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Relaxation dynamics and exciton energy transfer in the low-temperature phase of MEH-PPV

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Understanding the effects of aggregation on exciton relaxation and energy transfer is relevant to control photoinduced function in organic electronics and photovoltaics. Here, we explore the photoinduced dynamics in the low-temperature aggregated phase of a conjugated polymer by transient absorption and coherent electronic two-dimensional (2D) spectroscopy. Coherent 2D spectroscopy allows observing couplings among photoexcited states and discriminating band shifts from homogeneous broadening, additionally accessing the ultrafast dynamics at various excitation energies simultaneously with high spectral resolution. By combining the results of the two techniques, we differentiate between an initial exciton relaxation, which is not characterized by significant exciton mobility, and energy transport between different chromophores in the aggregate. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4918645]

I. INTRODUCTION

Molecular functional materials are currently subject to extensive studies because of their applications in organic electronics and photovoltaics. Among these materials, conjugated polymers are particularly attractive as they combine high absorption cross sections with low-cost production and deposition over flexible substrates. 1–3 However, typical efficiencies of solar cells based on conjugated polymers are currently limited to <11%. 4

The key parameters to understand photoinduced function in these devices are the interactions of polymer structural units (monomers), both within a single polymer chain and between neighboring polymer chains in aggregates. Indeed, such interactions affect the relaxation time scale of the excited states, the population yield of mobile excitons versus nonmobile species (e.g., excimers), the capability to transport the absorbed energy over long distances, the formation of charge-transfer states, and their dissociation into free charges in proximity of the donor-acceptor interface. Particularly, the efficiency of energy transport from the bulk of the donor material towards the interface with the acceptor is among the factors that have a significant influence on the performance of organic photovoltaic devices.

Conformational disorder, which is among the distinctive characteristics of conjugated polymers, has profound effects on the dynamics of excitons and energy transfer. Together with spatial variations in the polarization of the environment, conformational disorder breaks the conjugation along the polymer chains and forms short conjugated segments called “conformational subunits.” 5,6 Absorption of a photon populates exciton states which are initially delocalized over several conformational subunits but localize on sub-100 fs time scales on smaller domains due to dynamic coupling between electronic and nuclear degrees of freedom. 7 On a longer time scale, electronic energy transfer is typically described in terms of a sequence of Förster energy transfer steps between localized excitons, 8,9 although intermediate regimes characterized by coherent intrachain energy transfer have been reported for Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) in chloroform. 10 The dynamics of energy transfer differs significantly along the polymer chain (intrachain) and between different polymer chains (interchain). The latter is typically one to two orders of magnitude faster than intrachain energy transfer, 11–14 explaining the more efficient energy transport observed in films as compared to isolated polymer chains in solution. 12,15,16

The picture of exciton dynamics described above applies in general for conjugated polymers. However, the dynamics of the photoexcited species, as well as the rate, the efficiency, and the length scale of energy transport, can differ strongly for different systems. Additionally, the photophysics of conjugated polymers and their aggregates depends not only on the chemical nature of the compound but also on its structure and morphology. 12,17–21 Hence, understanding the key factors controlling exciton dynamics requires the capability to control the structure of the aggregate. A possibility in this respect is to use systems where both aggregation and the morphology of the self-aggregated state can be controlled by external parameters.

In this paper, we investigate the low-temperature self-aggregated phase of the polymer MEH-PPV in solution. In MEH-PPV, two classes of chromophores have been observed, one emitting at higher energy (“blue sites”) than the other (“red sites”). 22–25 The picture emerging from single-molecule spectroscopy suggests that MEH-PPV can be found in two distinct conformational classes, and that the relative amount...
of blue and red sites in a single chain is controlled by the presence of interactions between segments of the polymer chain that are brought into contact by chain folding. The red sites have been repeatedly ascribed to planarized segments characterized by an increased conjugation length compared to the blue sites.\textsuperscript{25,29} It was also suggested that the formation of the red sites might be related to aggregation.\textsuperscript{22,27} Recent studies showed that concentrated solutions of MEH-PPV in 2-methyltetrahydrofuran (MeTHF) undergo a phase transition from a coiled conformation ("blue phase"), characteristic of room temperature, to an aggregated and planarized phase at low temperatures ("red phase"), characterized by very long conjugation length.\textsuperscript{28} The phase transition is accompanied by the appearance of a low-energy band in both the absorption and emission spectra.\textsuperscript{26,29} In the following, we will refer to the blue (red) phase as coiled (aggregated) phase.

Although the ultrafast dynamics of the room-temperature coiled phase of MEH-PPV has been extensively studied both in solution and films,\textsuperscript{14,18,24,30,31} knowledge on the ultrafast dynamics of the aggregated red phase is still sparse. In the following, we use broadband transient absorption spectroscopy and coherent electronic two-dimensional (2D) spectroscopy to observe the exciton relaxation and energy transfer dynamics in the planarized aggregated phase of MEH-PPV. Combining the results from these experiments allows us to individuate two regimes of energy relaxation in the aggregated phase of MEH-PPV. In particular, we separate the initial exciton relaxation within a manifold of excitons sharing a common ground state (relaxation without significant energy transport) from the energy hopping between excitonic states located on different polymer segments. Furthermore, we show that the average time scale for energy hopping in the aggregated phase is comparable with the typical values reported for the red-emitting sites in single molecules.

