Observation of Very Narrow Linewidths in the Fluorescence Excitation Spectra of Single Conjugated Polymer Chains at 1.2 K

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(Received 26 February 2007; published 15 May 2007)

Fluorescence emission and excitation spectra of single poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] polymer molecules embedded in poly(methylmethacrylate) have been recorded at 1.2 K. The ubiquitous spectral diffusion causes large variations in the spectral shape and apparent linewidth in the emission spectra. Nevertheless, we find very narrow ($\sim 0.1\ \mathrm{cm}^{-1}$) purely electronic zero-phonon lines in the excitation spectra, which are 2 orders of magnitude smaller than previous estimates of the homogeneous linewidth. These results complement the molecular description of the low energy transitions in conjugated polymers.

DOI: 10.1103/PhysRevLett.98.208301 PACS numbers: 36.20.Kd, 33.20.Kf, 33.70.Jg, 78.55.−m

Optical spectroscopy has been crucial to elucidate the electronic structure and energy transfer processes in conjugated polymers [1,2]. According to our present understanding, conjugated polymers are viewed as a collection of "chromophores," each formed by a certain number of repeat units. After photon absorption, the energy is transferred efficiently between the chromophores until it is captured and emitted by low energy sites. Recently, optical studies have been extended to the level of single polymer chains, giving additional insights into the nature of the emissive species [3–5], chain conformations [6,7], and singlet/triplet excitons [8]. After cooling down the samples to temperatures as low as 5 K, narrowed emission spectra have been found, which allowed for distinguishing between several emitting sites [9–11] and for studying spectral diffusion over various energy and time scales [12,13]. Another important parameter accessible in low temperature single-molecule experiments is the optical linewidth, which is intimately connected to the nature of the corresponding electronic transitions and their coupling to the environment. Narrow linewidths ($\sim 4\ \mathrm{cm}^{-1}$) have been observed in the emission spectra of single polydiacetylene chains in a crystalline host at 10 K, a model system with exceptionally high structural order [14]. Considering the prototypical conjugated polymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), Schindler *et al.* have reported the narrowest linewidths so far, which were around $20\ \mathrm{cm}^{-1}$ and obtained at 5 K by emission spectroscopy of single chains embedded in polystyrene [13,15]. By comparison with other experimental data, the authors suggested that this is actually the homogeneous linewidth. Given the molecular picture of conjugated polymers, this conjecture is puzzling, because this width at 5 K is still orders of magnitude larger than the value given by the excited state lifetime which was reported to be around several hundred picoseconds [16].

All of the single-molecule results mentioned above have been obtained by emission spectroscopy. Typically, single-molecule emission spectra at cryogenic temperature suffer from two drawbacks. First, the achievable spectral resolution is intrinsically limited by the spectrograph, and, second, only the emissive sites are accessible. To overcome these limitations, we have measured for the first time both fluorescence excitation and emission spectra of isolated single MEH-PPV polymer chains embedded in poly(methylmethacrylate) (PMMA). We find linewidths as narrow as $0.1\ \mathrm{cm}^{-1}$, which, however, are still limited by the instrumental resolution. Because of spectral diffusion, which can lead to very large apparent linewidths, such sharp zero-phonon lines are observed only occasionally.

MEH-PPV with an averaged molar weight of $M_w \approx 200$ kDa and large polydispersity (PD = 5) was purchased from Aldrich. After size fractionation, a sample with $M_w \approx 50$ kDa and PD = 1.3 was selected, whereby the selected fraction was chosen according to the results from gel permeation chromatography (GPC). The MEH-PPV was first completely dissolved in tetrahydrofuran, and afterwards, 17 μl of this solution (ca. 1.3×10^{-8} mol/l) was diluted with 3 ml of toluene containing PMMA at a concentration of 20 g/l. From this solution, thin films (thickness: ~ 100 nm) were spin-coated onto thoroughly cleaned glass cover slides. During and after the spin coating process, the samples were constantly kept under argon. The sample to be investigated was transferred into an optical cryostat under a constant argon stream and kept under vacuum conditions before cooling down. For the measurements at 1.2 K, the sample was immersed in superfluid liquid helium. The fluorescence imaging and spectroscopy of single polymer molecules was conducted by a homebuilt confocal microscope [17]. The fluorescence emission spectra were taken with $\lambda_{\mathrm{exc}} = 488$ nm and a laser intensity of ca. $2.5\ \mathrm{kW/cm}^2$. A spectrograph equipped with a liquid-nitrogen-cooled CCD camera was operated in low (150 lines/mm grating; res.: $20\ \mathrm{cm}^{-1}$) and high (1800 lines/mm; res.: $2\ \mathrm{cm}^{-1}$) resolution mode. The fluorescence excitation spectra were recorded by using a tunable, circular polarized ring dye laser (linewidth ca.

