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Ultrafast depolarization of the fluorescence in a conjugated polymer

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The effect of the extent of π electron conjugation on the primary photophysics in semiconducting polymers is reported. A rapid depolarization of photoluminescence and transient absorption, which indicates a reorientation of the transition dipole moment by ~30° on a sub-100 fs time scale, is observed in the fully conjugated polymer poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV). In contrast, partially conjugated polymers exhibit a much slower depolarization. The results reveal rapid changes of exciton delocalization in the fully conjugated MEH-PPV driven by structural relaxation.

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I. INTRODUCTION

Conjugated polymers show attractive semiconducting and optical properties together with a great potential for applications in electroluminescent devices,[1] solar cells,[2] lasers,[3] optical switches,[4] and fluorescent biosensors.[5] Soluble polymers, particularly poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV), have received a lot of attention, because solution processing provides easy shaping and simplicity in device manufacturing. The primary optical excitations in these materials are correlated electron-hole pairs—excitons,[6–12] which show intermediate properties between small radius Frenkel excitons of molecular aggregates and large radius Wannier-Mott excitons in inorganic semiconductors. A very important parameter determining excited state dynamics is exciton delocalization length, which depends on electronic coupling, site energy disorder, and electron-phonon coupling. Instantaneous delocalization of the exciton over at least 50 repeat units, which corresponds to 400Å, was estimated from the measured anisotropy of the electroabsorption signal in films of oriented MEH-PPV,[13] which also showed a lower binding energy of the exciton[12] than the disordered films.[8,10] Exciton delocalization in solutions and unoriented spin-coated films of MEH-PPV as well as those of unsubstituted poly(phenylenevinylene) (PPV) prepared from a precursor was estimated to be between 6 and 17 repeat units from fits to absorption spectra.[14,15] This estimate depends on whether the blueshift and broadening of absorption originates from conjugation-disrupting defects, such as kinks and twists in the backbone[16] or from the "wormlike" conformational disorder, which gradually weakens the conjugation in the absence of abrupt conjugation breaks.[15,17] Quantum-chemical calculations indicate that topological defects, such as twists and kinks, do not result in a complete exciton localization on individual segments, they just shift electronic transitions towards higher energies.[18] Dynamic localization of the exciton is expected as a result of structural relaxation,[18–21] but it has not been experimentally proven for MEH-PPV. Such a localization could be the cause of the rapid decay of the three-pulse stimulated echo peak shift within 50 fs observed in MEH-PPV in solution at room temperature.[22] A much longer electronic dephasing time of 100–450 fs in PPV films following site-selective excitation at low temperature is inferred from the decay of resonant Rayleigh scattering[23] and fluorescence interferometry,[24] which is in good agreement with a homogeneous linewidth on the order of 1 meV measured by hole burning[25] and observed in the single-chain emission[26] of a ladder-type polyphenylene. Thus, the initial exciton delocalization and its dynamics in disordered polymers are not understood yet.

In this paper we investigate the role of the extent of π electron conjugation on the primary exciton dynamics in MEH-PPV. To do this we study a family of MEH-PPVs synthesized to have different degrees of conjugation. Earlier work showed a decrease of the charge mobility in partially conjugated polymers as compared to fully conjugated polymers,[27] but no comparison of ultrafast photophysics has been reported. We report that a much faster depolarization of photoluminescence (PL) and transient absorption (TA) is observed in the fully conjugated MEH-PPV than in the partially conjugated polymers. This can be explained by dynamic localization of the exciton in the fully conjugated MEH-PPV in contrast to static localization in the partially conjugated polymer. From the amplitude of rapid depolarization we estimate that the primary excitons in the fully conjugated MEH-PPV are delocalized over at least 14 conjugated repeat units.

II. EXPERIMENT

Fully and partially conjugated MEH-PPVs were synthesized from chloro precursors.[28] Control over the degree of conjugation was achieved by selective dechlorination of the precursor before base-catalyzed conversion to the conjugated

