Unraveling the Inhomogeneously Broadened Absorption Spectrum of Conjugated Polymers by Single-Molecule Light-Harvesting Action Spectroscopy

Manfred J. Walter and John M. Lupton

Department of Physics and Astronomy, University of Utah, Salt Lake City, Utah 84112, USA

(Received 15 May 2009; published 12 October 2009)

The distribution of chromophores in single polymer chains is revealed by photoluminescence excitation spectroscopy under excitation of the backbone and detection of emission from an end cap. Spectral broadening in excitation exceeds that in emission. An increase in vibronic coupling for shorter (higher energy) chromophores is resolved, leading to intrinsic spectral broadening and making higher energy units more effective donors. The results suggest routes to increasing absorption breadth while minimizing disorder as required for efficient photovoltaics.

DOI: 10.1103/PhysRevLett.103.167401 PACS numbers: 78.55.Kz, 31.15.at, 42.70.Jk, 78.66.Qn

The spectroscopy of single nanoscale entities, such as nanocrystals or large macromolecules, has significantly enhanced our understanding of the intrinsic electronic properties of these complex materials. Dissecting a bulk material, e.g., a film of a conjugated polymer as used in light-emitting diodes, into individual emitters is conceptionally and experimentally challenging. An individual π-conjugated polymer chain, the smallest spatially separable entity, may contain scores of emitting units, termed chromophores. A polymer chain is made up of alternating single and double carbon bonds, which enable the formation of a spatially delocalized electron system. This conjugation can be interrupted along the chain by structural or chemical defects. Single chain fluorescence spectroscopy has proven remarkably versatile in unraveling some of the inherent diversity of individual chromophores either within a chain or between different chains [1–3]. However, single chain luminescence, in analogy to ensemble site-selective fluorescence spectroscopy [4], inherently probes only a small subset of chromophores: those which emit. Absorption may occur in a higher energy unit of shorter conjugation length, but given the presence of lower energy segments in this primary unit's vicinity, excitation energy transfer (EET) can arise along the chain [5–7].

To fully unravel the energetic disorder of a conjugated polymer sample it is necessary to consider the absorption of individual subunits on the chains. This site-selective addressing of the chromophore distribution in the ensemble has previously been achieved by resonance Raman scattering [8], but the applicability of this approach is limited for luminescent materials. Ensemble absorption spectra are always broader than emission spectra as absorption probes the entire energetic distribution, whereas emission only identifies those lowest energy units to which EET has occurred. The difference between absorption and emission spectra rises with increasing chain disorder: the most ordered materials such as ladder-type poly(*para*-phenylenes) reveal approximate mirror symmetry between absorption and emission [4]. In view of the increasing significance of organic semiconductors to photovoltaics, the microscopic origin of spectral broadening of the ensemble absorption remains a crucial question. An ideal photovoltaic material must enable efficient charge transport, which requires minimal energetic disorder to minimize carrier trapping. On the other hand, the absorption spectrum must be broad to maximize overlap with the solar spectrum. This broadening is often attributed to energetic disorder: individual chromophores should have electronic characteristics of oligomers [8]. However, it remains an open question how the interaction between these units may modify the overall chain absorption compared to a set of isolated oligomers. Knowledge of the intrinsic chromophore absorption is also crucial for microscopic descriptions of EET in artificial and natural light-harvesting systems. Although the single chromophore absorption has been modeled quantum chemically previously, it has not been experimentally accessible [7].

Here, we reveal the intrinsic absorption of single chromophores in a polymer. Surprisingly, we generally identify only one dominant chromophore with oligomeric features, the lowest energy unit. The remaining chromophores add up to form a broad absorption continuum, enabling efficient excitation of the single chain over many wavelengths. Shorter chromophores display stronger electron-phonon coupling, which appears to enhance EET.