0.1 cm^{-1}) operated with pyrromethene 546. While scanning the dye laser across its tuning range (525–545 nm), all emission light transmitted by a 555 nm red pass filter was collected with an avalanche photodiode. The excitation spectra were taken with an intensity of ~10–100 W/cm^2.

Absorption and emission spectra of a bulk solution of MEH-PPV in toluene (not shown here) agreed with data reported in the literature [1]. Figures 1(a)–1(c) show three examples of emission spectra, which were taken from single MEH-PPV molecules in PMMA. In all three cases, the spectra are attributed to emission from a single chromophoric unit within the conjugated polymer molecule. Such one-chromophore spectra have been observed for 36% of all investigated single MEH-PPV chains. The remaining spectra were attributed to a superposition of emission from two or more sites. An example is given in Fig. 1(d), where the two peaks at 525 and 547 nm represent the electronic origins of two contemporaneously emitting chromophoric units. In total, 176 single MEH-PPV molecules have been investigated. The histogram of emission peak wavelengths derived from these measurements is well described by a single Gaussian (Fig. 2). The distribution clearly is not bimodal (''blue''- and ''red''-emitting site) as was found for high molecular weight MEH-PPV samples at 20 K [18,19]. In accordance with recent investigations of single polyfluorene copolymer molecules [20], our observation of a monomodal distribution is attributed to the short chain lengths of the MEH-PPV, which makes distinct red-emitting sites—supposedly caused by intrachain contacts [19,20]—less probable.

A closer look at the emission spectra shown in Fig. 1 reveals that at 1.2 K substantial differences exist between different molecules from the same sample. The spectra shown in Figs. 1(a) and 1(b) are similar to spectra recorded at 20 K by Barbara *et al.* [9,18]. Given the low temperature used in our investigation, the apparent linewidths, which clearly differ for both molecules, are extremely large. In contrast, the spectra in Figs. 1(c), 1(d), and 3(a) display intense and sharp features at the electronic origin which are the zero-phonon lines (ZPLs) of the $S_1 \leftarrow S_0$ transition of the emitting chromophores. These sharp peaks, which appeared for only 20% of the molecules studied, can become as narrow as 2–3 cm^{-1} [see inset in Fig. 1(d)]. Recently, it has been argued that the observation of a substantially blueshifted distribution of narrow emission lines of MEH-PPV may be caused by partial photooxidation [21]. To emphasize that our observation of narrow emission lines is not related to the spectral position, we have highlighted the ZPL emission wavelengths in the distribution given in Fig. 2.

Narrow ZPLs as shown in Fig. 1(c) are mostly subject to fluctuations in the spectral position. When the time scale of spectral diffusion becomes much faster than the recording time of spectra (20 s), the narrow features can be smeared out completely, leading to spectra of the types shown in Figs. 1(a) and 1(b). This behavior is seen in straightforward simulations, in which a spectrum as shown in Fig. 3(a) was allowed to perform Gaussian distributed random spectral shifts over several nanometers, a range which is in accordance with previous observations [13]. Furthermore, when