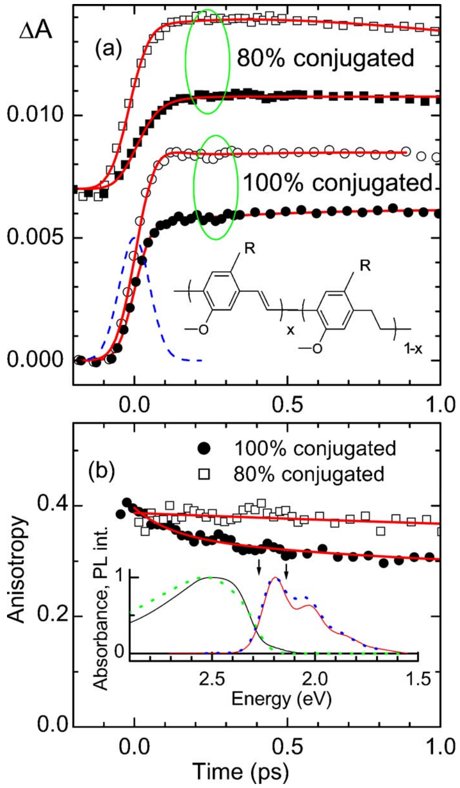

FIG. 1. (Color online). Parallel (open symbols) and magic angle (filled symbols) TA kinetics (a), the convoluted fits (solid lines) and the response function (dashed line). The kinetics in 80% conjugated are offset vertically. The inset shows the chemical structure of the polymers studied, R is 2-ethylhexyloxy. In (b) raw experimental anisotropy (symbols) and fits (solid lines) are shown with ground state absorption and time-integrated PL spectra of 100% (solid lines) and 80% conjugated (dotted lines) polymers are shown in the inset; arrows mark the excitation and probe energies.

polymer. Three polymers with different fractions of conjugated segments x [see inset in Fig. 1(b)] were prepared: $x=1$ (fully conjugated), $x=0.8$ (80% conjugated), and $x=0.66$ (66% conjugated). The weight-averaged molecular mass of the fully conjugated polymer was measured to be $\bar{M}_w=274\,000$ with a polydispersity ~ 3.8 by gel permeation chromatography using polystyrene standards as reference. The 80% and 66% conjugated polymers had $\bar{M}_w=123\,000$ and $\bar{M}_w=311\,000$ with polydispersities of 2.4 and 2 respectively. Measurements were performed in a dilute chlorobenzene solution, where MEH-PPV chains predominantly adopt extended conformations[29,30] avoiding significant interchain and chain-folding effects. TA of degassed polymer solutions was measured in a 1×1 cm^2 cell, which was stirred during measurements. The sample was excited by light pulses of 80 fs with a spectral width of 0.025 eV at a 5 kHz pulse repetition rate and a white light continuum probe was used,[9] giving an instrumental response function (IRF) of 120 fs (FWHM). Femtosecond PL was measured in a 1 mm rotating cell by fluorescence up-conversion, which had an IRF of 220 fs (FWHM). PL spectra on a picosecond time scale were measured with a synchroscan streak camera (IRF of 2 ps) in a 1 cm cell and solutions were stirred during measurements. In both cases excitation was by 100 fs pulses at 80 MHz repetition rate using the second harmonic of a Ti:sapphire laser. All measurements were performed at room temperature. The results were independent of polymer concentrations in the range of 0.1–5 mg/ml. The raw experimental anisotropy was calculated from TA or PL intensities, measured for parallel, $L_{\parallel}$, and magic angle (54.7°),L_m, relative polarizations of excitation and probe (or detection) using the well-known formula $r=(L_{\parallel}-L_m)/(2L_m)$. A sum of exponential decay functions convoluted with the IRF was fitted to the kinetics of L_m and the obtained parameters were used to fit the $L_{\parallel}$ kinetics, simulating the anisotropy decay as a sum of two exponential functions.

