration of 10^{-4} w/w dispersed in Zeonex. The fluorescence intensity transients extracted from fluorescence microscopy images as shown in (a) for 65 individual molecules for the polymer backbone emission (□) and 95 individual molecules for the endcap emission (○) are overlaid for comparison. The rise in the endcap acceptor emission is clearly discernible along with the rapid decay of the backbone donor fluorescence.

(d) Low-Temperature Single Molecule Spectroscopy. To obtain a deeper understanding of the energetic properties of the individual chromophoric sites on the polymer chain, we studied PL spectra of single chains of PEC-PIFTEH at a temperature of 5 K. Figure 5 shows a typical single molecule PL spectrum. The spectrum exhibits a narrow line of less than 10 meV (80 cm^{-1}) width, which we attribute to the purely electronic transition convoluted with a phonon sideband, followed by a number of vibronic peaks, the most significant offset by approximately 1320 and 1620 cm^{-1} from the 0−0 line. The single molecule PL line width provides an upper limit to the homogeneous line width of the system. Note that the single molecule spectrum in Figure 5 displays only one peak, which may be attributable to emission from only one single chromophore.[48] However, we frequently also observe multichromophoric emission as in the case of ladder-type poly(*para*-phenylene) (LPPP),[48] which is manifested by multiple peaks in the PL spectrum. Disorder due to different chain conformations and differences in the local nanoscale dielectric environment result in inhomogeneous broadening of the optical transitions. The distribution of the spectral positions of the 0−0 transition of single molecules is shown in the inset of Figure 5. It suggests an inhomogeneous broadening of 58 meV (centered at 422 nm), which is over twice as broad as that found in LPPP,[55] consistent with the somewhat greater chain flexibility. The overlaid

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(57) Herz, L. M.; Silva, C.; Friend, R. H.; Phillilps, R. T.; Setayesh, S.; Becker, S.; Marsitsky, D.; Müllen, K. *Phys. Rev. B* **2001**, *64*, 195203.

(58) Wang, C. F.; White, J. D.; Lim, T. L.; Hsu, J. H.; Yang, S. C.; Fann, W. S.; Peng, K. Y.; Chen, S. A. *Phys. Rev. B* **2003**, *67*, 035202.

(59) Kersting, R.; Lemmer, U.; Mahrt, R. F.; Leo, K.; Kurz, H.; Bässler, H.; Göbel, E. O. *Phys. Rev. Lett.* **1993**, *70*, 3820−3823.

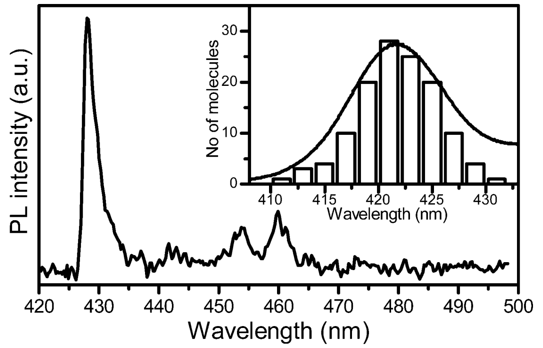

Figure 5. Single molecule PL spectrum of the polymer backbone emission of a PEC-PIFTEH molecule dispersed in a Zeonex matrix, excited at 395 nm at 5 K. Besides a narrow peak corresponding to the 0−0 transition of the backbone at 428 nm, vibronic peaks offset by roughly 1320 and 1620 cm^{-1} are visible. The distribution of peak positions of the 0−0 transition determined from single molecule spectra is shown as a histogram in the inset, providing direct access to the level of inhomogeneous broadening with a width of 58 meV (468 cm^{-1}). The PL curve of the 0−0 transition of an ensemble of isolated molecules dispersed in Zeonex at 5 K is superimposed over the histogram to demonstrate the correspondence between single molecule measurements and ensemble measurements (solid line).

ensemble spectrum of isolated PEC-PIFTEH molecules embedded in a Zeonex matrix at 5 K shows direct correspondence between single molecule and ensemble measurements.

To understand energy transfer on a microscopic scale, it is essential to consider both the homogeneous line width and the energetic distribution of the sites (i.e., the disorder).[17] Although there is no precise information on the homogeneous line width at room temperature, we can take the single molecule PL line width of LPPP (approximately 30 meV/242 cm^{-1}) as a crude estimate.[17] As the rate of energy transfer between chromophores depends on the spectral overlap between chromophores,[17,49] the broad inhomogeneous distribution with a width of 58 meV (468 cm^{-1}) results in a low average transfer efficiency between adjacent chromophores. Intrachain excitation energy diffusion on the polymer chain is therefore generally limited. Many molecules, however, appear to exhibit efficient energy transfer to the endcaps, which may be due to a continuous downhill transfer along the polymer backbone to chromophores of sequentially lower energy and finally to the perylene endcaps. In effect, coincidental arrangement of chromophores of different energy with a suitable overall energy gradient can therefore be thought of in terms of a microscopic cascade-like architecture.