Directly measuring the absorption spectrum of a single polymer chain is prohibitive, as this requires the observation of a miniscule drop in photon flux. Instead, photoluminescence (PL) excitation (PLE) spectroscopy can be used to probe any spectrally resolved absorption in the collection of chromophores by the resultant chromophore emission. Whereas PLE was the method of choice for the pioneering work on single-molecule spectroscopy [1,9,10], it does not lend itself immediately to considerations involving conjugated polymers. Single-molecule PLE is generally employed to reveal extremely narrow transitions of one single emitter [1,9–12], thus limiting the wavelength range required in an excitation experiment [11]. In this way, isolated narrow transitions could be

 © 2009 The American Physical Society

revealed in a conjugated polymer, without, however, accessing the ensemble absorption distribution [11]. Identifying different chromophores on single chains, in contrast, requires PLE to be carried out over a wide range of wavelengths, spanning a significant fraction of the ensemble absorption. A further complication arises when considering detection of the PL: the detector must be shielded from the exciting laser radiation, typically picking up luminescence in a vibronic band. As higher energy chromophores are probed, the sensitivity of the detector must be tuned to higher photon energies. This approach is not feasible in a large-range continuous excitation experiment.

We overcome these inherent limitations by studying PLE of a conjugated polymer—poly(indeno-fluorene) (PIF)—tagged with fluorescent perylene end caps [7,13]. Efficient EET can occur from the backbone to the end cap [13]. The perylene emission is spectrally distinct from the backbone absorption, so that the excitation energy of the backbone can be varied over a wide range without having to modify the detection conditions. The perylene absorption does not overlap that of the PIF, so that the backbone absorption can be probed selectively [7,13]. In effect, the experiment measures the dependence of EET on photon energy: light-harvesting action (LHA) spectroscopy, in analogy to photocurrent action. In conjunction, lower energy chromophores on the chain can also be probed by considering the direct emission of the PIF backbone. The PIF polymer contains 5–10 chromophores per chain [7]. Single chain PL spectra of a related material reveal spectrally resolved multichromophoric emission at 5 K [3]. We anticipate that the PLE spectrum under detection of the backbone emission should show a similar series of peaks due to the absorption of different chromophores. LHA spectroscopy, in contrast, will uncover those chromophores, from which an EET cascade to the end cap can be triggered. This cascade depends on the energetic and spatial ordering of chromophores. While we were previously only able to access discrete excitation wavelengths for LHA [13], we can now perform continuous excitation spectroscopy, enabling us to classify individual chains in terms of their lowest energy chromophores.

LHA spectroscopy is carried out on single PIF chains isolated in Zeonex in a low-temperature (5 K) fluorescence microscope [13]. The spectra are obtained by continuously varying the excitation wavelength at constant photon flux, typically between 370–435 nm in 1 nm steps, and measuring the emission intensity of the end cap. We spectrally select the emitting perylene with a 545 nm long pass filter. For excitation, frequency-doubled, circularly polarized Ti:sapphire laser radiation (140 fs pulses at 80 MHz repetition rate) is used. The band width (~2 nm) limits the resolution of the PLE spectra.

The red curve in Fig. 1 shows a typical single chain PLE (LHA) spectrum. To ensure that random blinking—the intermittency in intensity typical of single emitters—does not distort the spectrum, we averaged the emission intensity over up and down sweeps of the laser, discarding scans

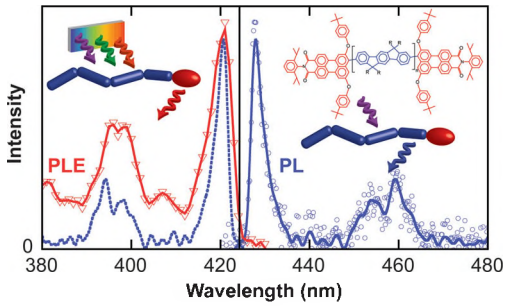

FIG. 1 (color online). Coincidence of PL and PLE features observed from single endcapped chains (structure inset). While the backbone PL spectrum (blue solid line) is excited at 400 nm, for PLE, the backbone excitation wavelength is changed and the end cap intensity is detected above 545 nm (LHA). The vibrational peaks of the mirror-imaged PL spectrum (dotted line) around 395 nm also appear in the PLE spectrum.

showing strong variations. The polymer absorption sets on at 420 nm, resulting in a distinct peak, followed by a broad continuum with pronounced peaks superimposed at shorter wavelengths. We propose that the dominant peak corresponds to excitation of the lowest energy chromophore in the polymer chain. This hypothesis is readily tested by comparison with a single chain PL spectrum (blue). The PL spectrum is mirrored and corrected for a Stokes shift of 0.05 eV due to structural relaxation (dotted line) [7], and can be superimposed on the PLE spectrum. The vibronic progression of the single chain emission at 454 nm (1360 cm^{-1}) and 459 nm (1600 cm^{-1}) is reflected in the excitation spectrum.

