

Photoexcitation dynamics in thin films of insulated molecular wires

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A study is presented on how encapsulation of conjugated polymer chains affects the motion of photoexcitations and the formation of interchain aggregates in solid films. It is shown that threading of a poly(diphenylene vinylene) backbone inside insulating cyclodextrins (rotaxination) and/or complexation of the chains with poly(ethylene oxide) are effective means of preventing the diffusion of excitons to nonradiative defect sites. Ultrafast time-resolved photoluminescence data reveal that excitation transfer between encapsulated chains is still possible and, for the case of rotaxination, is likely to be facilitated through close packing of end groups belonging to adjacent chains. © 2006 American Institute of Physics. [DOI: 10.1063/1.2398914]

Conjugated polymers have demonstrated great potential as materials for light-emitting diodes¹ and solar cells² via low-cost solution processing. Both optical and electronic properties of conjugated polymers are strongly modified by intermolecular interactions. The formation of closely packed aggregates and the associated electronic interactions between polymer chains in the solid films may trap excitons, quench the photoluminescence (PL) severely, and change its spectral characteristics.^{3,4} Such effects are unfavorable for light-emitting devices and demonstrate the need for control of material morphology at the molecular level. One promising scheme to reduce aggregation is encapsulation of single polymer chains^{5,6} through an approach based on supramolecular chemistry. Here, π -conjugated polymer backbones are isolated by threading individual chains with insulating sheaths. This method has been shown to increase the PL efficiency of polymer films,⁷ protect conjugated backbones from environmental contaminants, and enhance chemical stability.⁶

Several encapsulation techniques have been developed and discussed in recent reviews.^{5,6} In particular, we focus here on two strategies that have been employed to insulate conjugated polymer chains. The first is rotaxination where the conjugated polymer backbone is threaded with nonconjugated insulating macrocycles via hydrophobic interactions during polymerization.⁷ The second is complexation of the conjugated polymer with nonconjugated poly(ethylene oxide) (PEO) via ionic interactions in solution.⁸ For both encapsulation strategies, the photoluminescence and electroluminescence efficiencies in the solid were found to be dramatically enhanced compared with films of the uninsulated polymers.^{7,8} While the success of these schemes has been highly encouraging, the exact mechanisms leading to the improvement in device performance are still unclear. Specifically, insulation of the polymer chains in the solid may not only lead to a desirable increase in luminescence efficiency but also inhibit the motion of excitons and charges through the material. In this study, we use time-resolved PL

spectroscopy to address these issues by examining how insulation of conjugated polymer chains through rotaxination and complexation with PEO affects the motion of excitons and the associated potential landscape in solid films.

The chemical synthesis of the poly(diphenylene vinylene) (PDV) derivative and its rotaxane (β -CD-PDV) with β -cyclodextrin (CD) rings has been reported elsewhere⁹ (see Fig. 1 for chemical structure). PEO with average molecular weight of 100 000 g mol⁻¹ was used as purchased from Sigma-Aldrich. Solutions of the materials were prepared in de-ionized water at concentration of 14.5 mg/ml and blends were made by mixing the component solutions. Film samples were prepared by either spin or drop casting onto Spectrosil B substrates. Samples were processed under a N₂ atmosphere and held under a dynamic vacuum at 10⁻⁵ mbar during measurements. Time resolved PL measurements were conducted using the PL upconversion technique as described in detail elsewhere.¹⁰ The films were excited near the peak of the absorption at an energy of 3.06 eV using the frequency-doubled, 70 fs laser pulses supplied by a mode-locked Ti:sapphire laser. The PL was focused onto a β -barium borate crystal where the vertical polarization component was gated optically by an intense vertically polarized second pulse arriving at adjustable time delay. The resulting upconverted luminescence signal was dispersed in a monochromator and detected by a liquid-nitrogen cooled charge-coupled device. The polarization of the excitation beam was set by a half-wave plate and a Glan-Thompson polarizing prism. All PL spectra were corrected for instrumental response using a filament lamp of known emissivity.