A detailed understanding of energy transfer in guest−host systems also requires knowledge of the microscopic properties of the acceptor, that is, the perylene endcaps. Figure 6a displays ensemble absorption and PL spectra at room temperature of free isolated perylenemonoimide (not covalently attached to the polymer), together with a typical single molecule spectrum at 5 K. The properties of the perylene bound to the polymer chain are summarized in Figure 6b. The first striking difference between the free and the bound perylene is a red-shift of the bound perylene with respect to the free perylene of 24 nm in the ensemble absorption and of 34 nm in the ensemble PL. This may be a consequence of an extension of the π-system of the perylene dye onto the polymer backbone.[28] In the picture of Förster energy transfer, this red-shift is detrimental to backbone−endcap dipole−dipole coupling, as it reduces the spectral overlap of the polymer emission and the perylene absorption. The single molecule spectra show that whereas the free dye has a PL line width of less than 3 meV (24 cm^{-1}) at 5 K, the bound perylene dye exhibits a much broader feature of approximately 48 meV (387 cm^{-1}) line width at 5 K. In agreement with this, the PL for single perylene dyes bound onto a dendrimer has previously also been reported to be quite broad, even at 2 K.[60] The origin of this observation is not entirely clear, but the fact that the polymer backbone emission is over 5 times narrower than the endcap emission is rather surprising, as we generally associate single dye molecules with narrow transitions. These findings demonstrate the strong influence of grafting dyes covalently to a host polymer on the microscopic energy transfer and emission properties. This should be taken into account when designing blended systems for devices[5] and should also find consideration when developing microscopic quantum chemical descriptions of intramolecular energy transfer.[28] Although we cannot quantify the acceptor absorption, the low-temperature single molecule spectroscopy provides a rough measure for the perylene absorption line width. We conclude from the results in Figures 5 and 6 that the energetic separation between the backbone and endcap transitions is many times the spectral line width of the backbone emission. Spectral overlap between donor and acceptor is therefore negligible at low temperatures.[40] The fact that efficient energy transfer is observed in some molecules highlights the inadequacy of describing energy transfer in the entire molecule following nonradiative electrodynamic dipole or multipole coupling alone based on a coupling parameter derived from the far-field spectra.[25,43]

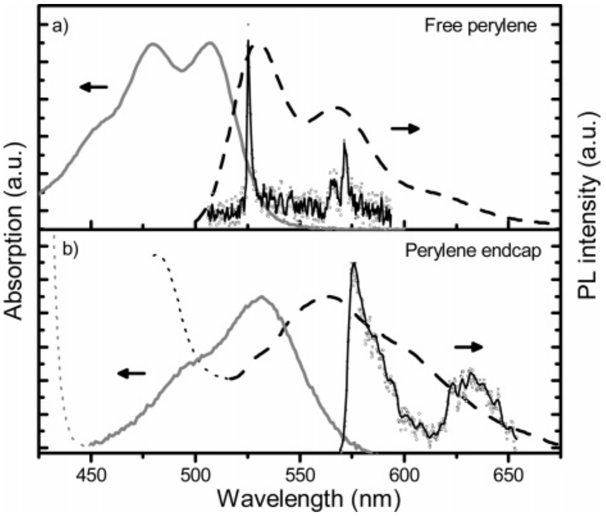

Figure 6. Ensemble absorption (solid line, measured at 300 K from chloroform solution), ensemble PL (dashed line, measured at 300 K for molecules dispersed in polystyrene at a concentration of 10^{-4} w/w), and single molecule spectra (solid line with circles, measured at 5 K from single molecules dispersed in a Zeonex matrix) of the free perylene dye (a) and of perylene endcaps attached to the indenofluorene polymer (b). The gray and black dotted lines in (b) correspond to the long-wavelength tail of the polymer backbone absorption and emission.

(e) Polarization Anisotropy in the Absorption and Emission of Single Polymer Molecules. It is well known that the structural conformation of a conjugated polymer molecule bears a strong influence on its photophysical properties.[61−63] To learn more about these structural properties of the polymer chain,

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(60) Christ, T.; Kulzer, F.; Weil, T.; Müllen, K.; Basché, T. *Chem. Phys. Lett.* **2003**, *372*, 878−885.
(61) Huser, T.; Yan, M.; Rothberg, L. J. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 11187−11191.
(62) Schwartz, B. J. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141−172.
(63) Grey, J. K.; Kim, D. Y.; Young, J. L.; Gutierrez, J. J.; Luong, N.; Ferraris, J. P.; Barbara, P. F. *Angew. Chem., Int. Ed.* **2005**, *44*, 6207−6210.

