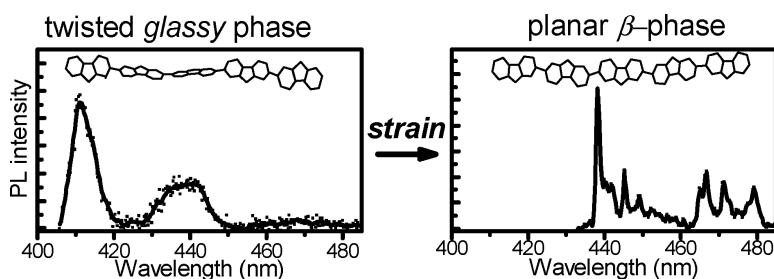


Dual Species Emission from Single Polyfluorene Molecules: Signatures of Stress-Induced Planarization of Single Polymer Chains

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Dual Species Emission from Single Polyfluorene Molecules: Signatures of Stress-Induced Planarization of Single Polymer Chains

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Conjugated polymers offer a broad spectrum of device applications but also raise many fundamental issues relating to the nature of excited-state species in complex macromolecules.¹ A driving force in their optical spectroscopy has been the desire to establish reliable relationships between chemical structure and physical properties. Polyfluorenes (PFs) are a particularly prominent class of materials, which can be employed in efficient light-emitting diodes.² Understanding the emissive species in PFs has been an active area of research due to the complexity of the emission spectrum and the apparent sensitivity to processing conditions.² Typically, the emission contains three components due to the presence of two distinct conformational phases (the glassy and the more ordered β -phase)^{2,3} as well as highly localized oxidative emissive defects.³ These three species contribute to ensemble emission, although their relative amplitudes depend strongly on both processing conditions² or detection schemes.³ Single molecule (SM) spectroscopy (SMS) provides unique insight into the fundamental emissive species of conjugated polymers by overcoming the influence of ensemble disorder.^{4–5} This is especially fruitful for studying the photophysics of the β -phase, which is always accompanied by the glassy phase in the ensemble.² Whereas room temperature SMS unravels stunning collective effects in high molecular weight multichromophoric systems,^{5–7} we have recently worked at low temperatures to address individual emissive units within the polymer chain.⁵ We present here SMS of single PF chains excited in the UV, constituting among the shortest wavelength SMS study to date. The two distinct and discrete PF phases are identified on the SM level and exhibit huge differences in photophysics despite the identical underlying chemical structure. This demonstrates that the spectral properties of conjugated polymers are predominantly *extrinsic* in origin and arise, for example, through backbone planarization.^{2e}

Single PF [poly(9,9-dioctylfluorenyl-2,7-diyl), American Dye Source Inc., $M_w = 220\,000$] molecules were dispersed in a 20 nm thin zeonex matrix at a concentration of 10^{-6} mg/mL and cooled to 5 K in an epifluorescence microscope setup described elsewhere.^{5c} A tunable femtosecond laser of 3 nm bandwidth was used for excitation. Figure 1 shows two typical photoluminescence (PL) spectra of single PF molecules. Whereas the spectrum in panel (a) displays a narrow ($\sim 60\text{ cm}^{-1}$; lines down to 10 cm^{-1} width were observed occasionally) zero phonon line at 2.829 eV followed by a well-defined vibronic progression, the spectrum in (b) peaks further in the blue at 3.015 eV and has a much larger line width ($\sim 380\text{ cm}^{-1}$) and a vastly different vibronic progression. Comparison with ensemble spectra² allows the assignment to the ordered β -phase and the “glassy” disordered phase (g -phase) of PF, which rather surprisingly can be identified on the SM level. The β -phase in the ensemble has previously been shown to be characteristic of a planarized conformation with extended π -electron conjugation,² while the g -phase signifies a twisted chain arrangement with shorter conjugation length.^{2,3} The appearance of the β -phase is a direct signature of stress-induced backbone planarization due to the

