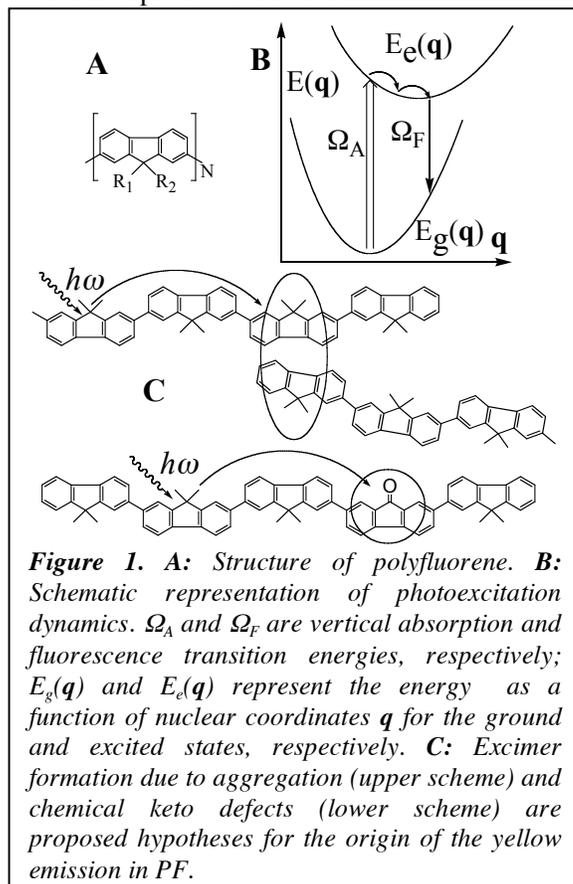


Electron-vibrational relaxation of photoexcited polyfluorenes in the presence of chemical defects

Light emitting conjugated polymers are of interest both for their broad technological applications and because they are model systems to gain fundamental understanding of the properties of soft organic and biological matter¹. Polyfluorenes (PF) and their derivatives (Fig. 1A) have received a great deal of attention lately and are evolving as a major class of materials for light emitting diodes (LEDs). They exhibit a very attractive pure blue emission an efficient electroluminescence, a high carrier mobility and a good processability². Frequently the fluorescence spectra of PFs exhibits an undesired low-energy emission band in the yellow region of the spectrum (2.2-2.3 eV), turning the desired blue emission into a blue-green color. Traditionally this band has been assigned to aggregation and/or excimer formation in the material in the solid state (Fig. 1C). A second, recently proposed hypothesis, suggests that fluorenone (keto) defects, and not aggregates, are the responsible for the novel yellow band emission (Fig. 1C)².

Given the technological and topical importance in understanding the origin of this undesired yellow emission, here we computationally explore the electronic excitations of polyfluorenes with and without chemical impurities (shown in Fig. 2). The first one consists of 5 fluorene units and was used to study pristine PF properties (O1). Keto doped PF were simulated with an oligomer 7 units long, where the second to the last monomer contains a defect site (O2). We focus on the lowest singlet excited state of PFs as it is determinant in absorption and fluorescence spectra. Vertical absorption transition energies were computed from the ground state optimal geometry which corresponds to the ground state potential energy minimum and describe the "hot exciton", created by an absorbed photon^{3,4}. This initial photoexcitation subsequently relaxes into the excited state minimum of potential energy hypersurface into a "cold exciton" which decays radiatively back to the ground state (vertical emission), Fig. 1B. For finding the ground and excited state optimal geometry we used a recently developed excited state molecular dynamics approach⁴, which propagates the Newtonian equations of motion

along the trajectory on the excited state molecular potential surface.



The structural changes induced by photoexcitation in both oligomers typically can be characterized by bond length alternation parameter, which measures the uneven distribution of π electrons over the bonds (Peierls distortion)^{3,4}. Fig. 2 (top) shows that bond length alternation in O1's ground state geometry is constant for equivalent bonds along the chain, and noticeably reduced in the middle of the molecule for the excited state geometry. As previously observed in poly(p-phenylene vinylene)⁴, this localized reduction of dihedral angles and bond length alternation is a characteristic signature of an exciton self-trapping. The introduction of a keto-defect into the system (O2) does not affect significantly the ground state geometry (Fig. 2, top). Drastic changes arise, however, when going to the excited state: A reduction of the bond-length alternation is clearly seen in the defect site. This indicates a trapping of the exciton by the defect.