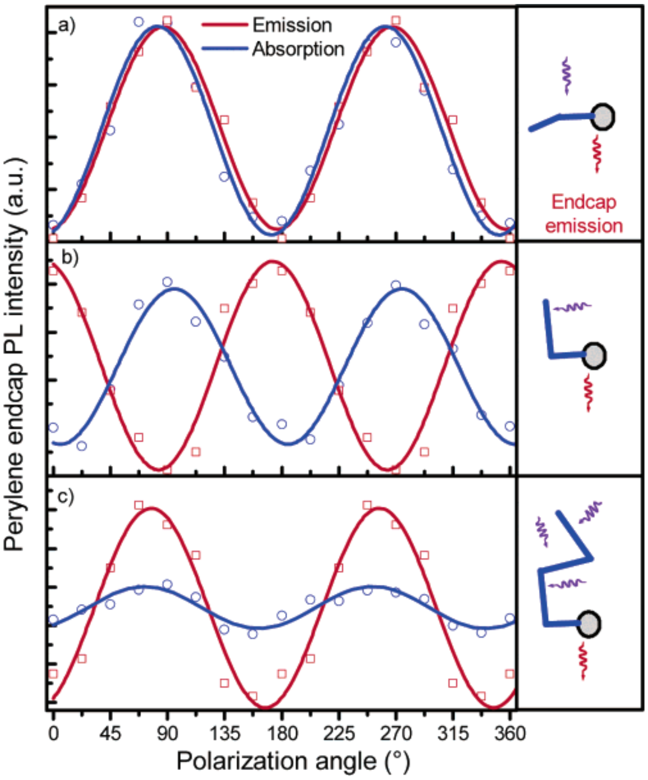

Figure 7. Degree of polarization of the absorption by the polymer backbone and the emission of the endcap of single characteristic PEC-PIFTEH molecules at 300 K. ○: Perylene endcap PL intensity as a function of the plane of polarization of the laser exciting the polymer backbone at 395 nm. □: Perylene endcap PL intensity as a function of the plane of polarization of an analyzer placed in the emission pathway. The cartoons indicate possible polymer chain conformations. (a) Linear polarization in excitation and emission due to energy transfer along an extended polymer chain. (b) Rotation of the plane of polarization between excitation of a single or multiple collinear chromophores on the polymer backbone and emission of the endcap due to energy transfer along an angled chain. (c) Nearly unpolarized excitation of multiple noncollinear chromophores on the polymer backbone with rapid energy transfer to a single perylene endcap.

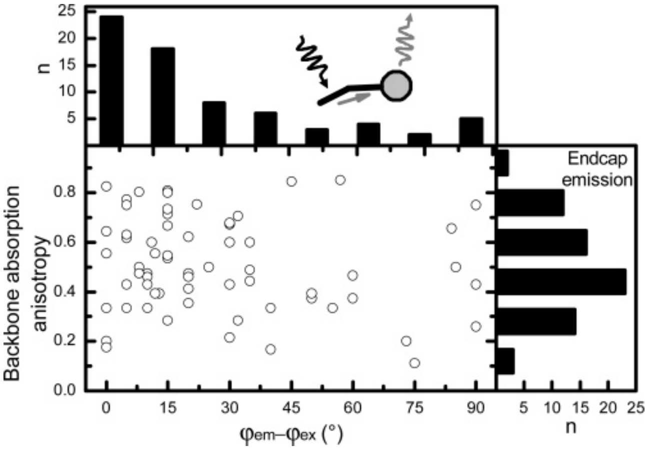

Figure 8. Role of polarization anisotropy and phase shift between emission and absorption polarization in the transfer of excitation energy from the polymer backbone to the dye endcap at 300 K. The polarization anisotropy in excitation of the polymer backbone at 395 nm (determined by the endcap emission intensity) and the angle of rotation of the plane of polarization between excitation of the backbone and emission from the endcap do not correlate for the 70 molecules studied.

polarization sensitive single molecule spectroscopy is a powerful tool for analyzing the orientation of the transition dipoles of the polymer backbone[40,51,63−66] and the dyes.[15,16,40] Figure 7 shows three typical polarization angle-dependent PL intensity curves for excitation of the polymer backbone at 395 nm and detection of the perylene endcap emission. In all three cases, the luminescence is almost completely linearly polarized, demonstrating that in these cases emission most likely occurs from one single perylene endcap.