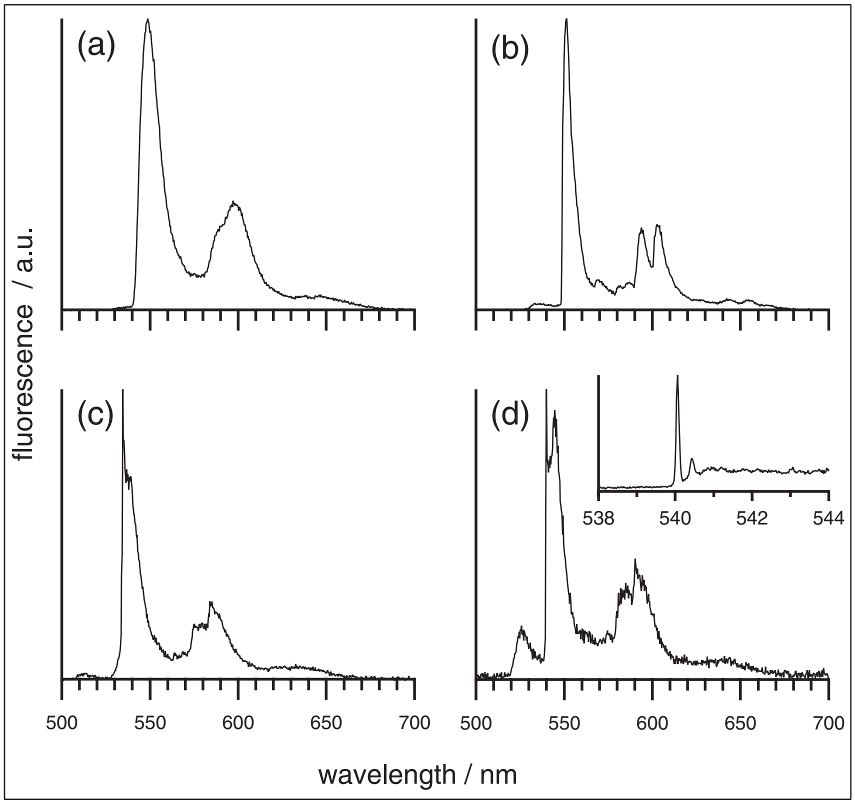

FIG. 1. Emission spectra of single MEH-PPV chains in PMMA taken at 1.2 K with an excitation wavelength of 488 nm. The spectra in (a)–(c) are attributed to emission from single chromophores. The substantial variations in spectral shapes are evident; in (c), a narrow zero-phonon line is visible. The spectrum shown in (d) results from the emission of two chromophores. The chromophore with lower transition energy displays a zero-phonon line. The inset presents the spectral region around this zero-phonon line acquired with higher spectral resolution.

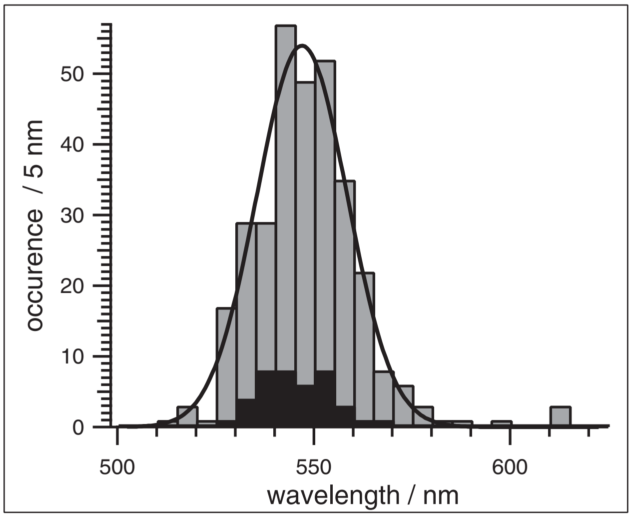

FIG. 2. Distribution of peak emission maxima observed for MEH-PPV at 1.2 K (gray bars). The drawn line is a Gaussian fitted to the data with a maximum at 547 nm and a FWHM of 27 nm. The black bars give the subpopulation of molecules for which zero-phonon lines could be detected.

decreasing the integration time to 1 s, in many instances we have found that the apparent linewidth of spectra as represented in Figs. 1(a) and 1(b) decreased appreciably. These observations at 1.2 K clearly indicate that spectral diffusion is a major contribution to the large variations of the emission linewidths of single MEH-PPV molecules. Hence, the large apparent linewidth of a spectrum as shown in Fig. 1(a) typically is not intrinsic. In addition to spectral diffusion, variations in electron-phonon coupling strength may also be partly responsible for the different types of spectra observed.

Besides experiments at 1.2 K, we also have conducted some measurements at 20 K. In no case could we observe narrow features in the emission spectra. Consequently, we assume that raising the temperature to 15–20 K leads to increased spectral diffusion, which, in addition to other line broadening mechanisms (phonon scattering), renders the observation of sharp ZPLs highly improbable [9,12].

The emission spectra shown in Figs. 1(a)–1(d) have been obtained in low resolution mode ($\sim 20\ \mathrm{cm}^{-1}$). In the inset in Fig. 1(d), the low energy fraction of the emission spectrum of the red-emitting chromophore (547 nm) is presented with increased spectral resolution. The width of the purely electronic ZPL is given by $3.2\ \mathrm{cm}^{-1}$. Although such linewidths are almost an order of magnitude smaller than values reported before for MEH-PPV in polystyrene [13,15], they are still limited by the resolution of the spectrograph ($\sim 2\ \mathrm{cm}^{-1}$). As will be shown below, the resolution can be greatly improved by fluorescence excitation spectroscopy using a narrow bandwidth laser. Interestingly, in the emission of the blue chromophore around 525 nm [Fig. 1(d)], no ZPL but only a broad line is found. Adopting the common description of conjugated polymers as multichromophoric systems, the two emissions seen in Fig. 1(d) originate from two chromophoric units along the chain. Since the behavior of the two chromophores needs not to be correlated, the blue chromophore may be subject to stronger spectral diffusion or electron-phonon coupling compared to the red chromophore. In addition, one has to take into account that energy may be transferred efficiently from the blue to the red chromophore (or other nonemitting chromophores), leading to appreciable homogeneous line broadening of the blue ZPL. All of these effects may lead to disappearance of the ZPL.