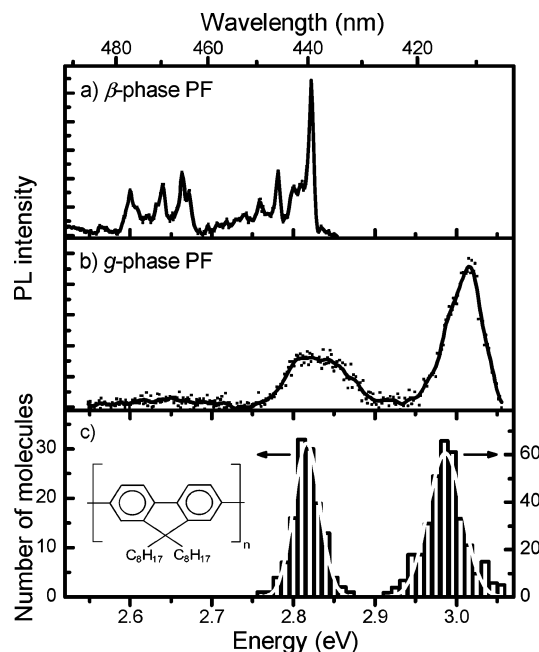


Figure 1. Single molecule PL spectra of PF at 5 K. (a) β -phase; (b) g -phase; (c) shows the distribution of peak positions of 480 single molecule spectra. The inset is the chemical structure of PF.

interaction with the host matrix.^{2e} We observe both spectral features simultaneously from different SMs under excitation at 393 nm, that is, close to the ensemble PF absorption maximum.^{2e} In contrast, the β -phase absorption peaks close to 430 nm in the ensemble.² We found that the SM β -phase emission (i.e., the number of molecules as well as the overall intensity per molecule) could be enhanced substantially by tuning the laser to 400 nm. This strong dependence of β -phase emission on excitation wavelength suggests that β -phase species in SMs are excited primarily by direct absorption and not by energy transfer from shorter, higher energy (g -phase) units on the chain.^{2e} Note that in agreement with SM β -phase emission, prior dilution measurements of PF in polystyrene showed that β -phase formation is not due to cooperative interchain interactions but arises primarily from intramolecular forces.^{2e} These may, however, be mediated by the polymer matrix.

The β -phase shows spectral features in the ensemble that are sharper than those in the g -phase.² This is generally taken as an indication of a lower degree of disorder induced inhomogeneous broadening.² SMS provides direct access to the relative contributions of homogeneous and inhomogeneous broadening within the ensemble spectrum. Figure 1c displays histograms of the peak positions of a total of 480 molecules. Both distributions exhibit a Gaussian shape. The β -phase distribution with a width of 36 meV is only slightly narrower than the bluer g -phase distribution of 49 meV width. This distribution is still over a factor of 5 narrower than what we recently found for poly(phenylene vinylene).^{5d} What

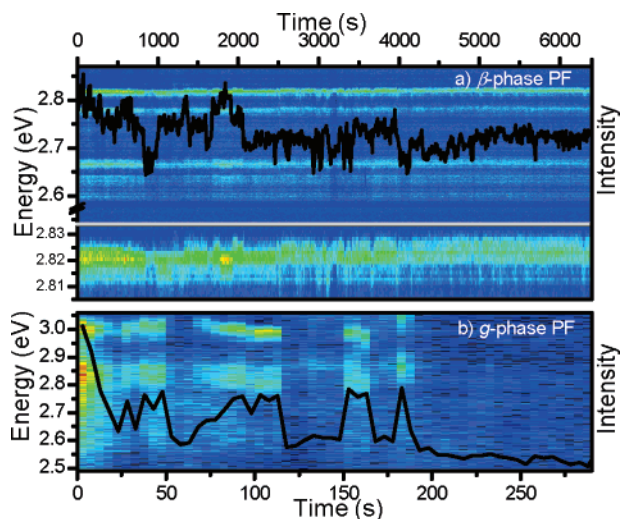


Figure 2. Temporal evolution of the PL of two single PF molecules at 5 K. The integrated intensity is overlaid as a black curve. A close-up of the zero phonon line of the β -phase PF is shown at the bottom of (a), which clearly displays spectral diffusion.

appears to give rise to the differences in the ensemble spectra² is the homogeneous line width, for which SMS provides an upper bound. The SM spectra of the g -phase are an order of magnitude broader than those of the β -phase.