To analyze the light absorption properties of single chains, we focus on the first dominant peak in the PLE spectrum, which we attribute to the 0–0 transition in absorption. The emission intensity does not drop to zero for any excitation wavelength below the 0–0 absorption. We expect that this apparent background in excitation arises from weaker absorption of higher energy chromophores on the chain. These units have shorter conjugation lengths and thus lower oscillator strengths, and, together with a superposition of different vibrational modes, average out to an apparent effective continuum in the PLE spectrum. To study the absorption characteristics of the dominant lowest energy and thus longest and most strongly absorbing chromophore quantitatively, we note that the spectra are accurately described by a superposition of two Gaussian peaks $P1$ and $P2$ (for the 0–0 and 0–1 transitions), and a sigmoid function C (for the remaining contributions to absorption), as shown in Fig. 2(a).

LHA spectroscopy allows us to unravel the different single chromophores contributing to absorption in the ensemble. Single chain excitation spectra can be grouped according to absorption onset. Figure 2(b) shows such a grouping of a total of 127 spectra. The lowest energy chromophore peak position is marked by a purple line, with the corresponding 0–1 transition indicated in orange. As the energy of the lowest energy chromophore showing

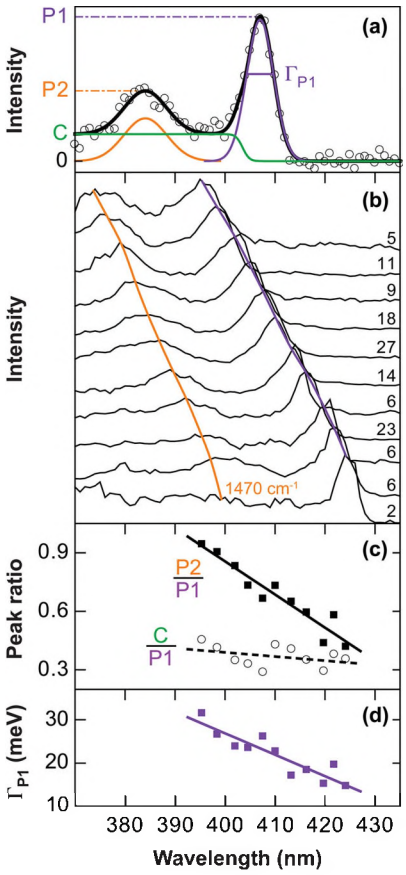

FIG. 2 (color online). LHA spectra grouped by lowest energy chromophore. (a) A typical spectrum (i.e., backbone excitation and end cap detection) is described by two Gaussians, corresponding to the 0–0 (purple) and 0–1 (orange) transitions of a single chromophore, and a sigmoidal offset (green) which averages the contributions of higher energy chromophores. (b) Grouped and averaged spectra. The number of single chains in a set is given. The normalized spectra are offset in intensity and the expected (1470 cm^{-1}) average position of the 0–1 peaks (orange line) with respect to the 0–0 transition (purple line) is marked. (c) Relative intensity of the vibronic band (squares) and the continuum (circles) as a function of $P1$ wavelength. (d) Increase of line width Γ_{P1} with decreasing chromophore size.

end cap EET increases, so does the electron-phonon coupling: the 0–1 intensity rises. The effect is quantified in panel (c), where the $P2$ to $P1$ ratio is plotted as a function of chromophore wavelength. While this ratio changes, the contribution of the continuum absorption remains constant. In addition, as the chromophore length decreases, the peak width Γ_{P1} increases [panel (d)]. This increase most likely stems from the stronger electron-phonon coupling and more pronounced contributions of low-energy vibrations to the absorption. Enhanced spectral diffusion, which is generally stronger in short segments [3], may also account for the change in Γ_{P1}. Increased line width of higher energy chromophores will facilitate intrachain EET.