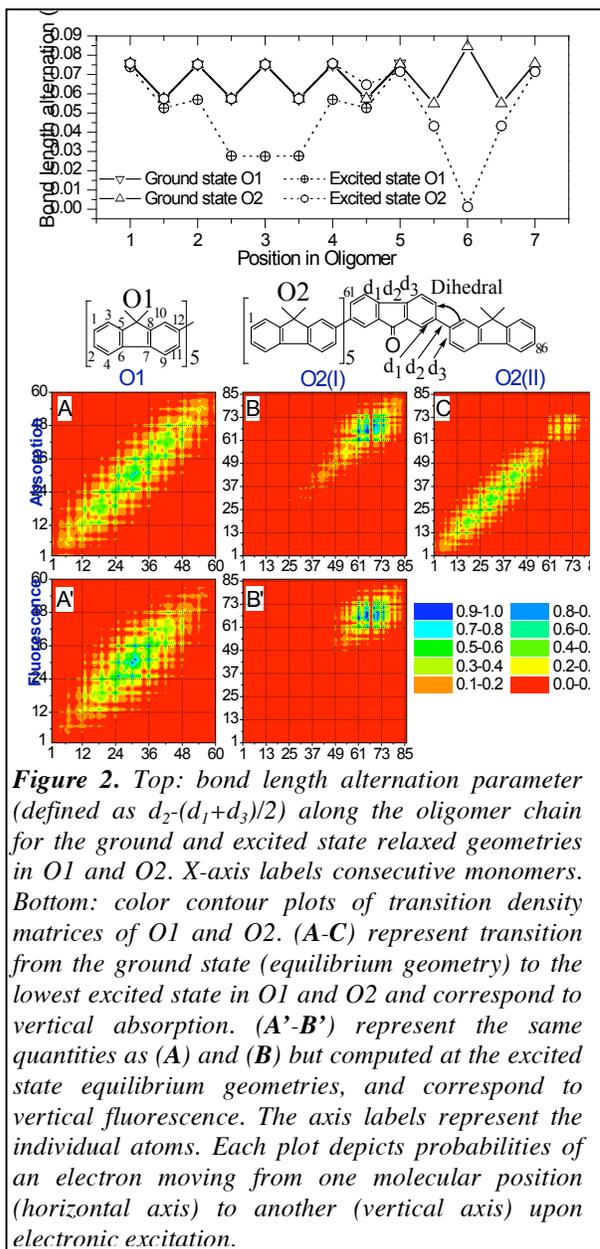


Figure 2. Top: bond length alternation parameter (defined as $d_2 - (d_1 + d_3)/2$) along the oligomer chain for the ground and excited state relaxed geometries in O1 and O2. X-axis labels consecutive monomers. Bottom: color contour plots of transition density matrices of O1 and O2. (A-C) represent transition from the ground state (equilibrium geometry) to the lowest excited state in O1 and O2 and correspond to vertical absorption. (A'-B') represent the same quantities as (A) and (B) but computed at the excited state equilibrium geometries, and correspond to vertical fluorescence. The axis labels represent the individual atoms. Each plot depicts probabilities of an electron moving from one molecular position (horizontal axis) to another (vertical axis) upon electronic excitation.

To connect these structural changes with distinct dynamics of the underlying photo-induced electron-hole pairs in doped and undoped oligomers we use two-dimensional real-space analysis of the transition density matrices^{3,4} related to the absorption and emission electronic spectra of O1 and O2 (Fig. 2 A-C). These provide a real-space picture of electronic transitions by showing accompanying motions of optically induced charges and electronic coherences^{3,4}.

The exciton created by absorption to the excited state in O1 (Fig. 2A) is delocalized over the entire chain (diagonal in the plot). The exciton diagonal size decreases at the excited state geometry (Fig. 2A'). This confirms exciton

self-trapping by vibrational relaxation in the middle of the chain. However, the exciton is still sufficiently delocalized so that a considerable portion of the oligomer participates in the emission. In contrast to O1, the lowest excited state (O2(I)) created by an absorbed photon in O2 does not correspond to the band-gap state. The exciton has the center of mass at the defect site (Fig. 2B) and is delocalized over the defect. The O2(I) state lies lower in energy and has a smaller oscillator strength than band-gap state in O1. We identify the third excited state (O2(II)) in O2 (Fig. 2C) as corresponding to the band-gap state in pristine PF oligomer (compare Figs. 2A and C). The O2(II) state has a strong oscillator strength and will subsequently dominate the absorption spectrum of doped PF making it similar to that of pristine PF. After absorption to the band-gap state O2(II) (Fig. 2C), the excitation is transferred to the lowest state O2(I) localized on the defect site. The effect of vibrational relaxation induces further localization of the excitation on the defect site (Fig. 2B'). Thus, the emission of PF with chemical defects originates from the exciton completely localized on the fluorenone unit which acts as a guest site for exciton recombination.

In conclusion, we have theoretically studied the effects of chemical defects on the dynamics of excitations in PF^{5,6}. Our analysis identifies exciton self-trapping in pristine oligomers and a non-quenching localization of the excitation in oxidative defects which results in a dominant low energy fluorescence band in support of recent experimental data².

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