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Vibrational fluorescence spectroscopy of single conjugated polymer molecules

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Fluorescence spectroscopy of conjugated polymers at the single molecule level provides unique insight into the nature of the emitting state of these organic semiconductors. We are able to verify the picture that molecular excitations form the primary photoexcitations in conjugated polymers by identifying individual chromophore units on rigid rod-like chains of a ladder-type polymer. The observation of a well-defined substructure in the vibronic progression as well as the presence of sum-frequency vibrational modes in the higher order vibrational bands demonstrate the sensitivity of the method. We find that conjugated polymers are excellent materials for single molecule experiments, exhibiting narrow transition lines accompanied only by a limited number of discrete vibrational modes offset by hundreds of cm^{-1}. We conclude that the high level of structural rigidity of the molecule as well as the presence of shielding sidegroups on the polymer chain reduces vibrational coupling both to the amorphous matrix as well as limiting the number of internal vibrational modes, in contrast to the case for small dye molecules. By studying the fluorescence from different single molecules we are able to image intramolecular and intermolecular disorder directly. We observe a distribution in energy of the electronic transitions due to the characteristic energetic disorder. The intensity of the vibronic side bands is also found to vary from molecule to molecule, which we propose to be related to conformational influence on the strength of coupling between the electronic excitation and vibrational modes. Structural relaxation and intramolecular energy transfer are studied by single molecule site-selective fluorescence. Our results suggest that even in rigid polymer molecules structural relaxation leads to a small Stokes shift of <70 cm^{-1} upon electronic excitation of a single chromophore on a polymer chain at low temperatures. The influence of vibrational and structural relaxation on intramolecular energy transfer in these multichromophoric systems is also discussed.

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I. INTRODUCTION

Single molecule spectroscopy is a powerful technique that allows direct insight into the photophysical properties of individual emitters in the absence of disorder effects.[1,2] Fluorescence microscopy of single emitters has been applied extensively to, among others, individual dye molecules localized in both amorphous and crystalline matrices,[1–7] probed either by excitation or emission spectroscopy, to biological light-harvesting complexes[8] and fluorescent proteins,[9] inorganic nanocrystals,[10] and conjugated polymers.[11–18] Remarkably, to date, single molecule spectroscopy of individual chains of a conjugated polymer has been limited to room temperature investigations under ambient conditions. Although these high molecular weight molecules, which are generally thought of as multichromophoric assemblies, exhibit a pronounced fluorescence intermittency indicative of quantum jumps of the emitting state,[11] it has thus far not been possible to extract high resolution spectroscopic features from single conjugated polymer molecules. This is most likely due to the strong tendency of polymer chains to form intramolecular aggregate states, which dominate the emission.[12,13,15] An exception to this has been studies of perfect chains of polydiacetylene polymerized in their monomeric crystal.[18] These defect-free chains have been shown to behave as perfect one-dimensional quantum wires, exhibiting only very weak coupling to vibrational modes in the ensemble[19] and ultrafast coherent energy transport along the chain.[18] As these quantum wires are, however, free of defects and therefore do not form multichromophoric systems, they bear little resemblance to conventional disordered conjugated polymers, which are widely used in optoelectronic devices such as light-emitting diodes, photodiodes, and transistors.

As electron-phonon coupling is typically very strong in conjugated polymers, coupling of the excited state to vibrational modes is an important feature of the photophysical properties of these systems. Besides providing an understanding of the nature of the emitting state as well as the origin of the fluorescence spectrum in this class of materials, a microscopic picture of vibrational relaxation is crucial to understanding charge carrier dissociation processes[20,21] as well as exciton thermalization and migration,[22–27] which are, for example, vital to the operation of polymer-based solar cells. High resolution vibrational spectroscopy on bulk polymer samples using site-selective fluorescence techniques has provided invaluable insight into vibrational relaxation processes.[28–30] Up until very recently, it has been assumed that vibrational relaxation precedes both charge and energy transfer.[20,23,27] However, the recent demonstration of long-lived vibrational coherence in conjugated polymers, which gives rise to characteristic beating oscillations in pump-probe transients for up to 1 ps after photoexcitation,[31,32] demonstrates that vibrational relaxation should be considered to be

much slower than has previously been thought. Long-lived vibrational coherence may therefore lead to both energy transfer from vibrationally excited molecular units[25] as well as influencing exciton dissociation giving rise to anomalously large photocurrent yields.[20]

The pathway and efficiency of intramolecular energy transfer in multichromophoric systems such as natural light-harvesting complexes, conjugated polymers, and well-defined macromolecular assemblies of dye molecules is an important issue, which has recently attracted substantial attention.[33–39] In conjugated polymers, for example, the efficiency of intramolecular energy transfer determines the rate at which excitation energy is funneled to intentional[35] or accidental[40] acceptor states. Besides moving between chromophores, at sufficiently high density and short intramolecular proximity molecular excitons may also interact with one another, leading to annihilation.[36,38] We recently demonstrated that the mobility of intramolecular excitations depends on the spectral linewidth of the individual chromophore units.[39] Due to the inherent intramolecular disorder and the energetic separation between the individual chromophore units, the spectral overlap between adjacent chromophores required for energy transfer depends on the chromophoric linewidth. The chromophore spectral linewidth broadens substantially with increasing temperature, leading to thermally activated intramolecular exciton diffusion.[39] A microscopic understanding of intramolecular energy transfer therefore requires an exact knowledge of the mechanisms of line broadening, which are linked to excited state coupling to vibrational and phonon modes.

A further important point related to the understanding of vibrational processes as well as energy transfer in conjugated polymers on a microscopic level is an identification of the origin of the Stokes shift between absorption and emission. Both measuring and interpreting the shift between excitation and emission energies has led to a considerable controversy in the literature.[24,28,30,41–43] Such a shift can arise through either direct coupling to vibrational modes (i.e, excitation in a higher lying vibrational level), structural relaxation, or energy transfer. Down (or up[44]) -shifting of the fluorescence by vibrational coupling is a trivial case, but structural relaxation and energy transfer are often not trivial to separate. By studying vibrational relaxation we demonstrate that it is possible to gain insight into both energy transfer and structural relaxation on a single molecule level.