III. RESULTS

Figure 1(a) shows the TA kinetics in the fully and 80% conjugated MEH-PPV measured after excitation with 2.25 eV photons and probing at 2.14 eV. In this case, the TA signal is dominated by amplification of the probe light due to stimulated emission. The magic angle TA kinetics in both polymers show a dominating instantaneous rise and a slower rise with a time constant of ~ 0.4 ps, which corresponds to $\sim 10\%$ of the full amplitude. The anisotropy shows an initial value of ~ 0.4 in both polymers [Fig. 1(b)], which is a theoretical maximum for an ensemble of randomly oriented, noninteracting chromophores with parallel dipoles of absorption and probe transitions. The striking difference is a much faster initial decay of anisotropy from $r_0=0.4$ to $r\approx 0.32$ in the fully conjugated polymer with a time constant of 90 ± 10 fs, whereas the 80% conjugated polymer shows a much slower depolarization with a time constant of ~ 4 ps for a similar loss of anisotropy. Figure 2 shows PL spectra measured with a streak camera at 3 ps and the 100 fs PL spectra obtained from fluorescence up-conversion using the streak camera spectra as a reference. The PL peak at 100 fs in all samples is at much lower energy than the excitation, implying that a substantial relaxation occurs within 100 fs. The PL peak in partially conjugated polymers is at higher energy and shows a bigger red shift on a picosecond time scale than in the fully conjugated polymer. Figure 3(a) shows the short time PL kinetics at 2.21 eV measured at magic angle. They show a finite rise of ~ 50 fs and a slower rise component of ~ 1 ps, which is more pronounced in the partially conjugated polymers. The PL anisotropy in the 66% conjugated polymer shows a decay from ~ 0.4 to ~ 0.26 with a time constant of ~ 1 ps [Fig. 3(b)], whereas in the fully conjugated MEH-PPV a much faster (~ 50 fs) decay to $r=0.2$ is observed. Depolarization in the 80% conjugated polymer is biphasic, showing a fast (~ 50 fs to $r\approx 0.3$) and a slower (~ 1 ps to $r\approx 0.2$) component.

IV. DISCUSSION

The polarization anisotropy of PL and TA signals provides information about the time-dependent orientation of the transition dipole moment. From the Perrin equation $r=(3\cos^2\alpha-1)/5$, where α is the angle between the transition dipole

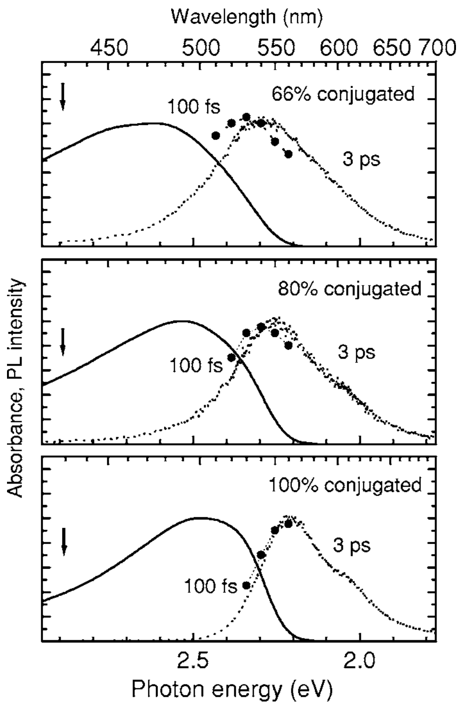

FIG. 2. Ground state absorption (solid lines) and time-resolved PL spectra taken at 3 ps (dashed line, streak camera data corrected for the wavelength-dependent sensitivity) and at 100 fs (symbols, reconstructed from the fluorescence up-conversion kinetics). Arrows mark the excitation energy (2.9 eV).

moments of absorption and emission, the sub-100 fs anisotropy decay to $r\approx 0.32$ for 2.25 eV excitation and to $r\approx 0.2$ for 2.9 eV excitation corresponds to reorientation of the transition dipole moment by 21° and 35° respectively. In partially conjugated polymers the exciton is localized by controlled conjugation breaks and the ~1 ps depolarization of the PL [Fig. 3(b)], which occurs with a similar time constant to the PL rise at 2.21 eV [Fig. 3(a)], can be attributed to incoherent excitation transfer along the disordered polymer chain[9,31] [Fig. 4(a)] or between chains in case of aggregation or chain folding. The much faster (<100 fs) depolarization of the PL and TA observed in the fully conjugated polymer cannot be explained by incoherent hopping, because it is not observed in the partially conjugated polymers. Interchain hopping associated with aggregation and chain folding is expected to be more severe in partially conjugated polymers due to kinks at the conjugation breaks.[16] Incoherent hopping on sub-100 fs would also be incompatible with the observation of a vibrational coherence time of 300 fs for high frequency modes in the excited state in a substituted PPV,[11] because coherence would then be lost much faster as a result of the stochastic nature of incoherent hopping. We have also considered the possibility of pure electronic relaxation to a state with a transition dipole moment in a different direction in the fully conjugated polymer. Absorption to a higher electronic state can be observed at 3.7 eV(Ref. 32) but is not excited in our experiment. An even parity state at 2.73–3.15 eV above the ground state in MEH-PPV has been observed using two-photon absorption and electroabsorption.[32] Linear absorption to this state is parity forbidden in conjugated polymers, but it may acquire some oscillator strength in MEH-PPV, where charge conjugation symmetry is partially broken by side substitution. However, it is negligible as compared to absorption by the lowest optical transition, which shows a vibronic progression up to ~3.2 eV[13,14,32] and is strongly polarized along the polymer chain.[33] Thus, the primarily excited and emitting electronic states have the same orientation of the transition dipole moment and hence a pure electronic relaxation is not a plausible explanation of rapid depolarization.