LHA spectroscopy on single chains allows us to identify the ensemble chromophore distribution. Knowledge of this distribution is crucial to computing energy transfer phenomena [7]. To a first approximation, chromophores on disordered polymer chains can be thought of as more or less isolated oligomers [8]. As the molecular energy decreases, so does the vibronic intensity [14]. This effect is a simple consequence of increased structural relaxation between ground and excited state: shorter, higher energy chains undergo a more pronounced change in bond length alternation and torsional angles upon photoexcitation, raising the Franck-Condon factor of vibrational transitions. The effect has previously been studied theoretically in the context of a series of indeno-fluorene oligomers to compute resonant dipole-dipole coupling for intrachain EET [7]. Our experimentally determined electronic to vibronic peak ratio agrees remarkably well with the predictions of Hennebicq *et al.* [7], as discussed in the supporting information [15]. We are indeed able to identify single, short oligomeric units within individual polymer chains, and ultimately within the ensemble. The number of single chains exhibiting EET to the end cap as a function of excitation wavelength scales directly with the onset of the ensemble absorption spectrum [13]. It is therefore the integral of the distribution of microscopic peak positions in Fig. 2(b) which relates to the macroscopic absorption as discussed in the supporting information [15]. In the ensemble with a large distribution of different conjugation lengths the increase in vibronic intensity with decreasing chromophore size is masked, leading to a broad featureless absorption [7,13]. Close inspection of the relation between single chain LHA and ensemble absorption suggests that EET is enhanced for the shorter chromophores due to the greater intrinsic spectral line width resulting from stronger vibrational coupling [15].

With a tool at hand to identify individual oligomeric units on a chain spectroscopically, we can investigate the influence of chromophore size, and spatial ordering of chromophores along the chain, on EET. To do this, we distinguish between PLE of the backbone alone, i.e., under detection of the vibronic side band (445–470 nm) of the PIF emission, and LHA under detection of the end cap. The spectra are analyzed in terms of the lowest energy absorbing chromophore. These units should correspond to the sites in a polymer chain from which PL occurs. In contrast, the shorter segments seen in Fig. 2 at shorter wavelengths should not be visible under backbone PLE: a longer unit will *always* be present on the chain which will absorb at lower energy. The highest energy chromophores should only become visible if EET occurs because they are spatially located immediately next to the end cap. Longer segments will then not show up in LHA spectroscopy, since EET is blocked from a long, low-energy chromophore to the end cap by a high energy unit in between. Figure 3 summarizes the distribution of lowest energy chromophore PLE peak positions under backbone (a) and end cap (b) detection. Panel (a) shows a continuous distribution of peaks. For comparison, the ensemble PL spectrum at 5 K is shown (solid line). The mirror image of this spectrum, shifted to account for structural relaxation, can

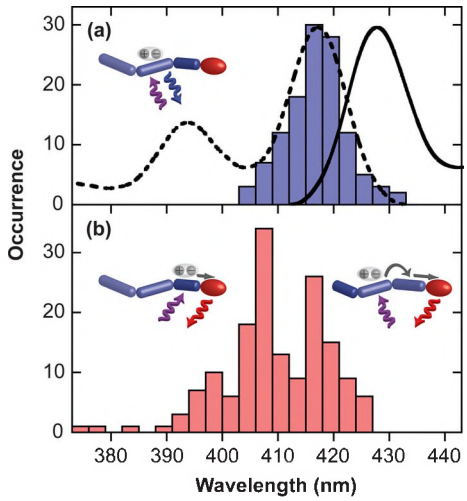

FIG. 3 (color online). Distribution of lowest energy chromophores on single chains, depending on detection condition. (a) PLE peaks under backbone excitation and backbone detection for 120 single chains. The distribution of chromophores coincides with the 0–0 peak of the mirror-imaged (dotted line) ensemble PL spectrum (solid line). (b) LHA peaks for 160 chains. The cartoons indicate the chromophore distribution: the shortest units are only visible as lowest energy chromophores in a chain if they couple directly to an end cap (left distribution). For lower energy chromophores, EET to the end cap may involve multiple steps (right distribution).

be accurately superimposed on the chromophore distribution. We conclude that PLE of the backbone does indeed reveal the absorption of the lowest energy units on the chain, which are always responsible for emission. Comparison with theory [15] allows us to estimate an effective conjugation length in excess of 9 repeat units.