We recently found that the SM PL line width depends sensitively on conjugation length by comparing oligomers and polymers of a ladder-type poly(paraphenylene) (LPPP).^{5b} This is consistent with the less conjugated g -phase exhibiting broader SM transitions. SMs often display spectral diffusion dynamics, that is, a temporal instability in emission.⁴ Whereas spectral jumps are usually rather discrete for small π -electron systems, such as dye molecules,⁴ spectral diffusion appears to be more gradual in extended π -systems, such as polymers.⁵ Figure 2 compares the temporal evolution of the emission of two single PF molecules. SM spectra are plotted on an intensity scale as a function of energy and time. The integrated intensity is overlaid as a black line. The β -phase molecule in panel (a) exhibits a remarkable temporal stability in both the zero phonon transition at 2.82 eV and the lower energy vibronic modes. Confirmation that the PL arises from SMs comes from both the weak random switching in PL intensity with time and the slight spectral jitter over a range of 5 meV (panel (a), bottom). Although aggregate formation may pose a problem in SM studies, we stress that besides the spectral dynamics, we have observed monotonic scaling behavior with molecular weight^{5b} and surface density^{5c} in very similar polymeric systems, providing compelling evidence for nonaggregated molecules. We tracked the SM PL for almost 2 h but found no substantial decrease in intensity. The case is very different for the g -phase SM in panel (b), which only emitted for 200 s. Here, the emission switches on and off, the typical “blinking” behavior seen in many single molecules.^{4–7} The spectral meander is much stronger and occurs over a range of 50 meV. We generally observe that the β -phase conformation gives rise to orders of magnitude enhancement in photophysical stability in terms of both increased lifetime and reduced spectral meander. We propose that this is a direct consequence of the increased π -electron delocalization in β -PF, which is prominently visible in X-ray scattering.^{2e} Polydiacetylenes polymerized in monomeric crystals can have conjugation lengths on the micrometer scale.⁸ These highly ordered polymers exhibit very little spectral diffusion and PL blinking and display PL line widths over 5 times narrower than those reported here.^{8a} Strong electronic delocalization, however, also leads to weak

vibrational coupling.^{8b} This is evidently not the case for PF. The β -phase not only displays a strong progression of discrete modes but also exhibits vibrations (e.g., at 362, 555, and 725 cm^{-1}) which are absent in the twisted conformation.

SMS provides access to the intrinsic photophysics of the conformational species of PF. A surprising result, which holds direct consequences for material design for optoelectronic devices, is the marked difference between the two phases in terms of photophysical stability. Apparently, increased conjugation through planarization reduces the tendency for dark species formation (i.e., blinking, which lowers the quantum yield in the ensemble⁷) and irreversible photobleaching. The β -phase of PF is often likened to LPPP.^{2c,3a} We find that this comparison is not entirely appropriate on the SM level. Although inhomogeneous broadening is similar for β -PF and LPPP,⁵ vibrational coupling is much stronger in β -PF. β -PF SMs appear to be more stable than LPPP SMs. The most striking difference is the apparent absence of multiple emitting chromophores in β -PF. The complexity of the LPPP SM spectrum scales directly with molecular weight, as each chromophore corresponds to a peak in the PL spectrum.^{5b} We have not observed this effect in β -PF. This suggests that the conjugation length in β -PF^{2e} is much greater than that in LPPP and may even extend along the entire chain, so that individual chains may even ultimately behave like polydiacetylene quantum wires.⁸ What makes this material system fascinating for SM experiments is that a slight conformational change entirely transforms the photophysics of the system. A challenging goal for the future is to trigger this conformational change reversibly by applying external stimuli, such as heat or mechanical strain.

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