In Fig. 3, the fluorescence emission [Fig. 3(a)] and excitation spectra [Fig. 3(b)] of a single MEH-PPV molecule are shown. A single sharp ZPL is visible in both spectra. Within the experimental accuracy, the spectral positions of both narrow lines are the same, giving clear evidence that in both cases the lowest energy purely electronic zero-phonon transition of one chromophore has been probed. Consequently, there is no Stokes shift between these two lines. Again, the linewidth extracted from the emission spectrum would be eventually limited by the spectrograph resolution of $\sim 2\ \mathrm{cm}^{-1}$. By analyzing the excitation spectrum, the width of the ZPL was found to be $0.11\ \mathrm{cm}^{-1}$. Although this value is 1 order of magnitude smaller, it is still not the true linewidth, because it is basically given by the spectral width of the dye laser ($0.1\ \mathrm{cm}^{-1}$). Besides spectra, we also have measured fluo-

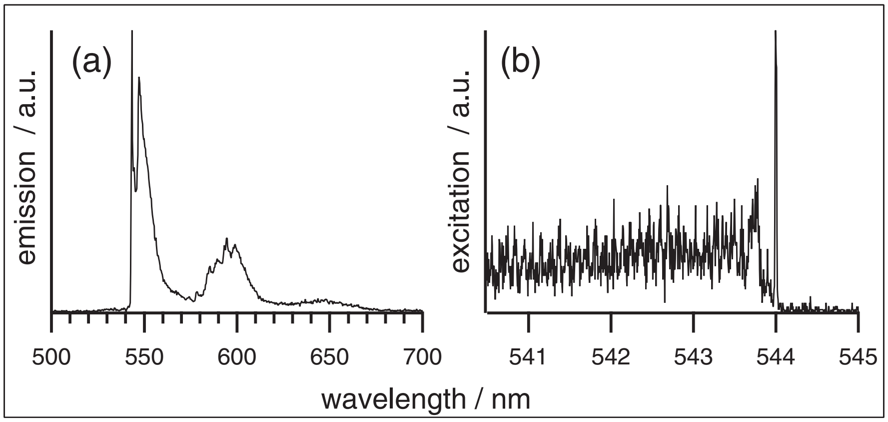

FIG. 3. (a) Fluorescence emission ($\lambda_{\mathrm{exc}} = 488$ nm) and (b) excitation spectra of a single MEH-PPV molecule. Both spectra show a purely electronic zero-phonon transition at the same spectral position. Please note the differences in wavelength scale.

rescence decay times of single MEH-PPV chains at 1.2 K. In accordance with other single-molecule [22] and ensemble measurements [16], values in the range of several hundred picoseconds were obtained. Assuming a fluorescence lifetime of 500 ps, the purely lifetime limited linewidth should be around 0.01 cm^{-1}. Because of additional dephasing processes, the homogeneous linewidth may be considerably larger. For the data shown in Fig. 3, an upper limit is given by the resolution limited value of 0.1 cm^{-1}.

The subsequent recording of ZPLs in emission and excitation spectra has been possible only in a very few cases where (light-induced) spectral diffusion was sufficiently weak. Furthermore, the few ZPLs that were reproducibly registered in the excitation spectra always showed up as the lowest energy feature. Not in a single case could we detect ZPLs at higher energies or multiple ZPLs in one excitation spectrum. At first glance, this observation seems to be in contradiction with the results from the emission spectra, where multichromophoric emission has been observed. Furthermore, assuming a chromophoric unit to be built by 5–10 repeat units, a single chain of our MEH-PPV sample should on average consist of about 20 chromophores. Hence, by scanning the dye laser across 20 nm in the region of the purely electronic transitions, the excitation lines of several chromophores should show up. The failure in observing higher energy transitions in the excitation spectra may be related to their linewidths. Considering the bichromophoric emission spectrum in Fig. 1(d), it is seen that in this case the emission from the blue site is represented by a broad band, which in an excitation spectrum over a limited wavelength range would barely be detectable. In accordance with the explanation given above, we assume that rapid energy transfer leads to significant homogeneous line broadening, making it very difficult to detect the excitation spectra of chromophores with higher transition energies. Spectral diffusion may be another detrimental contribution, taking into account that due to this effect already the observation of a single ZPL was very rare.

