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# Excited-State Dynamics of Oligo(*p*-phenyleneethynylene): Quadratic Coupling and Torsional Motions

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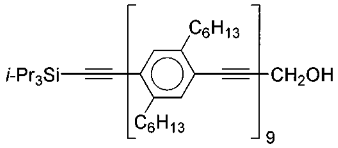
Poly(*p*-phenyleneethynylene)s (PPEs) are a class of conjugated polymers of growing importance.[1] Absorption and emission spectra of the oligo(phenyleneethynylene) nonamer **1** show unusual features that we attribute to quadratic coupling between the ground and excited states. The strong quadratic coupling results from twisting about the polymer axis that is relatively free in the ground state, but that becomes strongly constrained to the planar configuration in the excited state. These effects are heightened in PPEs because of the unique presence of a triple bond in the polymer chain. The spectral signatures of these processes mimic effects that are often attributed to energy migration,[2] mode mixing,[3] or other processes.



**1**

To avoid energy migration, we worked with dilute solutions of nonamer **1**, which was obtained as previously published.[4] All solutions were free of the narrow, red-shifted absorption band that indicates aggregation.[5] Thus, energy migration between chains is not possible. The conjugation length of PPE is close to $n = 10$.[4,6] The nonamer is long enough to contain a fully developed conjugation length and has spectra similar to those of the polymer. However, it is not long enough for energy migration along the chain.

Steady-state absorption and emission susceptibility spectra of the nonamer are shown in Figure 1. These were derived from fluorescence excitation and emission spectra respectively by correcting for instrumental sensitivity, transferring to a frequency axis, and dividing by the frequency or frequency cubed, respectively. Under the simplest assumptions, these spectra should show mirror symmetry.[7] However, in $CHCl_3$, the underlying Franck−Condon envelope of the absorption spectrum is broadened much more than the emission spectrum is (Figure 1, solid).

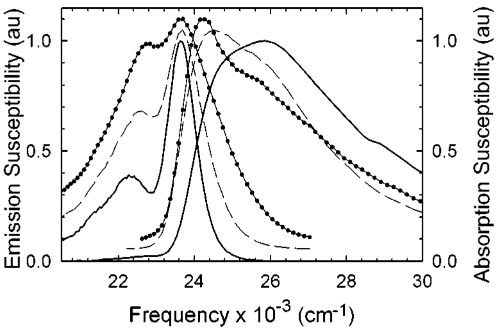


**Figure 1.** Absorption and emission susceptibilities of PPE nonamer **1** in $CHCl_3$ at 300 K (solid), in oligostyrene at 300 K (dashed), and in oligostyrene at 77 K (dotted). The spectra have been shifted vertically (+0.05, dashed; +0.1, dotted) and horizontally (+385 cm$^{-1}$, dotted) for clarity.

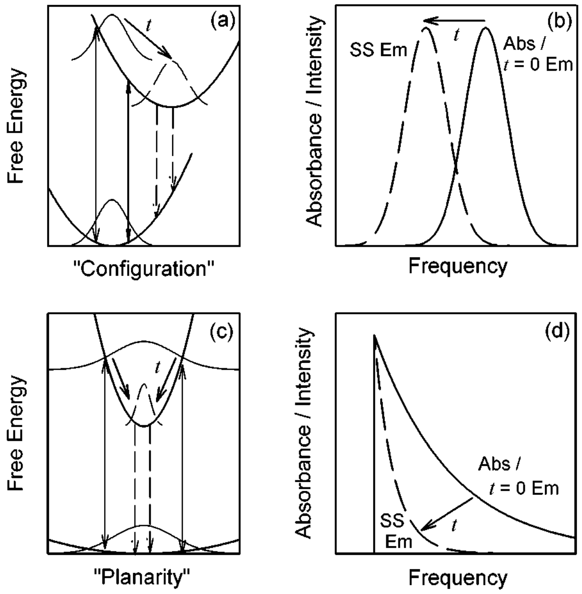


**Figure 2.** Schematic illustration of the differences between linear (a and b) and quadratic (c and d) coupling.

The results are quite different in a rigid matrix (oligostyrene, MW 800) at 77 K (Figure 1, dotted). As is common at low temperature, the absorption spectrum is somewhat narrower than it is at room temperature. In contrast, the emission spectrum broadens dramatically at low temperature. Moreover, the absorption and emission spectra become roughly mirror symmetric.

Spectral broadening of the envelope of Franck−Condon transitions is commonly described by linear coupling of the electronic states to the nuclear “configuration”. This configurational coordinate may represent either the displacement of low-frequency intramolecular vibrations and torsions or the positions of nearby solvent molecules. In linear-coupling models, the lowest energy configuration is different in the ground and excited states, but the restoring forces are the same (Figure 2a). The thermal distribution of configurations in the ground state maps onto a Gaussian distribution of absorption frequencies (Figure 2b). Immediately after excitation ($t = 0$), the emission spectrum is the same as the absorption spectrum. However, if the nuclear configuration has time to change during the fluorescence lifetime, the excited-state distribution moves to its energy minimum (Figure 2a), and the steady-state emission is red shifted (Figure 2b). Characteristics of linear coupling are symmetric, Gaussian broadening of the absorption and emission spectra, equal widths $\sigma$ for both spectra, and an adiabatic Stokes shift $\Sigma$ (i.e., one

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measured between 0−0 vibronic peaks) that is proportional to the square of the broadening, $\sigma^2 = kT\Sigma$.