To make the reconstruction of the energy transfer pathway easier, only those molecules showing linearly polarized emission from a single endcap were considered. The case of equal orientation of the transition dipoles of the absorbing chromophores on the polymer chain and the perylene endcap is observed in Figure 7a. Here, both excitation and emission are in phase. In contrast to this, a phase shift of 90° between excitation and emission shown in Figure 7b reveals the presence of at least one kink in the absorbing polymer chain because such a large angle between polymer chain and endcap is structurally improbable. Note that mere biaryl twists within the polymer chain should not change the orientation of the transition dipole moment and thus the plane of polarization of the backbone, as the curvature of the rigid rod structure is small in the absence of defects.[28] Twists alone may disrupt the conjugation, but a bend is required to change the polarization. In contrast, biaryl twists between the polymer and the endcap may modify the effective conjugation of the endcap and alter the orientation of the transition dipole moment in the perylene. Electronic structure calculations should be able to clarify this issue. As one chromophore absorbs and emits linearly polarized light in a fixed plane of polarization, this case suggests an intermediate step in the energy transfer pathway, providing direct evidence for excitation energy diffusion along the polymer chain prior to transfer to the endcap. Figure 7c shows a more extreme case, where the absorption by the polymer is only very weakly polarized. This situation corresponds to multiple absorbing chromophores on the polymer backbone oriented in different directions and may be an indication of a collapsed chain conformation,[64] although rather surprising for a nominally rigid-rod polymer.

These three scenarios are summarized in Figure 8 with the aid of a scatter plot of the angle of rotation of the plane of polarization between emission and excitation ($\varphi_{\mathrm{em}} - \varphi_{\mathrm{exc}}$) and the degree of polarization anisotropy of the excitation ($p = (I_{\max} - I_{\min})/(I_{\max} + I_{\min})$) determined by considering the endcap emission. For a total of 70 molecules the polarization anisotropy in absorption displays a large scatter. We take this as a signature of multiple absorbing noncollinear chromophores for typical chains of PIFTEH. In contrast, the substantial values of the polarization anisotropy in absorption observed for some molecules correspond to elongated, rodlike polymer chains. On the other hand, the picture of the polymer chain potentially supporting multiple kinks is underlined by the considerable number of molecules showing large phase shifts between the polarization of the excitation of the polymer backbone and the polarization of the perylene endcap emission.

We observe no correlation between a low degree of polarization anisotropy and a large phase shift between absorption and

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(64) Hu, D. H.; Yu, J.; Wong, K.; Bagchi, B.; Rossky, P. J.; Barbara, P. F. *Nature* **2000**, *405*, 1030−1033.

(65) Müller, J. G.; Lupton, J. M.; Feldmann, J.; Lemmer, U.; Scherf, U. *Appl. Phys. Lett.* **2004**, *84*, 1183−1185.

(66) Becker, K.; Lupton, J. M.; Feldmann, J.; Nehls, B. S.; Galbrecht, F.; Gao, D. Q.; Scherf, U. *Adv. Funct. Mater.* **2006**, *16*, 364−370.

emission. However, a collapsed chain would lead to both: (1) a low polarization anisotropy in absorption (due to random chromophore orientations) and (2) a random phase shift ($\varphi_{em} - \varphi_{exc}$) between the nearly isotropic absorption and linearly polarized emission if we assume a random orientation of the perylene endcaps within one collapsed polymer chain structure. Neither is the backbone polarization anisotropy particularly low (the distribution peaks at 0.45) nor is the distribution of $\varphi_{em} - \varphi_{exc}$ random, i.e., flat (it peaks at 0 and tails off to larger values), providing evidence against a generally collapsed chain conformation, in accordance with the fairly rigid structure of the molecule. We therefore conclude that the individual chains are kinked (once or multiply). However, they are not, as previously assumed,[28] strictly of rigid rod conformation.

(f) Thermal Activation of Energy Transfer. To arrive at a deeper understanding of intramolecular excitation diffusion prior to transfer to the endcap, we consider the emission properties of the polymer backbone of PEC-PIFTEH as a function of temperature. When a photoexcitation is created within the inhomogeneously broadened spectrum of states on the polymer chain, it can relax by resonant energy transfer to a neighboring chromophore with lower excitation energy, as long as the spectral overlap between emission and absorption of the neighboring chromophores is sufficient.[17,28,49] Alternatively, a coherent relaxation of the overall excited-state complex comprising multiple units may also take place on an ultrafast time scale.[25,41−43,65,67,68] Once the excitation has transferred to a lower energy site, absorption of a phonon is necessary to transfer it back to higher energy. For PEC-PIFTEH, the inhomogeneous broadening of ~58 meV is larger than the thermal energy at room temperature, so that exciton trapping on individual chromophores will still occur at 300 K. We therefore expect primarily downhill energy transfer even at room temperature. However, the lower the thermal energy, that is, the lower the temperature, the more the migration of the excitation on the polymer backbone will be limited by disorder. Consequently, the efficiency of the intramolecular energy transfer should at least in part be controllable by temperature.[9,17,18] This is demonstrated by the temperature dependence of the relative amount of fluorescence of the perylene endcaps as compared to the polymer backbone emission intensity when exciting the polymer at 395 nm, that is, upon excitation of the backbone. Figure 9 shows a plot of the endcap to backbone PL intensity ratio as a function of temperature for a highly diluted ensemble of molecules in a Zeonex matrix. The relative perylene emission intensity ranges from 15% at 5 K to just above 25% at room temperature. This provides clear evidence that the energy transfer process along the backbone to the endcaps has a weakly thermally activated component.