Figure 1(a) displays the PL spectra for drop-cast films of uninsulated PDV for different times after excitation. The emission spectra are broad and featureless indicating the presence of strongly aggregated chromophores.¹¹ The PL intensity decreases rapidly over the first ~ 10 ps, accompanied by a spectral redshift as excitations transfer to regions of the film where stronger interchain interactions lead to weaker oscillator strengths of the lowest electronic transition.³ The average energy of the emitted photons, $\langle E_{\text{PL}} \rangle$, was extracted from each spectrum through energy-weighted integration¹⁰

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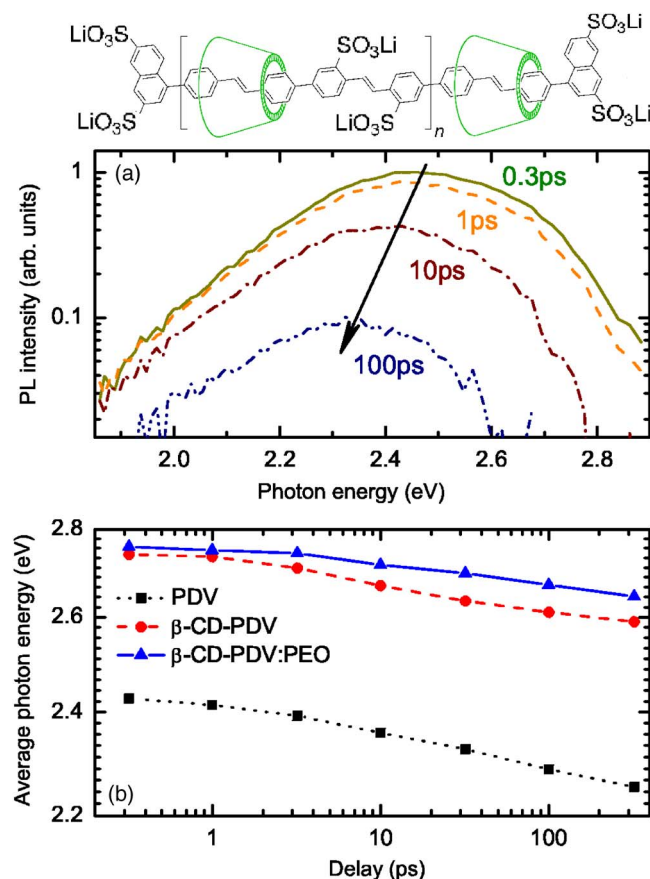


FIG. 1. (Color online) Chemical structure of β -CD-PDV. The PDV structure is identical but without CD (represented here by conical sheaths). (a) PL spectra of drop-cast PDV films at different times after excitation. (b) Average energy of emitted photons for drop-cast films of PDV (square), β -CD-PDV (circle), and the 50:50 blend β -CD-PDV:PEO (triangle).

and is displayed in Fig. 1(b) as a function of time after excitation. The figure also shows the $\langle E_{\text{PL}} \rangle$ values extracted using identical procedures for the polyrotaxane and its 50:50 blend (by weight) with PEO.

Distinct differences can be observed for the average emission energies at early times (0.3 ps) after excitation, that is, after nuclear relaxation has occurred but before any significant migration of excitons through the film has been undertaken. The redshifted emission from the un-insulated PDV at early times is a result of excitonic relaxation to the energetically lowest state of the aggregate on the time scale of nuclear motion, which may also be observed in coupled phenylene vinylene oligomers.¹² We will focus in the following on the processes associated with the slower exciton migration that occurs during the first few hundred picoseconds. Over these time scales, all films show a redshift in the emission energy in accordance with exciton migration to sites of lower energy within the density of states.¹³ For the un-insulated PDV film, this shift is very pronounced with a value of 174 meV over the first 320 ps, comparable to energetic shifts observed in a cyanosubstituted poly(phenylenevinylene) derivative¹⁴ for which they have been attributed to excimer formation. Polyelectrolyte materials have been shown to aggregate strongly in solution,⁴ making them useful for exploitation in chemical sensors.¹⁵ Interestingly, the extent of the redshift in the emission over the first 320 ps is reduced to 150 meV for the rotaxinated material and further to 110 meV for the chains that are both rotaxinated and then