In this paper, we present results on fluorescence microscopy of a highly ordered ladder-type polymer,[45] which tends to adopt a rigid rod-like molecular conformation and is generally considered as a model type material for π-conjugated polymers. Strongly polarized multichromophoric narrow band emission provides direct evidence for the picture of molecular excitations as the primary photo-excitation in conjugated polymers. However, in contrast to small molecules, the structural anisotropy and the dominance of a few strong vibrational modes[32] results in the presence of and therefore coupling to a substantially smaller number of vibrational modes than for the case of isolated dye molecules. We observe only a small number of discrete vibrational modes in the fluorescence, offset from the main transition line by hundreds of wave numbers. High resolution fluorescence spectra

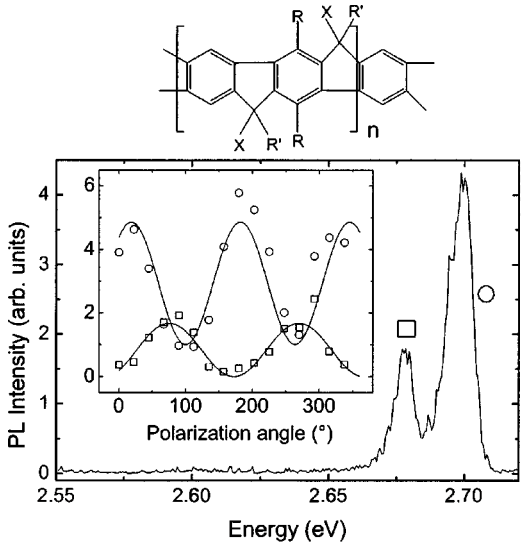

FIG. 1. Fluorescence from a single MeLPPP molecule at 5 K detected with a spectral resolution of ~2.5 meV under nonresonant, broadband excitation in the vibrational manifold of the molecule at 2.91 eV (laser line width 50 meV). The inset shows the polarization of the two emission lines (labeled with a square and a circle) which is determined by rotating a polarizer in the emission pathway of the microscope. The chemical structure of MeLPPP is also given (X: methyl, R: *n*-hexyl, R′: 1,4-decylphenyl).

provide an indication of weak, low frequency vibrational and phonon modes, which may be the origin of the temperature-dependent line-broadening mechanism observed.[39]

We find that the linewidths of the vibronic substructure and the 0-0 transition are the same, indicating that the ground state vibrational relaxation time is comparable to or larger than the electronic dephasing time, in marked contrast to the case for small molecules. We apply single molecule spectroscopy to image the effects of structural disorder on the fluorescence. Surprisingly, we find that chromophore units differ between each other not only in terms of their emission energy, but also with respect to the strength of vibrational coupling. Finally, we discuss the nature of structural relaxation and are able to place an upper limit on the Stokes shift arising due to excited state relaxation of 70 cm^{-1} as well as identifying intramolecular energy transfer between chromophores as a route to energetic relaxation.

II. EXPERIMENTAL

Methyl-substituted ladder-type poly(*para*-phenylene) (MeLPPP, structure shown in Fig. 1),[45] was dispersed in polystyrene in toluene at 10^{-6} molar concentration. The solution was spin-coated in a nitrogen atmosphere onto quartz substrates. The samples were mounted in a He cold finger microscope cryostat under a vacuum of $<10^{-6}$ mbar. The molecules were excited nonresonantly (i.e., not in resonance with the purely electronic transition of the molecule as is usually the case in single molecule spectroscopy[1,2,6,7]) in the vibrational manifold of the absorption [see Fig. 2(a)] by linearly polarized laser light from a pulsed frequency-doubled Ti:sapphire laser operating at 80 MHz repetition rate, sup-

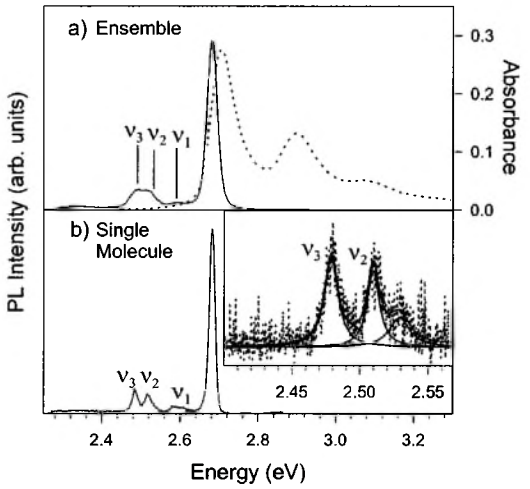

FIG. 2. (a) Ensemble fluorescence spectrum of MeLPPP dispersed in polystyrene at 10^{-4} molar concentration measured at 5 K. Three vibronic bands are identified and labeled. The absorption spectrum of a typical bulk film is also shown for reference (dotted line). (b) Single molecule fluorescence spectrum under nonresonant broadband excitation at 5 K measured with a spectral resolution of 10 meV. Inset: Vibronic progression of the single molecule fluorescence measured with a spectral resolution of ~2.5 meV. The solid lines correspond to Voigt fits.

plying pulses centered at 2.9 eV with a linewidth of 50 meV and a pulse length of 100 fs. The spectral width of the laser allowed nonresonant excitation of a number of different chromophores at once. The excitation was focused to a spot of ~100 μm in diameter. The excitation light was blocked using a nonfluorescent broadband interference filter. Photoluminescence (PL) was collected by a microscope objective (numerical aperture of 0.55) and imaged onto a LaVision Picostar gated intensified CCD, which was triggered by the laser and gated for typically 500 ps after the pulse. As the fluorescence lifetime of MeLPPP is ~300 ps, this allowed a reduction of the longer lived parasitic background luminescence of the matrix. Fluorescence spectra were recorded using either a 300 or a 1200 lines/mm grating in a 0.3 m monochromator. The maximal spectral resolution obtainable at the wavelength of the 0-0 transition of the polymer was ~2.5 meV. Polarized fluorescence spectra were recorded by rotating a polarization filter in the exit beam of the microscope and averaging over at least four complete cycles. Excitation of the polymer molecules in resonance with the purely electronic transition in emission and absorption at 2.7 eV [see Fig. 2(a)] could be achieved using an Argon ion laser operating at 2.708 eV. The excitation intensity of the epifluorescence microscope was ~6 W/cm^2 for pulsed excitation and 50 W/cm^2 for cw excitation using the Argon ion laser.