The situation is very different under detection of end cap luminescence (b), where a bimodal distribution is observed. The lower energy LHA spectra exhibit a similar distribution to that found in the absence of EET in panel (a). However, a second distribution extends into the ultraviolet, revealing chromophores not visible under backbone detection. These chromophores correspond to conjugation lengths of between 2 and 6 repeat units [15].

The distribution of LHA spectral peaks exhibits a pronounced minimum around 412 nm. Two distinct cases of EET can be identified conceptually: either the end cap is immediately adjacent to the absorbing chromophore from which EET occurs, or an energetic cascade exists along the chain prior to EET to the end cap. In the latter case the chromophore distribution should mirror the ensemble PL spectrum. In contrast, if absorption occurs in a unit immediately adjacent to the end cap, a much broader distribution of chromophores will be observed. We therefore propose that the lower energy part of the distribution in Fig. 3(b) arises from EET along the chain to the end cap, whereas the higher energy distribution results from EET from only the final chromophore in the chain to the end cap.

The single chain PLE spectra are significantly broader than the PL. Single molecules, such as perylene, tend to show narrower electronic structure in excitation than in emission as spectral diffusion is reduced in the former due to resonant excitation [9]. The nature of homogeneous broadening in conjugated polymers remains intriguing [11,16]. Ultrafast dephasing of the primary polarization may result from interchromophoric coupling [5], and could give rise to broader than expected single chain PLE spectra. Now that quasioligomeric units (down to two monomers in size [15]) can be identified in single chains, it will be crucial to compare oligomer and polymer PLE directly to illuminate any additional contribution to spectral broadening arising from interchromophoric coupling. From an application point of view, the excitation continuum demonstrates that the absorption of single polymer chains is not necessarily discrete [11]. Maximal spectral overlap between the solar spectrum and the absorbing medium is generally achieved by increasing energetic disorder, which impedes charge transport. If the underlying absorption is intrinsically broad in select single chains, disorder can be avoided to combine efficient charge transport with effective excitation. The challenge for future research lies in identifying which physical or chemical variables (e.g., chain shape, backbone substitution) control the breadth of a particular single chain excitation spectrum, and how to generate ensembles of polymers with minimal inhomogeneous broadening, i.e., in which individual chains have near-identical properties.

We are indebted to K. Müllen, A. Grimsdale, and S. Setayesh for provision of the PIF polymer. Financial support by the donors of the Petroleum Research Fund, the NSF (CHE-ASC), and the David & Lucile Packard Foundation is gratefully acknowledged.

[1] W. E. Moerner and M. Orrit, Science **283**, 1670 (1999).
[2] P. F. Barbara *et al.*, Acc. Chem. Res. **38**, 602 (2005).
[3] F. Schindler *et al.*, Angew. Chem., Int. Ed. Engl. **44**, 1520 (2005).
[4] H. Bässler and B. Schweitzer, Acc. Chem. Res. **32**, 173 (1999).
[5] E. Collini and G. D. Scholes, Science **323**, 369 (2009).
[6] T. Q. Nguyen *et al.*, Science **288**, 652 (2000).
[7] E. Hennebicq *et al.*, J. Am. Chem. Soc. **127**, 4744 (2005).
[8] M. L. Shand *et al.*, Phys. Rev. B **25**, 4431 (1982).
[9] A. Kiraz *et al.*, J. Chem. Phys. **118**, 10 821 (2003).
[10] A. M. van Oijen *et al.*, Science **285**, 400 (1999).
[11] F. A. Feist *et al.*, Phys. Rev. Lett. **98**, 208301 (2007).
[12] R. Métivier *et al.*, Phys. Rev. Lett. **98**, 047802 (2007).
[13] M. J. Walter *et al.*, Nano Lett. **8**, 3330 (2008).
[14] K. W. Hausser *et al.*, Z. Phys. Chem. **29**, 391 (1935).
[15] See EPAPS Document No. E-PRLTAO-103-035943 for a comparison of experiment with theory, and ensemble absorption. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[16] G. D. Scholes *et al.*, Phys. Rev. B **61**, 13 670 (2000).