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Formation of a Defect-Free π-Electron System in Single β-Phase Polyfluorene Chains

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Supporting Information

ABSTRACT: Single-molecule spectroscopy can help to uncover the underlying heterogeneity of conjugated polymers used in organic electronics, revealing the most effective molecules in an ensemble in terms of the transport of charge and excitation energy. We demonstrate that β-phase polyfluorene chains can form a near-perfect π-electron system, whereas conventional polymers exhibit chromophoric localization due to perturbation of the conjugation. Broad-band excitation spectroscopy demonstrates that only one absorbing and emitting unit is present on the polymer chain with an average length of ~500 repeat units, illustrating that the material effectively behaves as a molecular quantum wire with strong electronic coupling throughout the entire system.

Conjugated polymers are often likened to a bowl of cooked spaghetti: bent, twisted, and interweaving chains forming an interpenetrating mesh in the solid state. Charge carriers, or excitons, can wander through this mesh, a process which constitutes the backbone of organic electronics. Disorder in the π-electron system leads to localization which limits the inherent mobility of charge carriers and excitons.[1] But what if, to stay with this analogy, a strand of uncooked spaghetti exists within this mesh? Once a charge (or excited-state species) comes across this strand, it could be propelled throughout the disordered mesh: the rigid strand forms a highway through the disorder. Here, we present evidence that the so-called β-phase of the conjugated polymer poly(9,9-dioctyl-fluorene) (PFO) forms precisely such a highly ordered unit. Broad-band single-molecule photoluminescence (PL) excitation (PLE) spectroscopy reveals the presence of only one absorbing and emitting species per chain, indicating that the entire polymer chain consists of just one π-electron system.

Topological or chemical defects on the polymer chain generally disrupt π-conjugation, leading to the formation of localized units termed chromophores.[1] This picture is readily upheld in single-molecule spectroscopy of rigid polymers,[1c] where the number of spectral features observed at low temperatures increases with chain length. However, dipole−dipole coupling can occur between chromophores on the chain so that the emission spectrum only probes a particular subset of chromophores, the lowest-energy units. Thus, to probe all chromophores on a chain, an absorption or excitation technique is needed. We recently unraveled the inhomogeneously broadened absorption spectrum of a conjugated polymer through broad-band single-chain PLE, thus revealing chromophores as short as two repeat units which are otherwise invisible in regular PL measurements.[2] With this technique at hand, we can now assess the degree of π-electron localization in a variety of conjugated polymers. PFO is particularly intriguing as the monomer units (see inset of Figure 1a) can either be twisted with respect to each other (the so-called glassy phase) or all lie in one plane (the β-phase).[3] These two phases are distinguishable in the ensemble by X-ray scattering[3a] and are spectroscopically distinct, allowing for unambiguous indentification on the single-molecule level.[4]

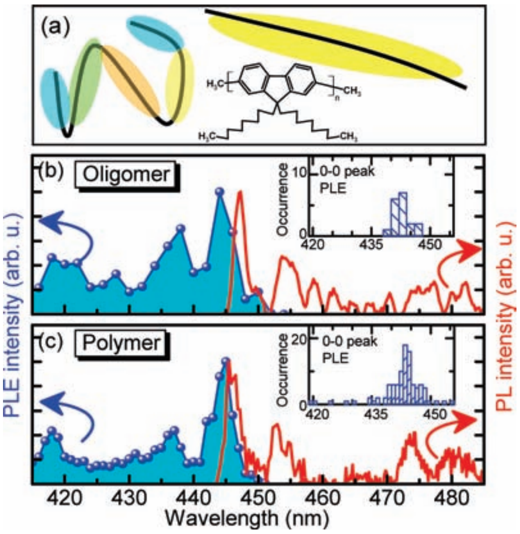

Figure 1. PLE and PL spectra of single β-phase chains. (a) Illustration of the structure of the planarized polymer chains. Either π-conjugation is disrupted, leading to the formation of chromophores (left), or the π-system extends along the entire chain. (b) Excitation and emission spectra of single β-phase fluorene nonamers. The distribution of 0−0 transitions for different molecules is shown in the inset. (c) As for (b), for a single PFO chain.