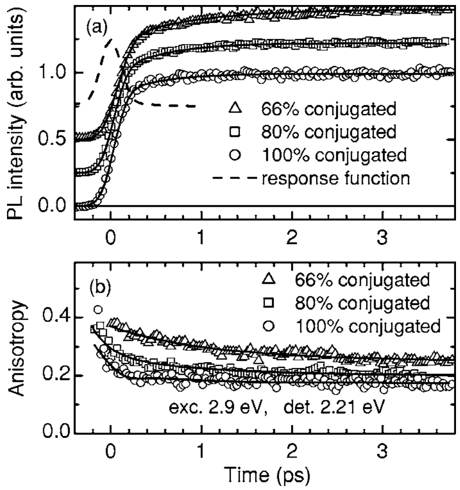

FIG. 3. Magic angle PL kinetics at 2.21 eV (a) and the convoluted fits (solid lines). Kinetics and response function are offset vertically. Symbols in (b) show raw anisotropy data and solid lines represent the anisotropy calculated from fits.

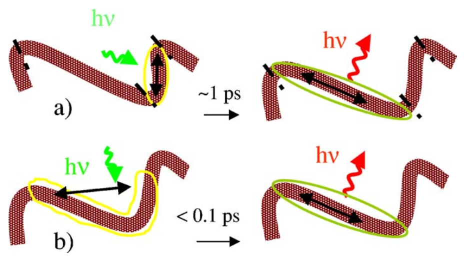

FIG. 4. (Color online). Sketch of static exciton localization by conjugation breaks in partially conjugated polymers (a) and dynamic localization due to structural relaxation in the fully conjugated MEH-PPV (b).

We propose that the sub-100 fs depolarization is due to rapid changes in exciton delocalization along twisted segments of the fully conjugated polymer [Fig. 4(b)]. We can estimate the extent of the primary exciton delocalization in the fully conjugated polymer from the fact that the amplitude of the sub-100 fs anisotropy decay in the fully conjugated MEH-PPV is similar to the depolarization in the first 10 ps for the partially conjugated polymers. This indicates that the exciton samples a similar size of the twisted polymer chain within 100 fs in the fully conjugated polymer as it does by incoherent hopping in the partially conjugated polymers in the first 10 ps, assuming that conformational disorder of these polymers is similar. In alkoxy-substituted PPV oligomers, only those with four and more repeat units have significant absorption at the excitation photon energy of 2.9 eV.[34,35] This means that in the time-resolved PL experiment in the partially conjugated polymers the initially excited state must be delocalized over four or more repeat units. The distribution of conjugation lengths statistically is expected to peak at short length in partially conjugated polymers.[27] The position of the PL maximum in the partially conjugated polymers at 3 ps is at 2.25 eV, indicating that emission comes predominantly from the conjugated segments of >10 repeat units long, because shorter PPV oligomers show emission peaks at significantly higher photon energies.[34] PL depolarization in the partially conjugated polymers within 10 ps represents at least one excitation hop to a neighboring conjugated segment; thus, adding the lengths of the initially excited and emitting segments in the partially conjugated polymers, we estimate that the primary exciton in the fully conjugated MEH-PPV is delocalized over a minimum of 14 repeat units (~ 110 Å). We note that our estimate is a lower limit, because partially conjugated polymers are expected to show kinks at the conjugation breaks and a single excitation hop between segments is likely to give a greater depolarization than exciton relaxation in the smoothly curved segment of the fully conjugated polymer. Also, the initially excited segment in the partially conjugated polymers is likely to be more than four repeat units, which would also increase the estimate for exciton delocalization in the fully conjugated polymer.