According to the literature [6], our preparation conditions should lead to a coiled conformation of the polymer chains, giving rise to efficient intramolecular energy transfer. Using a different solvent (chloroform instead of toluene), more extended conformations may prevail, reducing in turn the energy transfer efficiency. Consequently, higher energy transition ZPLs might be accessible, the width of which will directly report about energy transfer rates to lower transition energy chromophores [23]. Another fascinating perspective would be to employ a single mode dye laser to determine the true homogeneous linewidths of single chain excitation spectra and measure their temperature dependence. Such measurements would give unprecedented insights into low frequency excitations coupled to the electronic transitions in conjugated polymers.

We thank Eva Wächtersbach for GPC size fractionation of the MEH-PPV sample. Financial support from the Graduate School POLYMAT (F. A. F.), the German Science Foundation (SFB 625), and the Fonds der chemischen Industrie is gratefully acknowledged.

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[1] B. J. Schwartz, Annu. Rev. Phys. Chem. **54**, 141 (2003).
[2] A. J. Heeger, Rev. Mod. Phys. **73**, 681 (2001).
[3] D. A. Vanden Bout, W.-T. Yip, D. Hu, D.-K. Fu, T. M. Swager, and P. F. Barbara, Science **277**, 1074 (1997).
[4] D. Hu, J. Yu, K. Wong, B. Bagchi, P. J. Rossky, and P. F. Barbara, Nature (London) **405**, 1030 (2000).
[5] P. F. Barbara, A. J. Gesquiere, S.-J. Park, and Y. J. Lee, Acc. Chem. Res. **38**, 602 (2005).
[6] T. Huser, M. Yan, and L. J. Rothberg, Proc. Natl. Acad. Sci. U.S.A. **97**, 11 187 (2000).
[7] S. S. Sartori, S. De Feyter, J. Hofkens, M. Van der Auweraer, F. De Schryver, K. Brunner, and J. W. Hofstraat, Macromolecules **36**, 500 (2003).
[8] A. J. Gesquiere, S.-J. Park, and P. F. Barbara, J. Am. Chem. Soc. **127**, 9556 (2005).
[9] Z. Yu and P. F. Barbara, J. Phys. Chem. B **108**, 11 321 (2004).
[10] C. Rønne, J. Trägårdh, D. Hessman, and V. Sundström, Chem. Phys. Lett. **388**, 40 (2004).
[11] F. Schindler, J. Jacob, A. C. Grimsdale, U. Scherf, K. Müllen, J. M. Lupton, and J. Feldmann, Angew. Chem. **117**, 1544 (2005).
[12] T. Pullerits, O. Mirzov, and I. G. Scheblykin, J. Phys. Chem. B **109**, 19 099 (2005).
[13] F. Schindler, J. M. Lupton, J. Feldmann, and U. Scherf, Proc. Natl. Acad. Sci. U.S.A. **101**, 14 695 (2004).
[14] F. Dubin, R. Melet, T. Barisien, R. Grousson, L. Legrand, M. Schott, and V. Voliotis, Nature Phys. **2**, 32 (2006).
[15] F. Schindler and J. M. Lupton, Chem. Phys. Chem. **6**, 926 (2005).
[16] K. M. Gaab and C. J. Bardeen, J. Phys. Chem. B **108**, 4619 (2004).
[17] T. Christ, F. Kulzer, T. Weil, K. Müllen, and Th. Basché, Chem. Phys. Lett. **372**, 878 (2003).
[18] Y. J. Lee, D. Y. Kim, J. K. Grey, and P. F. Barbara, Chem. Phys. Chem. **6**, 2404 (2005).
[19] D. Y. Kim, J. K. Grey, and P. F. Barbara, Synth. Met. **156**, 336 (2006).
[20] J. K. Grey, D. Y. Kim, C. L. Donley, W. L. Miller, J. S. Kim, C. Silva, R. H. Friend, and P. F. Barbara, J. Phys. Chem. B **110**, 18 898 (2006).
[21] Y. J. Lee, D. Y. Kim, and P. F. Barbara, J. Phys. Chem. B **110**, 9739 (2006).
[22] J. Yu, D. Hu, and P. F. Barbara, Science **289**, 1327 (2000).
[23] R. Métivier, F. Nolde, K. Müllen, and Th. Basché, Phys. Rev. Lett. **98**, 047802 (2007).