The question remains as to whether the temperature dependence is due to changes of intrachain interchromophoric interactions on the polymer backbone or accelerated transfer from the polymer to the endcap. A clear signature of temperature-dependent interchromophoric interactions can finally also be derived from single molecule polarization anisotropy by considering both absorption and emission from the polymer backbone. Figure 10 displays the distribution of the degree of polarization anisotropy for a total of 172 molecules at 5 and at 300 K. We generally observe only a moderate degree of polarization anisotropy in the absorption of the polymer backbone (hatched bars), corresponding to the simultaneous absorption of multiple noncollinear chromophores as visualized in the cartoons in Figure 10. For the polarization anisotropy in absorption, only the orientations of the chromophores of the polymer backbone are relevant. As the polymer chain morphology should not change substantially with temperature, the degree of polarization anisotropy in absorption is temperature independent. At the same time, the degree of polarization anisotropy of the backbone emission is considerably larger at room temperature than at 5 K. This results in a shift of the histograms to larger anisotropies when going from 5 K (panel b) to 300 K (panel a). The large degree of polarization anisotropy of the

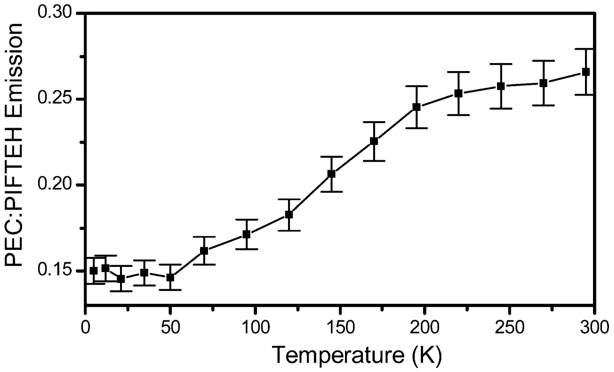

Figure 9. Temperature dependence of the relative amount of endcap emission with respect to the backbone emission of the PEC-PIFTEH polymer (excited at 395 nm), measured for a diluted ensemble of isolated molecules (10^{-5} w/w dispersed in Zeonex). The perylene endcap emission intensity increases somewhat with rising temperature as intrachain energy transfer along the backbone becomes more efficient.

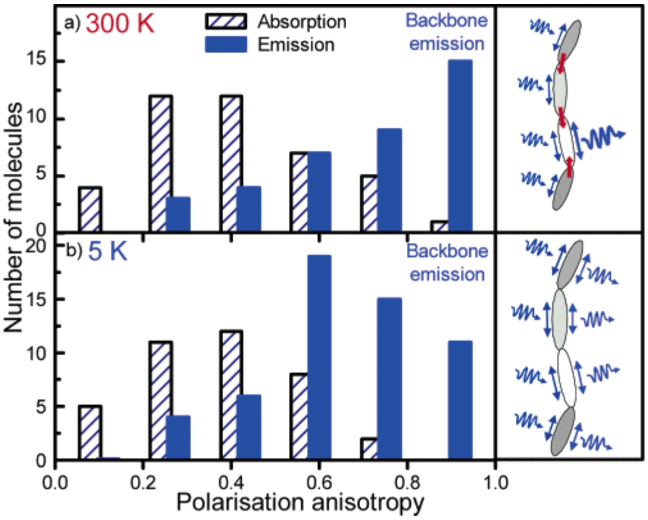

Figure 10. Polarization anisotropy of excitation (hatched bars) at 395 nm (determined by the backbone emission intensity) and emission (solid bars) of the polymer backbone for a total of 172 PEC-PIFTEH molecules. The endcap emission is not considered in this case. (a) Measured at 300 K: the absorption is only moderately polarized due to the presence of multiple noncollinear chromophores. Rapid downhill energy transfer along the polymer backbone (red arrows in the cartoon) followed by exciton trapping leads to strongly polarized emission from a small number of chromophores. (b) Measured at 5 K: the absorption is moderately polarized and virtually identical to the 300 K case. In comparison to (a), the degree of polarization in emission is reduced significantly as energy transfer along the polymer backbone is hindered at lower temperatures. Emission therefore occurs from multiple chromophores of different orientations.

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(67) Ranasinghe, M. I.; Wang, Y.; Goodson, T., III. *J. Am. Chem. Soc.* **2003**, *125*, 5258−5259.