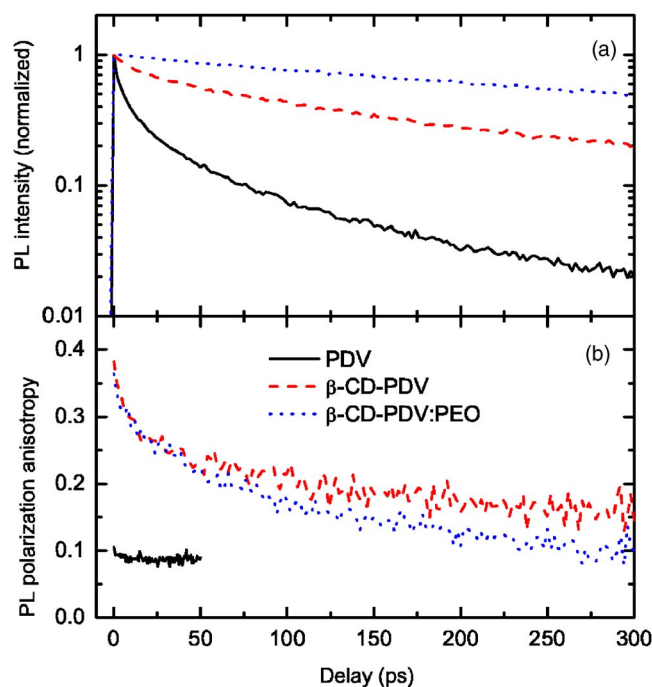


FIG. 2. (Color online) (a) Polarization-independent PL intensity [$I_{||}(t) + 2I_{\perp}(t)$] and (b) PL polarization anisotropy dynamics for drop-cast films of un-insulated PDV (solid), β -CD-PDV (dashed), and β -CD-PDV:PEO (50:50) (dotted line) at detection energies of 2.45, 2.71, and 2.71 eV, respectively.

blended with PEO. This reduction in energetic relaxation may be caused by a decreasing exciton diffusivity as the chains are separated further and also by a concomitant reduction in energetic disorder associated with a distribution of intermolecular interaction strengths. However, even for the most insulated chains in β -CD-PDV:PEO films, some exciton migration evidently occurs between chromophores. Scanning-force microscopy images of similar rotaxane:PEO blends have shown that PEO forms a complex with the rotaxinated polymers on the single-strand level⁸ indicating efficient separation of the chains. Since the average degree of polymerization for the materials investigated is relatively short [11 for β -CD-PDV and 12 for PVD Ref. 9], the observed energy shifts are unlikely to arise solely from intra-chain exciton migration. We therefore conclude that some interchain transfer of excitations occurs even between PEO-wrapped polyrotaxanes, in agreement with the observation of electroluminescence from devices based on these materials.⁸

To examine the exciton lifetime in all three films, PL decay curves shown in Fig. 2 were taken at the peak of the respective initial emission spectra. The PL dynamics of the un-insulated PDV film are strongly nonexponential with a fast initial component that is typical of exciton diffusion in a material incorporating nonradiative traps, such as strongly aggregated chains, chemical defects or contaminants.¹⁶ Rotaxination strongly reduces this fast component, while additional shielding with PEO yields an almost monoexponential decay with a lifetime of 420 ps. These findings are consistent with the substantial increase of emission efficiency with encapsulation reported recently^{7,8} for these materials.

Given the efficient encapsulation of the individual PDV backbones, it is surprising that charges and excitons are still able to transfer between the chains. Proton NMR and matrix-assisted laser desorption/ionization time-of-flight analyses of