Proof of single molecule detection came from the following observations. Firstly, individual spots observed in the fluorescence image on the CCD were found to turn on and off reversibly at room temperature, providing evidence for reversible fluorescence quenching of a single emitter.[11] Secondly, the number of fluorescent spots on the CCD image scaled linearly with the polymer concentration in polystyrene and corresponded to the area density expected from the concentration. Although polymer molecules can aggregate under certain conditions, particularly due to phase segregation in polymeric blends as in the present case, we believe that the polymer concentration is much too small for this to occur. We found no dependence of the average intensity per fluorescent spot on MeLPPP concentration over several orders of magnitude in concentration, which again provides firm evidence that the single spots observed indeed correspond to individual, nonaggregated molecules. Finally, we note that the measured average count rates per molecule of 30 s^{-1} correspond well to what we expect from the excitation rate of $\sim 2 \times 10^4$ s^{-1}, which depends on excitation density and molecular absorption cross section, the molecular quantum efficiency of ~40% and the microscope detection efficiency of 0.6%. The formation of molecular aggregates, even if only structural and not electronic in nature, would lead to much stronger absorption and thus emission rates.

III. RESULTS AND DISCUSSION

A. Single molecule detection

Figure 1 shows a fluorescence measurement of a MeLPPP molecule in polystyrene at 5 K. Two narrow lines are identified at 2.70 and 2.68 eV with full widths at half maximum of 11 and 7.5 meV, respectively. These lines are peaked in the region of the 0-0 transition of MeLPPP.[45] At first glance, it is not possible to say whether the two lines correspond to two individual molecules in close proximity, or to two emitting species on a single molecule. However, most of the spatially well separated fluorescent spots identified in the far field fluorescence image of the microscope gave rise to multiple peaks upon spectral dispersion. In view of the large average separation between molecules of over 10 μm and the regular occurrence of multiple fluorescence peaks we propose that the two narrow emission features in Fig. 1 correspond to emission from two separate chromophore units on a single chain. Both peaks exhibit a marked polarization anisotropy, which is shown in the inset of Fig. 1. Rotating a polarizer in the emission pathway of the microscope yields a $\cos^2\theta$ dependence for both emitting peaks. Interestingly, the stronger peak at 2.70 eV does not appear to be fully polarized. As this peak is also somewhat broader than the lower energy peak, we propose that the emission spectrum results from more than one chromophore unit with slightly different energies and different orientations. We note that, although MeLPPP should be considered as a rigid rod-like polymer, it has been proposed that on-chain structural defects exist, which lead to a branching of the polymer chain.[46] This could explain the observation of differently polarized species on a single polymer molecule.

Our demonstration of virtually fully polarized emission lines is similar to results from single dye molecules at room temperature,[4] but in contrast to previous single molecule spectroscopy of conjugated polymer molecules, which only exhibited a comparatively small degree of fluorescence anisotropy.[13,16] Previous polarization anisotropy studies on stretch aligned polymer films have suggested the possibility of polymer chains possessing an emission contribution from

off-axis transition dipoles.[47] In the present study, we are able to identify spectral features almost 100 times narrower than those previously observed from single polymer molecules.[11–16] These features are virtually fully polarized and we therefore conclude the off-axis component of the transition dipole to be less than 1%.

B. Single molecule vibrational modes

We note that the narrow fluorescence spectra shown in Fig. 1 bear little resemblance to low temperature fluorescence spectra of small molecules.[1–7] Typically, small dye molecules exhibit a narrow zero-phonon line, which is superimposed on a broad fluorescence background resulting from coupling to vibrational modes as well as scattering from low energy phonons in the matrix.[3,6,7] In some cases, spectrally broad (tens of nanometers) fluorescence has been reported from dye molecules such as perylenemonoimide down to temperatures as low as 2K.[3] The fluorescence lines seen in Fig. 1 are considerably broader than the spectral resolution. It is conceivable that a number of almost isoenergetic chromophores are excited at once, which cannot be distinguished by their polarization. Furthermore, spectral diffusion, (i.e., temporal changes in molecular conformation and the dielectric environment), may also occur and give rise to spectral broadening, although we will argue later that this is unlikely. Figure 2(a) shows the emission spectrum of an ensemble of MeLPPP molecules highly diluted in polystyrene. Three vibronic features are identified and labeled. A typical absorption spectrum of a bulk MeLPPP film is also shown in Fig. 2(a). It peaks at 2.7 eV and has vibronic sidebands with a significant absorbance at 2.9 and 3.1 eV. In order to enable direct fluorescence spectroscopy of the 0–0 transition, we excited the polymer nonresonantly at 2.9 eV in the vibrational manifold of the absorption. A single molecule spectrum is shown in Fig. 2(b) under such nonresonant broadband excitation. Both the 0–0 line as well as the vibronic sidebands appear narrower in the single molecule spectrum in the absence of inhomogeneous disorder broadening inherent to the ensemble measurement. A high resolution spectrum of the ν_2 and ν_3 modes is shown in the inset of Fig. 2(b). The two peaks are well separated and a further shoulder is observed to the blue of ν_2. Raman spectroscopy as well as site-selective fluorescence of MeLPPP have previously led to the identification of the ν_2 and ν_3 modes at 1318 and 1578 cm^{-1}, which have been assigned to inter- and intraring C–C stretch modes, respectively.[30,48,49] The vibrational mode ν_1 at around 750 cm^{-1} has been observed in some Raman spectra of MeLPPP, but not in all.[48,50] A possible assignment of this rather broad feature on the basis of quantum chemical calculations is to in-plane C–H vibrations,[51] although there are most likely a number of weaker vibrational modes involved.