(68) Varnavski, O. P.; Ostrowski, J. C.; Sukhomlinova, L.; Twieg, R. J.; Bazan, G. C.; Goodson, T., III. *J. Am. Chem. Soc.* **2002**, *124*, 1736−1743.

polymer emission at room temperature along with the difference in polarization anisotropy of absorption and emission provide evidence that thermally activated energy transfer occurs along the polymer chain, without having to consider the endcap. This results in the excitation energy being funneled to a few or possibly only one emitting chromophore on the chain, leading to linearly polarized emission.[61,64] Note that in this case, however, emission preferentially occurs from the global energetic minimum of the backbone and not from the endcap (the global energetic minimum of the entire molecule). At 5 K, the degree of polarization anisotropy of the emission is still larger than that observed for excitation, a signature of intrachromophoric energy transfer occurring even at low temperatures.[65] The difference between absorption and emission anisotropy is, however, much less pronounced than at room temperature, as the exciton is less mobile on the polymer backbone and cannot migrate to the global energetic minimum on the backbone. Both situations are depicted in the cartoons in Figure 10, which show excitation funneling to one emitting chromophore for room temperature (the backbone global energetic minimum[69]), while at low temperatures the reduced mobility of the excitation on the polymer backbone can lead to trapping in and emission from multiple local backbone minima.

IV. Discussion

When compared to ensemble measurements, single molecule studies of intramolecular energy transfer along a polymer chain to a fluorescent endcap reveal a broad spectrum of characteristic behavior. The efficiency and nature of energy transfer differs from molecule to molecule because of variations in relative chromophore disposition. Such variations may be purely geometric in nature, i.e., due to the microscopic local chain conformation, or arise from even more subtle effects such as the local strength of electron−phonon coupling or screening or polarizing influences of the immediate environment. We summarize the key observations in the following:

(1) Intramolecular energy transfer may be inefficient on average but can be extremely efficient in individual molecules.

(2) This efficient intramolecular energy transfer from the backbone to the endcap occurs without the need of spectral overlap between endcap absorption and backbone emission.

(3) Backbone to endcap energy transfer is consequently almost independent of temperature, which controls the transition line width and thus the strength of nonradiative dipole−dipole coupling.

(4) In contrast, energy transfer along the backbone depends on temperature as manifested by preferential exciton trapping on a single site and enhanced polarization anisotropy in emission at room temperature.

(5) Besides the statistical (or spatial) scatter in energy transfer efficiency, there are strong temporal fluctuations in the backbone−endcap coupling strength.

The key observation is that the simple Förster-type approximation for dipole−dipole coupling breaks down in strongly covalently bound systems such as the backbone−endcap complex.[40] This is clear from the experimental far-field spectra at low temperatures, and the weak temperature dependence of backbone−endcap coupling does not suggest that the coupling mechanism at elevated temperatures should be markedly different. Rather, endcap and backbone form a strongly coupled excited-state complex. A precedence for this is, for example, also found in energy transfer in dendritic systems,[41,67,68] which exhibit extremely fast (sub 100 fs) fluorescence depolarization due to strong interactions between conjugated arms of different orientation.[70,71] Furthermore, ultrafast fluorescence depolarization has previously also been observed in conjugated polymers due to the relaxation in the excited-state manifold of the individual spectroscopic units on the polymer chain.[42] This is effectively a signature of exciton self-trapping on a single curved conjugated segment[42] originating from the fact that the extension of the absorbing unit is greater than the extension of the emitting, relaxed exciton.[48] Such a rapid depolarization can, however, only occur on highly flexible chains such as poly(phenylenevinylenes), which also have a strong tendency to self-aggregate, thereby further enhancing intramolecular relaxation.[29,55] Signatures of strong dipole coupling and indeed energy transfer efficiencies inexplicable within the Förster picture have also been observed in a number of molecular aggregates,[72] most notably in biological light-harvesting complexes.[23−25,43]

We can consider the depolarization dynamics either in the time[70,71] or in the frequency domain, as we do in the present case. Our findings that the polarization anisotropy of the backbone emission increases with increasing temperature at first sight appears to be somewhat at variance with our previous study of LPPP molecules. Müller et al.[17,65] reported that the polarization anisotropy of the PL emission decreases with increasing temperature in LPPP. This can be explained by the substantially narrower inhomogeneous broadening found for LPPP (about one-half the value of 58 meV reported here for PIFTEH), which is lower than the thermal energy at room temperature. For LPPP, this results in an incoherent spreading of the excitation among multiple chromophores as a large spectral overlap between neighboring chromophores develops so that thermal equilibrium between the chromophores can be established by energy transfer. In the case of PIFTEH, as the exciton mobility along the chain rises with increasing temperature, emission occurs from fewer lower energy sites so that the polarization anisotropy increases. An important point to note is the similarity in the backbone excitation polarization anisotropy determined either by the endcap emission (Figure 8) or by the backbone emission (Figure 10). This suggests that light harvesting and energy transfer to the endcap occurs equally well from any segment on the chain.