the threading ratios for similar polyrotaxanes⁹ have revealed that the CD macrocycles do not completely shield the conjugated backbones and retain some degree of free motion along the chains. It has therefore been suggested that polyrotaxanes may still exhibit π - π stacking interactions at typical short (~ 0.4 nm) interchain separation between exposed regions of the backbone.⁷ In this case, the steric hindrance imposed by the bulky CD rings to either side of the exposed segment would lead to a relatively large angle between stacked chains. Alternatively, close contact may be established at the chain ends, where the exposed naphthalene derivative used to prevent the rotaxane from unthreading may form a π stack with that from an adjacent chain. Such end-group interactions have been found by x-ray structure analysis on crystals of shorter rotaxanes⁶ for which the adjacent conjugated backbones are relatively aligned. In order to examine which of the two options is most significant, we conducted transient PL depolarization measurements on the same three films. The time-dependent PL polarization anisotropy $\gamma(t)$ is defined as the difference between the luminescence intensity polarized parallel [$I_{\parallel}(t)$] and that polarized perpendicular [$I_{\perp}(t)$] to the excitation polarization, normalized by the total luminescence intensity [$I_{\parallel}(t) + 2I_{\perp}(t)$]. Figure 2(b) shows $\gamma(t)$. For the insulated chains, the initial polarization anisotropy is close to 0.4, the value expected for a random distribution of weakly interacting dipoles¹⁷ reemitting before any reorientation of the dipole moment may have occurred. As time progresses, excitons transfer to chain segments with different orientations leading to a decay of the PL anisotropy. Interestingly, the PL originating from the β -CD-PDV:PEO film depolarizes faster than that from the pure polyrotaxane film, even though exciton migration is slower in the former according to our PL decay and energy relaxation data. This is only possible if the angles between dipole moments on neighboring chromophores tend to be larger for β -CD-PDV:PEO films than for β -CD-PDV. These results therefore strongly suggest that the transfer of photoexcitations between polyrotaxanes is aided by end-group interactions in an aligned head-to-tail geometry, rather than the stacking at large interchain angle via exposed sections of the backbone. Such end-group-to-end-group interactions are a common feature in the crystal structures of related rotaxanes¹⁸ and are thus likely to occur in the films examined here. Complexation with PEO may disrupt such end-group interactions leading to larger angles and spacings between adjacent chains.

Finally, we have examined the effect of blending uninsulated PDV with different weight fractions of PEO without rotaxination, as shown in Fig. 3. Addition of only 20% of PEO leads to a strong reduction of the fast PL decay component observed for the pure dumbbell film. Increasing the PEO content leads to a gradual increase in the exciton lifetime with almost exponential decay dynamics observed over the first 50 ps for a weight fraction of 50%. Taken together with the PL efficiency enhancement observed previously for similar blends,⁸ these results again demonstrate the reduction of trapping of photoexcitations at nonradiative defect sites as a result of molecular insulation.

In conclusion, we have demonstrated that insulation of conjugated polymer chains has a strong effect on the transfer and energetic relaxation of excitons in the solid film. Both

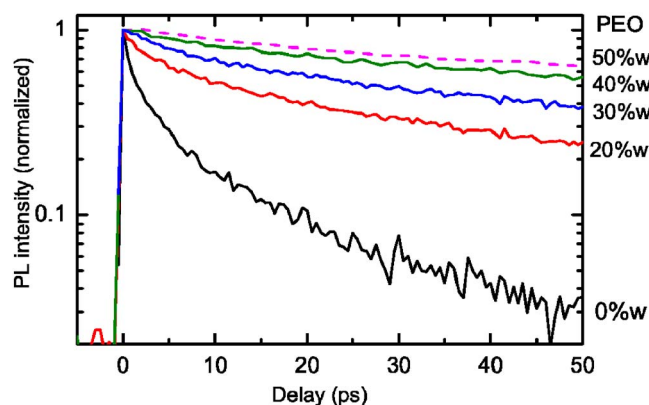


FIG. 3. (Color online) Decay of the polarization-independent PL intensity for spun-cast PDV:PEO blend at various PEO concentrations (by weight) taken at a detection energy of 2.6 eV.

rotaxination and complexation with PEO are highly effective at preventing the diffusion of excitons to nonradiative defects, and inhibit the formation of chain aggregates. The trade-off between prevention of weakly emitting aggregates and optimization of charge mobility clearly requires such encapsulation of the chains to be carefully balanced. However, the recent observation of electroluminescence enhancement with rotaxination⁷ and PEO complexation⁸ shows that sufficient charge injection can be maintained. Our results demonstrate that for the case of rotaxination, end-group stacking effects may be important in maintaining close contact between successive chains.

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