Direct excitation into the 0-0 absorption of the polymer using a narrow band laser allows us to image both the 0-1 and the 0-2 vibronic progression of the fluorescence of a single polymer molecule. This is shown in Fig. 3. The sum-frequency modes $\nu_2+\nu_3$ as well as $2\nu_2$ and $2\nu_3$ are clearly visible in the 0-2 transition peaked around 2.32 eV. The solid line indicates a fit using two Voigt-type curves and fixed center frequencies ν_2 and ν_3. The frequencies of the vibrational modes are identical under resonant and nonresonant excitation, which demonstrates that the molecule is fully relaxed and that excessive energy is dissipated before the radiative transition from the excited to the ground state occurs. Note that, in contrast, organic molecules in the gas phase have been shown to exhibit differences in vibrational coupling upon resonant and nonresonant excitation.[52]

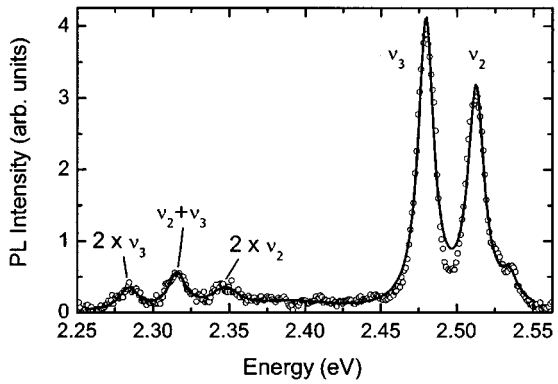

FIG. 3. Fluorescence from the first and second vibronic bands of a single MeLPPP molecule under narrow band resonant excitation of the 0-0 transition. The solid line corresponds to a Lorentzian fit and demonstrates the presence of the $\nu_2+\nu_3$ sum-frequency transition in the 0-2 vibronic sideband.

The observation of sum-frequency modes in the vibronic progression of a single polymer molecule demonstrates that it is possible to conduct single molecule experiments with conjugated polymers with only a very small contribution from intramolecular inhomogeneous broadening. The multichromophoric emission in Fig. 1 demonstrates that chromophore units on a single chain can lie 20 meV apart energetically. Such a distribution in energy would lead to a strong smearing of the beating in the vibronic progression in Fig. 3, rendering the sum-frequency feature unobservable. We therefore propose that we are indeed able to address a single chromophore on the polymer chain, and observe the intrinsic electronic properties of this molecular complex. We also note that this level of vibronic resolution has not previously been achieved in high resolution fluorescence studies of ensembles of conjugated polymers. Site-selective fluorescence has enabled the identification of narrow zero-phonon lines coupled to well-defined vibronic progressions in monomers and oligomers, but not in polymers.[29] Note that, in contrast to narrow band resonant excitation, where the observation of narrow vibrational lines can also be due to resonant Raman scattering, the fact that we observe the same fluorescence features at identical energies under both resonant and nonresonant narrow and broadband excitation (i.e., independent of excitation energy) demonstrates that we are indeed detecting fluorescence rather than scattering.

We note that the ν_2 and ν_3 vibrational modes dominate the gain spectrum in most conjugated polymers. On the basis of site-selective fluorescence measurements at high excitation fluence, it has previously been suggested that vibrational emission from nonthermalized excitations in the tail of the density of states acts as the seeding process in stimulated

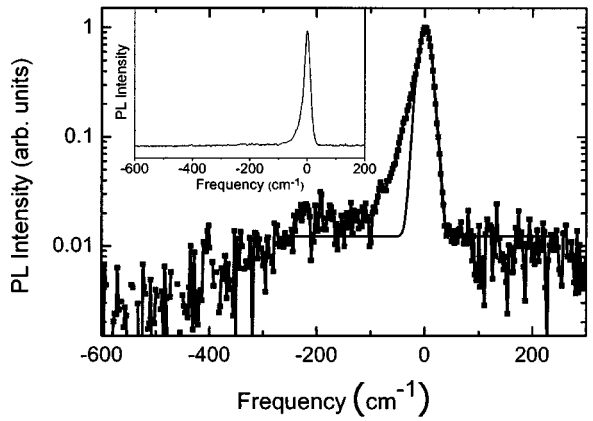

FIG. 4. High resolution fluorescence spectrum of a single MeLPPP molecule shifted by its center frequency and plotted on a logarithmic scale. The solid line shows a Gaussian fit to the high energy tail, which reveals a small degree of broadening to the red of the main transition. Besides a very weak feature at 190 cm^{-1}, no low frequency vibrational modes are apparent. The inset depicts the same spectrum on a linear scale.

emission.[53] Similar data have, however, also been interpreted in terms of stimulated Raman scattering under resonant excitation of the 0-0 transition.[54] Our observation of spontaneous emission into well-defined narrow vibrational features provides support for the former model of the dominance of vibrational relaxation in stimulated emission.