We next consider the nature of relaxation, which leads to depolarization on the sub-100 fs time scale. Trapped exciton states are predicted to form on the lower energy side of the one-dimensional Wannier exciton along the sharp bend of the polymer chain due to a stronger attractive potential.[36] However, rapid population of such trapped states would be inconsistent with the exciton diffusion length of ~ 20 nm observed in MEH-PPV films.[37] Thus, we do not expect trapped Wannier-type excitons to play a significant role in the photophysics of MEH-PPV. It is more likely that <100 fs depolarization is caused by dynamic localization, which is driven by structural relaxation of excited segments. According to calculations, the relaxed lowest excited singlet state ((S_1) in PPV shows a decrease of bond alternation in the vinylene linkages, which leads to a much steeper potential energy surface against the interring torsional motion as compared to the ground state (S_0).[19–21] Excitations created by Franck-Condon $S_1 \leftarrow S_0$ transitions in segments, which are distorted by torsional motions, are far from equilibrium and will relax towards an energy minimum. The amplitude of structural relaxation increases with conformational disorder and is as high as 0.6 eV in highly twisted polymers.[7,38] Modeling of absorption and PL spectra of oligomers predict structural relaxation in long conjugated PPV chains at room temperature to be of the order of 0.14 eV,[19,20] very similar to the difference between a shoulder at 2.35 eV in the absorption spectrum of fully conjugated MEH-PPV [Fig. 2], which corresponds to 0-0 vibronic peak, and the PL peak at 2.21 eV. This relaxation can lead to exciton localization on one side of the topological defect[18] or in the middle of the extended conjugated segment.[19–21] The time scale for exciton localization can be of the order of the period of the dominant vibrations coupled to the $S_1 \leftarrow S_0$ transition. These are high frequency stretching modes of the double and single C bonds with a vibration period of 21–27 fs,[7,11] and low frequency torsional modes (period of 160 fs and longer[39]). Low frequency torsional modes are predominantly excited at low photon energy (Fig. 1), and torsional relaxation mediated by these modes is expected to be slower, consistent with a slower depolarization (90 fs) as compared to higher energy excitation (~ 50 fs in Fig. 3). The reorientation angle of the transition dipole moments is smaller after excitation into the absorption tail, which is compatible with selective excitation of extended conjugated segments.

Our interpretation is consistent with the results of photon echo peak shift studies of MEH-PPV in chlorobenzene solution by X. Yang *et al.*,[22] which showed a fast decay of the energy gap correlation function for the optical transition at 2.34 eV within 50 fs. The magnitude of the rapid Stokes shift deduced from the echo peak shift data was $\sim 1400\ \mathrm{cm}^{-1}$ (0.17 eV), very similar to our PL data (Fig. 2). The ultrafast changes in the TA spectra and the dynamics of vibrational wave packets in polydiacetylene have been explained in terms of the geometrical relaxation of a free exciton to a self-trapped state within 100 fs.[40] In addition, ~ 30 fs depolarization component was observed in the stimulated emission signal from amorphous films of polythiophene,[41] which could not be explained by incoherent hopping and may also represent a signature of dynamic localization. All these observations suggest that structural relaxation and dynamic localization phenomena are common in conjugated polymers.

In some cases (TA experiment in the 100% conjugated MEH-PPV with 2.25 eV excitation and PL dynamics in the 80% conjugated polymer with 2.9 eV excitation), the initial decay of anisotropy required at least two exponential functions to fit the data. This is because two processes are involved: dynamic localization and incoherent hopping. For the TA experiment excitation is to the low energy tail of the absorption, so a fraction of the primary excitons are likely to be localized by conformational defects, while others are delocalized. The localized excitations will depolarize relatively slowly (picoseconds) by incoherent hopping, whereas the more delocalized excitations will depolarize much faster (<100 fs) due to dynamic localization. Excitation at 2.9 eV in the 80% conjugated polymer is also likely to generate delocalized and localized excitons, which again results in a fast (~ 50 fs) and a slower (~ 1 ps) component to the anisotropy decay.

V. CONCLUSION

The use of samples with a range of conjugation lengths has enabled us to explore the delocalization length of primary excitations in the widely used polymer MEH-PPV. In partially conjugated polymers the exciton is localized by controlled conjugation breaks, whereas in the fully conjugated polymer it is much more delocalized, at least on a very early time scale. Transient absorption and fluorescence measurements show a much faster depolarization in fully conjugated MEH-PPV (sub-100 fs) than in the partially conjugated polymer (>1 fs). The results can be explained by dynamic localization of initially delocalized excitons in the fully conjugated polymer driven by structural relaxation of excited segments. From the degree of depolarization, we estimated that the primary exciton in the fully conjugated MEH-PPV is delocalized over at least 14 repeat units (~110 Å). This estimate is a lower limit and the actual delocalization could be much bigger.

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