None of these features applies to the PPE spectra, so none of the specific mechanisms that fall within the class of linear coupling is satisfactory. We suggest that PPE's spectral features and excited-state dynamics are dominated by the collective twisting of the phenyl rings relative to a fully planar configuration. In the ground state, **1** has an energy minimum at the planar configuration, but can twist into nonplanar configurations with a low energy cost. As a result of the shallow ground-state potential, there is a broad thermal distribution of planarity in the ground state (Figure 2c).

The first excited state of PPE is strongly influenced by quinoidal/cumulenic configurations. As a result, the excited-state potential favors the planar configuration much more strongly than the ground-state potential (Figure 2c). This assumption is supported by quantum calculations of PPE dimers and trimers.[8] The distribution of ground-state configurations results in a broad, single-sided-exponential absorption line shape (Figure 2d). Immediately after absorption ($t = 0$), the distribution of configurations in the excited state is equally broad, and the emission line shape is the same as the absorption line shape. In a rigid matrix such as oligostyrene at 77 K, planarity cannot be achieved despite the strong driving force. The steady-state emission spectrum reflects the original broad distribution of twisted configurations and mirrors the absorption spectrum. However in a low-viscosity solvent like $CHCl_3$, the PPE chain quickly twists into a few nearly planar configurations. As a result, the steady-state emission spectrum is greatly narrowed (Figure 2c,d).

To test this model further, we measured steady-state spectra in an intermediate viscosity solvent, oligostyrene at room temperature (Figure 1, dashed). The spectra are between those in fluid $CHCl_3$ and frozen oligostyrene. At this viscosity, the time required for planarization in the excited state is similar to the fluorescence lifetime (350 ps), so the steady-state spectrum is a mixture of relaxed and unrelaxed emission.

Reexamination of the steady-state spectra in Figure 1 also supports our model. Taking the $CHCl_3$ fluorescence spectrum as an upper bound on the vibronic broadening, the absorption spectra are seen to be very asymmetrically broadened toward the blue. The Stokes shift is also small despite the broad absorption spectra. The predicted single-sided exponential broadening suggests that the frequency of the half-intensity point on the low-frequency edge of the absorption spectrum is a good estimate of the position of the 0−0 vibronic transition. Gauged on this basis, the adiabatic Stokes shift in the experimental spectra is very small, in agreement with our model. A more quantitative analysis of these spectra confirms the asymmetry of the spectral broadening and the smallness of the Stokes shift.[6b]

As an even more definitive test, we time-resolved the emission spectrum. In linear-coupling models, the emission spectrum's peak shifts toward lower frequency with time, but there is no change in its width (Figure 2b). In contrast, our model predicts that the peak position will not change, but that the blue side of the spectrum will collapse with time (Figure 2d).

Measurements were made by time-correlated single-photon counting with an instrument response function of 45 ps. Second-harmonic generation of a mode-locked Ti:sapphire laser produced excitation pulses at 397 nm. Wavelength-dependent fluorescence decays were inverted to time-dependent spectra by standard methods.[9]

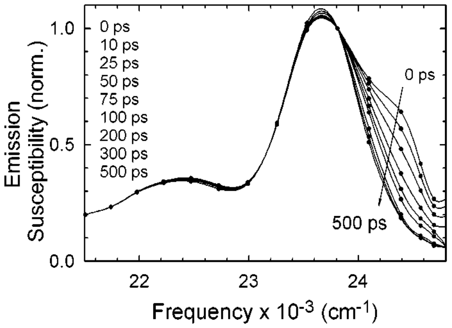

**Figure 3.** Time-resolved emission from PPE 9-mer in $CHCl_3$ at 297 K.

The results in $CHCl_3$ are shown in Figure 3. The spectra have been normalized at 420 nm to compensate for the overall decay of fluorescence intensity with time. As predicted, there is almost no shift of the peak of the spectrum, but there is a dramatic collapse of the blue edge. The time constant for the collapse is 60 ps, significantly faster than the fluorescence lifetime. Thus the steady-state spectrum is relaxed (narrowed) in this solvent (Figure 1). Preliminary results in oligostyrene show similar relaxation, but on a longer time scale (∼0.5 ns) that is close to the fluorescence lifetime. As a result, the steady-state spectrum is only partially relaxed in this solvent.

Both the steady-state and time-resolved spectra show that the rate of relaxation is directly connected to the solvent viscosity. This connection indicates that the relevant motions must displace a significant amount of solvent. Energy migration, coupling to low-frequency intramolecular vibrations, or changes in the Franck−Condon envelope would not show this viscosity dependence. Torsional motion is expected both to cause large solvent displacement and to have strong quadratic coupling. It is for these reasons that we identify it as the primary relaxation mechanism.

The earliest spectrum we infer from the time-resolved spectrum, i.e., the extrapolation to zero time, is still not as broad as the absorption spectrum. This result suggests that a partial planarization occurs more quickly than we can detect and that only the slower portion of the planarization is observed here. The fast portion could be associated with twisting of the phenyl rings by stretching the hexyl side chains, followed later by dragging the side chains through the solvent into their equilibrium positions.

Recognizing the role of planarity in PPEs has several important implications. Because the ground-state potential is shallow, environmental and supramolecular forces can strongly influence the planarity of the polymer and consequently its spectral properties.[10] Our model also shows that a broad absorption spectrum does not necessarily imply strong breaking of conjugation along the chain in the ground state. In our model, the breaking of the conjugation is primarily in the twisted excited state, not in the ground state. Finally, narrowed emission spectra are common in other conjugated polymer systems and are often attributed to energy migration. Torsional dynamics similar to those seen here may not be as dominant in other polymers, but they should be considered as a potential contributor to the spectral dynamics.

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