C. Vibrational coupling and dephasing

Most single molecules excited nonresonantly in the vibrational manifold exhibit narrow zero-phonon lines accompanied by broad phonon sidebands.[3,6,7] As the lifetime of vibrational states in molecules is rather short, typically in the range of picoseconds, the vibrational states generally appear very broad in comparison to the narrow, lifetime-limited zero-phonon line. In contrast, in the present polymer system, only a very limited number of vibrational modes appear to be available, giving rise to a rather isolated appearance of the 0-0 transition. Figure 4 depicts a PL spectrum on a logarithmic scale of a particularly narrow line from a MeLPPP molecule, shifted to the red by its peak energy. A Gaussian line is superimposed on the emission line, which reveals a small degree of asymmetry of the spectrum with slight broadening to the red. The broadened red tail is over an order of magnitude weaker than the main emission. The broadening, which extends to up to 50 cm^{-1} from the main transition line, may be due to the presence of a further, much weaker chromophore, but is most likely a result of inelastic scattering on low energy acoustic phonons in the matrix. This leads to the formation of a characteristic phonon wing. A broad feature, two orders of magnitude weaker in intensity than the main transition and just above the background level, is observed around 190 cm^{-1} from the main transition. This feature may be a signature of a low frequency vibrational mode. Site-selective fluorescence spectroscopy has suggested the presence of a weak 120 cm^{-1} vibrational mode in MeLPPP,[30] although the origin of this in the stiff and rigid polymer structure is not clear. The high energy tail falls off rapidly and shows no indication of an anti-Stokes phonon wing, as expected for low temperature measurements.

The width of the line of 2.5 meV is close to the resolution limit of the setup. Such a narrow line corresponds to a dephasing time of >520 fs. This is extremely fast compared to single dye molecules.[1,7] However, recent measurements of resonant Rayleigh scattering on conjugated polymer films have suggested a loss of electronic coherence within ~ 0.5 ps.[55] Due to the many forms of scattering events an excitation can undergo in a polymer, rapid dephasing and therefore a comparatively broad zero-phonon line is not very surprising. Estimates for the size of a single chromophore in MeLPPP are in the range of 10 or more repeat units,[56] which is much larger than any normal dye molecule and therefore dramatically enhances the possibility of coherence loss on, for example, structural defects. It should also be noted that even highly ordered single molecules of polydiacetylene in monomeric crystals, which essentially form defect-free one-dimensional quantum wires—and therefore cannot be described by the molecular chromophore model—exhibit dephasing times as short as 2 ps.[18] Furthermore, photon echo studies on aggregated chains of poly(phenylene-vinylene) in toluene solution have suggested room temperature dephasing times as short as 50 fs, leading to substantial spectral broadening in the ensemble.[57]

Detailed inspection of the spectrum in Fig. 4 shows that the 0-0 transition is not accompanied by any significant vibronic emission and only weak phonon scattering from the matrix within the first 600 cm^{-1} to the red of the 0-0 transition. The fact that such narrow lines are observed in an amorphous matrix from a multichromophoric macromolecule suggests that the coupling to the environment may actually be rather weak at low temperatures. In addition, the stiff backbone structure of the fully planarized ladder-type polymer inhibits low energy intramolecular vibrations. The result is that a large proportion of the excitation energy is channeled into the purely electronic transition, rather than being dissipated in phonon scattering processes. It is also conceivable that the bulky sidegroups on the polymer backbone lead to a reduction of the polymer surface area with respect to the volume occupied in the matrix, thereby providing an effective shielding of excitations from phonons in the matrix.

It is interesting to note that the coupling of π-electrons to only a very limited number of vibrational modes of the polymer chain is an underlying assumption of the band model of conjugated polymers, where vibrational coupling is required to drive dimerization and thus the formation of a bandgap, and can only occur with a small number of modes that exhibit the correct symmetry.[32] In effect, the dominance of a very limited number of high energy vibrational modes poses a deviation from the conventional model of conjugated polymers, although of course the observation of well-defined, nonisoenergetic chromophore units, most likely defined by structural defects rather than by vibrational coupling, is in full agreement with this picture.

The dominant vibrational modes of the system are set off by over 1200 cm^{-1} from the purely electronic transition. In small molecules, the vibrational features are expected to be broader than the zero phonon line as the lifetime of the vi-

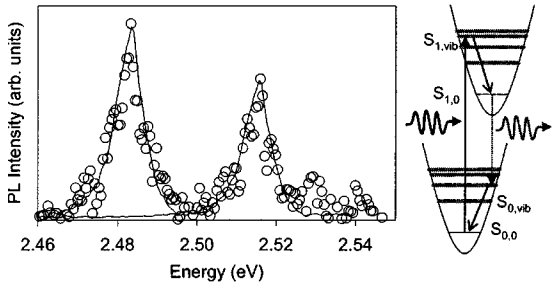

FIG. 5. Comparison of the linewidths of the 0-0 and vibronic emission bands in a single molecule. The lines show the 0-0 transition at 2.7 eV, which is shifted in energy and rescaled to overlay the ν_2 and ν_3 vibronic bands (symbols).

brational states is typically on the picosecond time scale, which gives rise to a smearing out of the emission energy due to the Heisenberg uncertainty principle. A similar effect is also observed in PL excitation spectra of inorganic quantum dots, where the homogeneous linewidth of the exciton ground state increases monotonically with increasing energy of the discrete excited states of the exciton.[58] This appears not to be the case for the polymeric systems presently under investigation. Figure 5 shows a comparison of the 0-1 vibrational lines (symbols) and the 0-0 transition (solid line), with the 0-0 line shifted to lower energy to superimpose the 0-1 transitions. Note that the spectra are not resolution limited. Evidently, the superposition is perfect, and we conclude that the vibronic and 0-0 transitions have the same width. This implies that the contribution to spectral broadening due to fast vibronic relaxation is minimal, in stark contrast to the case for small molecules. The energy level scheme is also sketched in Fig. 5. Vibrational transitions are marked by nonvertical open arrows, whereas electronic transitions are marked by closed vertical arrows. In molecular systems, the vibrational levels are generally smeared out in energy due to their short lifetime in both the excited and ground states, whereas the width of the electronic $S_{1,0} \rightarrow S_{0,0}$ is simply limited by the excited state lifetime in the absence of scattering mechanisms and is therefore much smaller.