Whereas energy transfer along the backbone qualitatively matches the expectations of line width-limited Förster energy transfer,[17] the final transfer step from the backbone to the covalently bound endcap clearly does not. While elucidation of the precise nature of this final step must be left to future theoretical studies, there are a few points besides the aforementioned precedences on strong intrachromophoric couplings we would like to make. First of all, we have to consider the possibility of highly efficient energy transfer occurring from the backbone to a higher-lying state of the endcap. While this appears improbable in view of the fact that we cannot excite

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[69] Bässler, H.; Schweitzer, B. *Acc. Chem. Res.* **1999**, *32*, 173−182.

[70] (a) Varnavski, O.; Menkir, G.; Goodson, T.; Burn, P. L.; Samuel, I. D. W.; Lupton, J. M.; Beavington, R. *Appl. Phys. Lett.* **2000**, *77*, 1120−1122. (b) Varnavski, O.; Menkir, G.; Goodson, T.; Burn, P. L.; Samuel, I. D. W.; Lupton, J. M.; Beavington, R. *Appl. Phys. Lett.* **2001**, *78*, 3749.

[71] Lupton, J. M.; Samuel, I. D. W.; Burn, P. L.; Mukamel, S. *J. Phys. Chem. B* **2002**, *106*, 7647−7653.

[72] Métivier, R.; Kulzer, F.; Weil, T.; Müllen, K.; Basché, T. *J. Am. Chem. Soc.* **2004**, *126*, 14364−14365.

the endcap directly using a laser operating at the wavelength of the peak emission of the PIFTEH,[40] we cannot exclude the possibility that higher lying states of the dye endcap play a role in energy transfer. In any case, dissipation of energy is very efficient in these macromolecules as over 0.7 eV is removed from the system upon transfer of the excitation to the endcap. In view of the fact that structural relaxation is extremely small in LPPP[21] and most probably also in PIFTEH, this implies rapid multiple phonon emission, a potentially inefficient process.[73]

A further interesting point is that charges couple strongly to the lattice in polymeric semiconductors so that the exciton can be ascribed polaronic character. Polaronic effects should therefore be considered in models of energy transfer.[74] Polarons in LPPP have been shown to exhibit a considerable degree of delocalization,[75] which most likely also holds for the structurally not dissimilar material PIFTEH. Interestingly, LPPP can also support a long-range exchange interaction, which can even acquire intermolecular character.[76] This is a further signature of long-range electronic interactions occurring in rigid poly(*para*-phenylenes), and links up perfectly with the effective strong backbone−endcap coupling observed. Besides the question of the microscopic coupling pathway, however, it is also important to understand why the coupling efficiency can vary with time and why different molecules can display such vastly different coupling efficiencies. We have previously illustrated how single polymer molecules display both static and dynamic energetic disorder, where the latter is manifested in spectral diffusion.[77] The influence of disorder on energy transfer in multichromophoric aggregates is well established.[78] Furthermore, the strength of electron−phonon coupling can also vary substantially from molecule to molecule.[21] As the relaxation of the bound backbone−endcap complex requires efficient energy dissipation, we propose that it is in part controlled by the strength of electron−phonon coupling. This may also govern the microscopic nature of polaron formation on the polymer chain, which could further influence the dye−polymer coupling. Finally, we would like to point the reader to our recent observation of permanent dipoles on the polymer backbone, which give rise to a striking linear Stark effect in the emission of the single molecule.[79] Such dipoles, which can differ in strength and orientation from molecule to molecule and can also change with time, could clearly also modify the relaxation of excited state species in the covalently coupled dye−polymer complex. On one hand, dipoles may lead to effective potential minima on the polymer chain, thus trapping the exciton or amplifying self-trapping. On the other hand, static dipoles could also play a role in passing excitation energy along the polymer chain by virtual exchange of charge. Our observations may, therefore, constitute a signature of the previously described influence of a third body, or chromophore, on resonance energy transfer.[80]

We conclude by noting that the observation of efficient intramolecular energy transfer to dye acceptors is also acutely relevant to understanding the role of on-chain defects in the performance of high molecular weight conjugated polymers in optoelectronic devices. A particularly important case is the formation of oxidative defects such as nonemissive carbonyls in poly(phenylene-vinylenes)[81] or emissive fluorenones in polyfluorenes.[18,19] It was recently proposed that the on-chain energy transfer efficiency to fluorenone defects should be inefficient due to the poor spectral overlap between the weak fluorenone absorption and the backbone emission.[82] This observation was used to support the view that intermolecular interactions give rise to the contamination of the emission spectrum of polyfluorenes, rather than monomolecular on-chain fluorenone emission.[82] However, we recently succeeded in identifying the fluorenone emission in single polyfluorene molecules, thus demonstrating the monomolecular nature of the emission.[66] We therefore stress that, as in the present case of perylene endcaps, highly efficient transfer of excitation energy can occur to the oxidative fluorenone units even without the requirement of spectral overlap between donor emission and acceptor absorption. Strong coupling of donor and acceptor on a polymer chain can therefore potentially be detrimental to the operation of organic optoelectronic devices. On the other hand, however, it is exactly such a coupling that is desirable in photovoltaic cells where efficient light harvesting as discussed in the present contribution is required, along with directional transport to a charge separation site. In this context, it appears interesting to link charge acceptors covalently to the π-system of the backbone rather than attaching them in the place of side groups or nonconjugated endcaps.[83]