Generally, an anisotropic π-electron system supports a linear transition dipole moment which should lead to dipolar emission with a well-defined plane of polarization.[1d] However, in our previous work on PFOs, we reported a deviation from this rule in the case of single β-phase chains: the emitted light is not always completely polarized.[4b] As only one narrow transition was observed in the emission spectrum, we speculated that the entire chain may form one chromophore and that exciton recombination

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occurs randomly throughout the chain.[4b] Loss of polarization arises because the chain can be slightly bent, even if it is completely planarized in the β-phase. However, such extensive electronic delocalization in a conjugated polymer chain has only previously been reported for polydiacetylenes polymerized in their monomeric crystals[5] and would be quite extraordinary for a disordered polymer in an amorphous matrix. Emission spectroscopy alone is inadequate to detect such delocalization since it is not possible to conclusively differentiate between all of the chromophores present on the chain; energy transfer can funnel all excitations to a single chromophore, or multiple isoenergetic units of slightly different spatial orientation may give rise to a loss of emission polarization.[4b]

PLE allows us to conclusively demonstrate that the π-conjugation extends along the entire chain of β-phase PFO molecules by scanning the excitation wavelength across much of the spectral region of the PFO ensemble absorption and monitoring the fluorescence. Single-molecule samples were prepared by dispersing PFO in a Zeonex matrix at a concentration of 10^{-6} mg/mL in toluene; the resulting solution was then deposited via spin-coating on a thin quartz substrate. The samples were then mounted on the cold finger of a microscope cryostat, as described previously,[2] and cooled to the temperature of liquid helium (4 K). PLE spectra were recorded by scanning the laser over the absorption spectrum and recording the emission intensity in the vibronic progression (i.e., above the 0−0 emission line). In previous experiments, we did not need to spectrally resolve the PL.[2] However, as the glassy and β-phases of PFO both emit in the blue, selection between the two requires spectrally dispersing the emission by means of a monochromator.

Figure 1 shows PL and PLE data recorded on single chains of the polymer and an oligomer with more than nine repeat units. The cartoon in panel (a) illustrates the conceptual question to be addressed in the experiment: either the chromophore comprises the entire chain (right), or the π-system is disrupted (left) so that different and spectroscopically distinct conjugated units emerge. We have previously shown that the nonamer is the shortest chain segment which supports formation of the planarized β-phase.[4c] Panel (b) displays two representative PL and PLE spectra of single nonamers, with the scatter of PLE peaks between different molecules shown in the histogram (inset). The same situation is summarized in panel (c) for a single *polymer* chain. In both cases, PLE and PL display a clear mirror symmetry anticipated for such rigid molecules, suggesting that the same species is responsible for absorption and emission. The spectra consist of a high intensity peak around 445 nm, assigned to the 0−0 transition. Additional spectral features can be attributed to the characteristic vibrational modes of the molecule.[4a] The spectra for the oligomer and the polymer are virtually indistinguishable. We conclude that one single PFO chain, although over 50 times larger than the exciton, does not support multiple chromophores. Out of 100 single-polymer chains studied, we never observed multiple 0−0 transition peaks. This observation is in stark contrast to our prior PL investigations in ladder-type poly(paraphenylenes),[1c] and recent PLE spectroscopy of polyindenofluorenes,[2] which both exhibit spectral signatures of multiple chromophores on the chain.

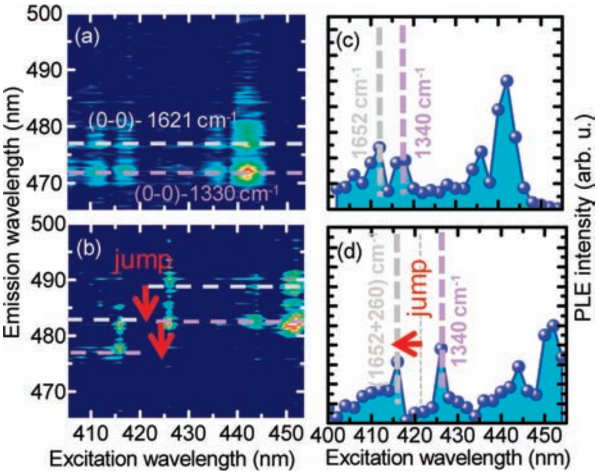

Figure 2. (a,b) Two-dimensional plots of the color-coded emission intensity as a function of emission and excitation wavelength for two single PFO chains, each containing precisely one chromophore. A sudden jump occurs in (b) due to spectral diffusion. (c,d) Corresponding PLE spectra highlighting the position of vibronic transitions and spectral jump.