Our observations suggest that vibrational relaxation in the ground state occurs on a time scale similar to or even longer than electronic dephasing,[55] in marked contrast to small molecules. This is in agreement with the recent observation of vibrational coherence in the excited state, assuming that vibrational relaxation in the ground and excited states are similar and both of order 1 ps.[31] The vibrational lines are therefore not broadened due to the short lifetime of the vibrational sublevels, but are due to the intrinsic linewidth of the 0-0 transition. Note that if the lifetime τ of the vibrational excitation were indeed shorter than 100 fs, as widely assumed,[20,23] even in the absence of any further broadening mechanisms such as electronic dephasing or spectral diffusion, the linewidth of a single vibronic transition would have to exceed $2\hbar/\tau = 13$ meV. This is evidently not the case, and even for the comparatively broad 0-0 transition in Fig. 5, a width of only 8 meV is found for the vibronic sideband.

A consequence of long-lived vibrational coherence in conjugated polymers may be either energy transfer from the nonrelaxed state[25] or even emission. To test for this emission,

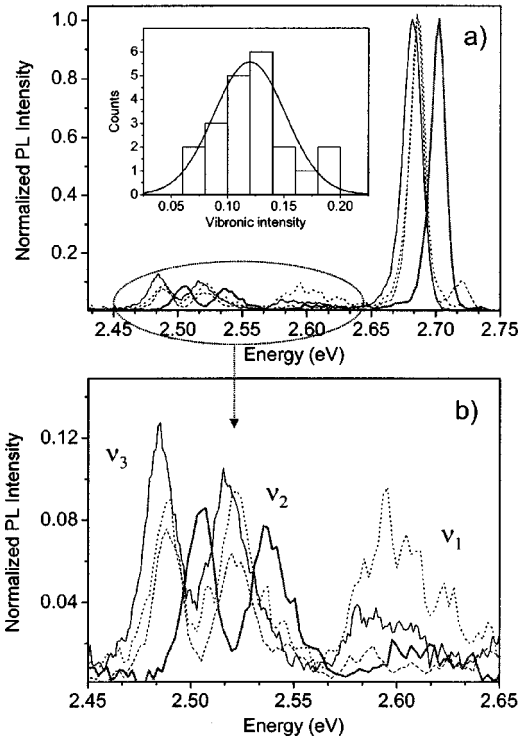

FIG. 6. (a) Four different single molecule fluorescence spectra normalized to the 0-0 transition line, which is limited in width by the instrument response. The strength of the vibronic side bands differs from molecule to molecule. The inset shows the distribution of measured intensities of the ν_3 vibronic sideband. (b) Magnification of the spectra shown in (a).

we performed ultrafast fluorescence measurements on MeLPPP solutions using a streak camera setup with a temporal resolution of 2 ps. Upon UV excitation, we observed an instantaneous onset of PL. We identified a weak spectral feature present only in the first few picoseconds to the blue of the MeLPPP PL, which we were able to attribute to Raman scattering from the 3000 cm^{-1} mode of the solvent. The absence of any further detectable feature suggests that if there is any emission from hot excited states, its intensity is below 0.01% of the relaxed PL, in accordance with the initial measurements of time resolved PL by Kersting *et al.*[23]

Using single molecule spectroscopy, we are able to demonstrate that the strength of vibrational coupling differs strongly from molecule to molecule. Figure 6 shows a comparison of four single molecule spectra of MeLPPP normalized to the 0-0 transition around 2.70 eV. The spectra are peaked at slightly different energies, but all exhibit vibrational peaks offset by the same energies. Figure 6(b) shows a close-up of the vibrational peaks. Evidently, the intensities of the vibronic sidebands vary dramatically from molecule to molecule. The variation is particularly pronounced for the ν_1 peak, which is entirely absent for some molecules. The inset in Fig. 6(a) shows a histogram of the vibronic intensity of the ν_3 peak relative to the 0-0 line for 21 different molecules, which shows a variation within a factor of 2. Note that the data were obtained under the premise of resolution-limited detection, which implies that the peak height scales with the peak area, thus permitting us to consider the peak ratios.

Evidently, the concept of disorder not only applies to the actual π-π^* gaps of the individual molecules, but also to the strength of coupling of electronic excitations to vibrational modes. This direct observation of two manifestations of structural disorder in conjugated polymers provides important input into a microscopic understanding of the role of disorder in organic semiconductors.

It has previously been pointed out that the vibrational coupling strength in ensembles of conjugated polymers can change depending on the film morphology.[42,59] Recent quantum chemical calculations have shown that the Franck-Condon progression in both absorption and emission can be very sensitive to small changes in the actual molecular conformation.[60–62] Careful interpretation of single polymer molecule spectra with well-defined vibrational structure could therefore be used in combination with suitable quantum chemical models to derive insight into the conformation of a single chain. We note that the number of degrees of conformational freedom are limited for rigid-rod ladder-type polymers. The difference in vibrational coupling between nominally identical molecules however suggests a substantial variation between molecules. This could be induced by localized defects or even chain branching points.[46] If the chain is not fully planarized, it is also conceivable that the ladder-structure obtains a certain degree of torsional stress due to interactions with the matrix. The degree of twisting and therefore of torsional stress could depend on the overall chain length, which differs from molecule to molecule. Intermolecular variations in the strength of vibrational coupling have been observed in the vibrationally rich fluorescence spectra of terrylene molecules.[5,6] It has been suggested that certain vibrational modes may exhibit a particular sensitivity to slight changes in the molecular conformation or the local environment, which has also been supported by quantum chemical calculations.[6] The recent development of novel quantum chemical techniques to describe excited state relaxation in conjugated polymers as well as vibrational coupling[60] in combination with our spectroscopic results promises further insight into fundamental structure property relationships in organic semiconductors.