V. Conclusions

In this contribution, we presented detailed single molecule studies on intramolecular energy transfer in a conjugated polymer with perylene dyes grafted covalently to the ends of the chain. This system can be regarded as a photonic wire where both the individual chromophores on the polymer chain with respect to each other as well as the chromophore−endcap group act as donor−acceptor systems. Besides being an interesting material for highly efficient and color tunable light-emitting diodes, this system provides an ideal model for studying two important steps of intramolecular energy transfer: (1) the diffusion of an excitation along the polymer backbone and (2) the final energy transfer step from the polymer to the dye. Our results reconfirm the inefficient and thus slow intramolecular energy transfer in an ensemble of isolated molecules.[28] However, single molecule microscopy and spectroscopy allow a suppression of the averaging over a large ensemble and demonstrate that, in contrast to the ensemble expectations, many individual molecules show highly efficient energy transfer along the polymer backbone to the perylene endcap. Polarization sensitive single molecule spectroscopy reveals that the polymer chains typically contain one or more structural kinks. The substantial inhomogeneous energetic broadening of the chromophores (58 meV) within the polymer backbone is identified to be the main

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(73) Barford, W. *Phys. Rev. B* **2004**, *70*, 205204.
(74) Markvart, T.; Greef, R. *J. Chem. Phys.* **2004**, *121*, 6401−6405.
(75) Wohlgenannt, M.; Jiang, X. M.; Vardeny, Z. V. *Phys. Rev. B* **2004**, *69*, 241204.
(76) Reufer, M.; Walter, M. J.; Lagoudakis, P. G.; Hummel, A. B.; Kolb, J. S.; Roskos, H. G.; Scherf, U.; Lupton, J. M. *Nat. Mater.* **2005**, *4*, 340−347.
(77) Schindler, F.; Lupton, J. M. *ChemPhysChem* **2005**, *6*, 926−934.
(78) Yeow, E. K. L.; Ghiggino, K. P. *J. Phys. Chem. A* **2000**, *104*, 5825−5836.
(79) Schindler, F.; Lupton, J. M.; Müller, J.; Feldmann, J.; Scherf, U. *Nat. Mater.* **2006**, *5*, 141−146.
(80) Daniels, G. J.; Andrews, D. L. *J. Chem. Phys.* **2002**, *116*, 6701−6712.
(81) Yan, M.; Rothberg, L. J.; Papadimitrakopoulus, F.; Galvin, M. E.; Miller, T. M. *Phys. Rev. Lett.* **1994**, *73*, 744−747.
(82) Sims, M.; Bradley, D. D. C.; Ariu, M.; Koeberg, M.; Asimakis, A.; Grell, M.; Lidzey, D. G. *Adv. Funct. Mater.* **2004**, *14*, 765−781.
(83) Ramos, A. M.; Rispens, M. T.; van Duren, J. K. J.; Hummelen, J. C.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2001**, *123*, 6714−6715.

reason for the inefficiency of energy transfer along the polymer backbone. Excitation trapping in local minima arises primarily due to downhill transfer steps. Depending on the specific details of the local energetic structure of the individual molecules or of individual adjacent chromophores, however, efficient intramolecular energy transfer may also occur. The mobility of the excitation on the polymer chain is shown to be temperature dependent, leading to excitation energy funneling to predominantly one emitting chromophore and therefore strongly polarized emission at elevated temperatures. At low temperatures, however, uphill steps in the inhomogeneous energy distribution of the chromophore sites cannot be accomplished, resulting in less efficient exciton diffusion along the polymer chain. Additionally, a strong influence on the absorption and emission properties of the perylene dye is observed when grafted covalently to the ends of the polymer chain. This leads to a pronounced red-shift and an increase in the single molecule fluorescence line width.

We conclude by pointing out that our single molecule measurements of intramolecular energy transfer are not fully consistent with microscopic models derived from ensemble averaged measurements.[28] Local energetic inhomogeneities, conformational variations, and even temporal modifications of intramolecular couplings have to be taken into account. Importantly, it appears to be the transfer along the backbone and not the final step to the endcap that is rate limiting for intramolecular energy transfer. The great disparity between the lack of spectral overlap between individual donor and acceptor units on a single chain at low temperatures[40] and near complete multistep energy transfer from the backbone to the endcap in some molecules highlights the need for including coherent redistribution processes of excitation energy[24,25,41,43,67,68] such as intramolecular excited-state relaxation[42] in a complete description of energy transfer and light harvesting in conjugated polymers.

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