Although the scatter in peak wavelength of different single chains, shown in the insets of Figure 1, suggests that multiple on-chain chromophores should, on average, be spectrally distinct, it is still possible that several chromophores are formed with the same transition energy within the spectral resolution. To exclude this possibility, we made use of the random spectral jitter which accompanies single chromophore transitions.[6] If a random modification in the transition energy occurs due to, e.g., photoinduced rearrangement of the immediate dielectric environment of the molecule, a simultaneous change in absorption and emission should arise, provided there is only one absorbing and emitting entity. Figure 2a,b shows two-dimensional plots of the color-coded emission intensity as a function of emission and excitation wavelength for two single PFO chains. Note that the PL spectrum is cut off at wavelengths below 465 nm to block the excitation laser, leaving only the vibronic progression in emission (modes at 1330 and 1621 cm^{-1} for the chain in panel (a) of Figure 2). A very similar progression is observed for the single chain in panel (b) of Figure 2, although this chromophore shows emission at longer wavelengths with respect to the one in (a), (0−0)−1330 cm^{-1} mode at 482 nm. The single chain in panel (a) shows spectroscopic features with a remarkably stable emission wavelength position, while the excitation laser is scanned upwards in wavelength. Here PL emission from the vibronic progression occurs whenever the excitation laser overlaps with a resonance of the absorption spectrum. It is again worth pointing out the mirror symmetry between excitation and emission, as demonstrated by the corresponding excitation spectrum (panel (c)), showing the two vibronic modes with very similar energetic spacing when compared to those in emission. An example of a chain exhibiting spectral jitter observed both in PL and PLE is shown in panels (b) and (d), respectively. As the excitation laser is tuned below 425 nm in panel (b), the chromophore exhibits a random *jump* of the whole PL vibronic structure by 220 ± 10 cm^{-1} to shorter wavelengths.[7] This spectral jump is also seen in the integrated PLE spectrum (panel d) as the peak expected to lie around 1652 cm^{-1} (indicated as a thin dashed line) is shifted to lower wavelengths by ~260 cm^{-1}. The synchronous random spectral jumps indicate that emission and absorption arise from the same conjugated unit on the chain. We stress that, since PLE spectra are constructed point by point in time, integrating the PL signal for each wavelength step, the jump in the PLE spectrum appears only at a specific energy or resonance, although the entire PLE spectrum is shifted by 260 cm^{-1}, including the 0−0 transition. Since only one molecular resonance is observed as the laser is tuned over the entire absorption, we conclude that only one optically active unit exists on the chain. The single chain constitutes the entire chromophore.

In contrast to some polydiacetylenes,[5] the delocalized π-system in β-phase PFO is not quite a perfect quantum wire. Although excitation and emission occur anywhere along the chain, leading to a distinct signature in the polarization of absorbed and emitted light,[4b] weak structural relaxation arises upon excitation, leading to a shift between the 0−0 transitions in PLE and PL of ~0.5 nm (25 cm^{-1}). As a consequence of this exciton localization, vibronic coupling appears much stronger in β-phase PFO than in polydiacetylene.[5]

We have uncovered highly delocalized states in single chains, which can be thought of as one-dimensional π-systems with weak disorder localization. The most appropriate way to picture the electronic structure of these chains is as an arrangement of strongly coupled units, reminiscent of natural and synthetic light-harvesting complexes.[9]

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures and sample preparation. Additional data on two-dimensional plots of PFO chains showing a spectral jump. This material is available free of charge via the Internet at http://pubs.acs.org.

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