Finally, it is interesting to note that interparticle variations in the strength of electron-phonon coupling have also been observed for colloidal nanocrystals.[63] The variation in coupling strength, which was also observed on one single particle undergoing spectral jumps, was related to Fröhlich-type electron-phonon interactions due to a change in the ionic crystal's charge distribution.[63] This modifies the degree of electron-hole wave function overlap. Although such a process is rather unlikely to influence tightly bound electron-hole pairs in organic semiconductors, we do note that the intramolecular charge distribution in π-conjugated systems is closely coupled to the molecular conformation. Although the vibrationally resolved fluorescence of a molecule is a signature of the ground state vibrational manifold, the intensity of the vibronic band may be a signature of the degree of excited state structural relaxation, which can also be influenced by the charge distribution. The single molecule Franck-Condon factor should thus be related to the structural relaxation following the $S_1 \leftarrow S_0$ transition.

D. Stokes Shift

Solid state organic materials typically exhibit a substantial shift between absorption and emission maxima. This is in general a favorable property, as it prevents reabsorption of light emitted in a photonic device. Four processes can give rise to an apparent shift between the absorption and emission of an organic semiconductor. Firstly, excitation in the vibrational manifold above the fundamental transition energy should generally lead to rapid vibrational relaxation and a conversion of excitation energy into thermal energy. Secondly, a structural reorganization may occur in the excited state, which can account for a shift of hundreds of meV.[28,30,43,64] Both inter- as well as intramolecular transfer of excitation energy can occur in polymeric semiconductors, which typically leads to a further redshift in the emission as energy is transferred to the lowest energy molecular sites in the inhomogeneously broadened density of states[23,26,27,65]. Finally, efficient exciton transfer to emissive chemical defects on the polymer chain[40,66] or exciton trapping on inter- or intramolecular aggregate or excimer sites[65,67,68] can lead to a further substantial redshift of the apparent emission due to the involvement of an entirely different emissive species. The presence of on-chain defects with a considerable ground state absorption has, for example, rendered the observation of resonant features in site-selective fluorescence of MeLPPP polymers impossible, whereas model oligomeric compounds exhibited resonant features under identical conditions.[29]

Both site-selective and time-resolved techniques can be used to differentiate between these processes. However, site-selective fluorescence measurements have thus far always indicated a finite Stokes shift in polymers of tens of meV due to structural relaxation or intramolecular energy transfer.[28,30,43] This is in contrast to oligomeric model compounds, which exhibit much smaller Stokes shifts.[30] We can perform site-selective excitation of single polymer molecules by resonantly exciting the 0-0 transition at 2.708 eV. The ν_2 and ν_3 vibrational modes in emission are offset by a constant value from the 0-0 transition, independent of the molecule. The energetic difference between the narrow laser line in resonance with the 0-0 absorption and the ν_2 and ν_3 emission bands therefore provides a measure of the Stokes shift on a single molecule.

Figure 7(a) shows a PL spectrum recorded under resonant excitation at 2.708 eV. A small amount of excitation light was recorded to allow an accurate detemination of the position of the laser line. Offset by an energy $E_{\mathrm{Exc}}-E_{\mathrm{PL}}$ to the red, the vibronic sidebands ν_2 and ν_3 are observed. The energetic difference between excitation and PL is plotted for both vibrational peaks in Fig. 7(b). The dashed lines indicate the energetic position of the ν_2 and ν_3 lines in the absence of a Stokes shift. Evidently, the actual energetic difference between the excitation and emission energy is larger than the energy of the vibrational modes. The energy differences are plotted for six different molecules, and are found to vary between 70 and 250 cm^{-1}. Intramolecular energy transfer accounts for part of this energy difference. Its contribution can, however, be as small as zero, if the emitting chromophore is identical with the chromophore excited by the laser. The smallest offset of the measured difference to the expected

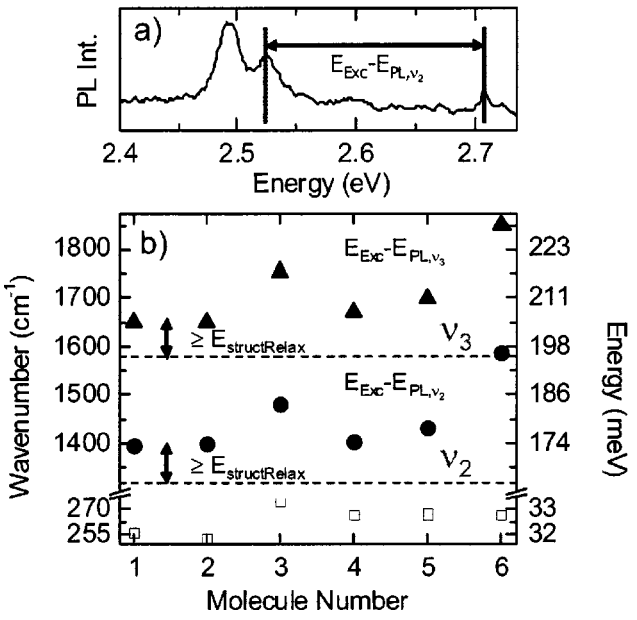

FIG. 7. (a) Single molecule PL spectrum under narrow band resonant excitation at 2.708 eV. The vibronic doublet of the 0-1 transition is visible around 2.5 eV as well as the laser line at 2.708 eV. The energetic difference between the ν_2 vibronic peak and the laser peak, which is resonant with the 0-0 transition, is extracted from the figure and is defined as $E_{\mathrm{Exc}}-E_{\mathrm{PL},\nu_2}$. (b) Energetic difference between the laser line and the vibronic fluorescence band for the ν_2 (▲) and ν_3 (•) peaks. The energy of the ν_2 and ν_3 transitions are marked by dashed lines, which should correspond to $E_{\mathrm{Exc}}-E_{\mathrm{PL}}$ in the absence of structural relaxation and energy transfer. The lower panel shows the difference $E_{\mathrm{PL},\nu_3}-E_{\mathrm{PL},\nu_2}$ (□), demonstrating that the peak positions are determined within a precision of 15 cm^{-1}.

shift of ν_2 or ν_3 is 70 cm^{-1}. We propose that this value gives an upper estimate for the Stokes shift arising due to structural relaxation and therefore term it $E_{\mathrm{structRelax}}$. The lowest panel in Fig. 7(b) shows the difference between the two vibronic peaks observed in the PL spectra. The value is constant to within 15 cm^{-1} for the six molecules studied, providing an estimate for the accuracy in determining the positions of the vibronic sidebands relative to the excitation line.

Molecules exhibiting Stokes shifts larger than 70 cm^{-1} are most likely subject to energy dissipation in the form of intramolecular energy transfer from higher to lower energy chromophores. We note that the largest shift we observe on a single molecule is 270 cm^{-1}. Assuming an energy transfer process with the involvement of at least two chromophores, a donor and an acceptor unit, which each exhibit a Stokes shift of 70 cm^{-1} due to structural relaxation, an energetic shift of 130 cm^{-1} remains to be accounted for by energy transfer. By determining the average energetic distribution of different chromophore units present on a single chain—as seen, for example, in Fig. 1—we arrive at an estimate for the level of intramolecular disorder of approx. 14 meV (112 cm^{-1}).[39] As the narrow laser line at 2.708 eV excites the polymer ensemble in the higher energy tail of the density of states, it is reasonable to assume that intramolecular energy transfer can give rise to an additional energetic shift of order the intramolecular disorder. This can account for the apparent Stokes shift of up to 270 cm^{-1}.

IV. CONCLUSIONS

We have presented results on single molecule spectroscopy of a ladder-type conjugated polymer. Single molecule studies provide an important addition to site-selective fluorescence studies in ensemble systems. We find that single conjugated polymer molecules are excellent materials for single molecule experiments, exhibiting a high degree of photostability, narrow spectral emission lines, weak interaction with the environment, and relatively weak coupling to a selected number of vibrational modes. We have provided evidence that we are able to identify individual chromophores on a single polymer chain, which emit fully linearly polarized light. We can resolve the vibrational modes constituting the vibronic progression in the emission up to the 0-2 band. We find that, in contrast to previous studies of the fluorescence of single dye molecules, the polymers investigated display only very weak emission due to low frequency phonons or vibrations with energies below 600 cm^{-1}. This suggests that most of the oscillator strength is channeled into the purely electronic transition. We cannot exclude the possibility of slight spectral diffusion giving rise to spectral broadening even at low temperatures. However, as our linewidths, which correspond to a dephasing time in the range of 0.5 ps are in good agreement with previous measurements of the electronic dephasing time in conjugated polymers,[18,55] we conclude that the zero-phonon line in the polymeric system under investigation should not be much narrower than the feature we observe in fluorescence (e.g., in Fig. 4). Furthermore, we observe no direct evidence for discrete spectral jumps, which can be as large as hundreds of wave numbers in dye molecules or colloidal nanocrystals.[7,8]

The nature and speed of vibrational relaxation of polymers in the ground and excited states have been debated extensively in the literature. Whereas rapid vibrational relaxation in the ground state is a general prerequisite for achieving population inversion and stimulated emission, excessive vibrational energy in the excited state may lead to photoionization[21,69] which is important in, for example, organic photodiodes. As the primary photoexcitation in all applications of conjugated polymers, such as light-emitting diodes, is generally a hot, nonrelaxed exciton, obtaining insight into the relaxation pathways is crucial to understanding device operation. Furthermore, the role of nonthermalized excitons in energy transfer has also been discussed previously.[25] Measurements of the ultrafast fluorescence decay in conjugated polymers have suggested that excess vibrational energy is dissipated in under 100 fs.[23] This assumption is frequently used in microscopic models of charge carrier generation and exciton migration. However, the recent observation of long-lived (up to 1 ps) vibrational coherence in a conjugated polymer is at variance with these assumptions and rather suggests that excitons can remain in an excited vibrational state for a considerable amount of time.[31] Our observation that the linewidth of the 0-0 transition is identical to that of the vibrational sidebands is in agreement

with the picture that vibrational dephasing occurs on a time scale longer or comparable to the excited state dephasing, which we estimate to be 0.5 ps.

Sample-dependent differences in the Franck-Condon progression exhibited in the fluorescence of conjugated polymers have previously been observed in bulk films and attributed to changes in molecular conformation. Single molecules display strong variations in the strength of vibrational coupling, pointing to the possibility of a range of molecular conformations. The study of single polymer molecules therefore allows a differentiation between purely energetic disorder, manifested in a distribution of emission energies, and disorder in terms of vibrational coupling strength, which controls the intensity of the vibronic sidebands. We anticipate that combinations of sophisticated quantum chemical techniques with vibrational single molecule spectroscopy will allow a powerful insight into conformational properties of single polymer molecules.

Finally, we are able to exploit the site-selective nature of resonant single molecule fluorescence spectroscopy to arrive at an estimate for the intrinsic Stokes shift of a single chromophore. Both intramolecular energy transfer between individual chromophores and structural relaxation are found to contribute to the Stokes shift. Using resonant excitation of individual chromophores, we are able to suppress intramolecular energy transfer and observe a maximal Stokes shift of 70 cm^{-1}, which is substantially smaller than the shift of 240 cm^{-1} previously determined in films of poly(phenylenevinylene) using resonant excitation and time-resolved detection to extract the component due to exciton migration.[24] To the best of our knowledge the Stokes shift of 70 cm^{-1} is the smallest shift reported for a conjugated polymer thus far.

We conclude by pointing out that the spectral purity and stability, the control over polarization, the narrow spectral width, and large oscillator strength as well as the small Stokes shift all suggest that single conjugated polymer molecules at low temperatures are ideally suited to performing single molecule quantum optical experiments.

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