II. EXPERIMENTAL METHODS

MEH-PPV was purchased from Sigma Aldrich (CAS 138184-36-8). Gel permeation chromatography measurements were performed (PSS Polymer Standards Service GmbH in Mainz) using polystyrene as the calibration standard and solving the MEH-PPV in 1,2,4-trichlorobenzol at a temperature of 150 °C to make sure that it was completely dissolved. This measurement provided the weight-average molecular weight of the batch of sample used for our experiments ($M_w = 218.8$ kDa) and the number-average molecular weight ($M_n = 58.12$ kDa), resulting in a dispersity of $D = M_w/M_n = 3.76$. The sample was dissolved in distilled MeTHF (Sigma Aldrich) at a concentration of 0.2 mg/ml. The solution was stirred and heated at $\sim$40–45 °C for 24 h, until no macroscopic particles could be observed anymore. Absorption and emission spectra at different temperatures were recorded with a home-built setup which is described in detail elsewhere.\textsuperscript{32}

For the time-resolved measurements, the 0.3 mm thick sample cell was placed in a continuous-flow cryostat (Oxford Instruments) operated with liquid nitrogen. Upon cooling the sample from room temperature to 140 K, an optical density of $\sim$0.4 OD at 2.11 eV was achieved.

The light source for the ultrafast spectroscopy experiments was a commercial Spitfire Pro-regenerative amplifier (Spectra Physics) providing 120 fs, 2.5 mJ pulses at 800 nm with a repetition rate of 1 kHz. A small portion ($<1 \mu$d) of the 800 nm pulses beam was focused onto a CaF$_2$ window to generate the white-light continuum probe. About one quarter of the laser intensity was used to pump a commercial non-collinear parametric amplifier (TOPAS White, Light Conversion) to generate the tunable excitation pulses. For the experiments described here, the excitation pulses were centered at 2.10 eV and 2.03 eV and pulse lengths were 42 fs and 60 fs, respectively. Beam diameters at the sample position were $\approx$50 $\mu$m and $\approx$30 $\mu$m for the excitation and probe beams, respectively. For all the experiments, we made sure that excitation-pulse energies were within the linear regime of excitation, where exciton-exciton annihilation processes are negligible (see also Fig. S1 in the supplementary material).\textsuperscript{33,80} For the transient absorption experiments, photon flux of $9.4 \times 10^{12}$ photons/cm$^2$ and $4.9 \times 10^{11}$ photons/cm$^2$ were used upon 2.10 eV and 2.03 eV excitation, respectively.

The setup for 2D spectroscopy was described extensively elsewhere.\textsuperscript{34} Briefly, 35 fs excitation pulses centered at 2.10 eV were generated by the TOPAS White and split into four replicas, which served as three excitation pulses and local oscillator in an inherently phase-stabilized fully noncollinear four-wave mixing setup with heterodyne detection. The time delay between the local oscillator and the third pulse was set to 2.8 ps. The coherence time $\tau$ was sampled in steps of $\Delta \tau = 5.5$ fs, covering a range of $\pm 143$ fs. Scattering contributions may lead to distortions of the 2D signals and possible errors in the phasing procedure, since they add up to the projection of the signal on the detection axis. This might lead to errors in the phasing procedure or misinterpretation of cross-peaks and oscillating contributions. Therefore, it is important to efficiently subtract these undesired scattering contributions. Working with samples in the liquid phase often requires circulation of the sample to reduce photodamage, but this might lead to dynamic scattering. This dynamic scattering can be effectively reduced by double-modulation lock-in detection.\textsuperscript{35} In our experiment, where the sample is still above the glass temperature but is not circulated inside the cryostat, we can perform scattering correction by acquiring certain scattering contributions at each delay point and subtracting them from the spectral interferograms before Fourier evaluation of the data.\textsuperscript{36} In addition to our scattering correction routine, we added a polarizer in the signal beam to reduce remaining unpolarized scattered light. Data sets were phased to spectrally resolved pump-probe data acquired in the same setup (see also Fig. S2 in the supplementary material).\textsuperscript{80} Optical signals were recorded with a CCD-array spectrometer (Acton SpectraPro 2500i equipped with PIXIS 2K CCD camera).

III. RESULTS AND ANALYSIS

A. Transient absorption

Figure 1(a) shows the normalized steady-state $S_1 \leftrightarrow S_0$ absorption (red solid) and $S_1 \rightarrow S_0$ emission spectra (red
Static absorption (solid) and emission (dashed) of the aggregated phase (red) and coiled phase (blue) of MEH-PPV at 140 K and 180 K, respectively. The laser spectra used in the experiments are also shown (black and green dotted). Selection of transient absorption spectra at 140 K and different population times upon excitation at (b) 2.10 eV (1.69×10^4 cm⁻¹) and (c) 2.03 eV (1.64×10^4 cm⁻¹).

The low-energy absorption feature at 2.1 eV only appears below a critical temperature (here 180 K, see also the steady-state absorption at temperatures immediately above the phase transition, plotted in blue in Fig. 1(a)) and is attributed to the 0–0 transition of the aggregated phase. The emission at 140 K is characterized by three major bands at 2.04 eV, 1.88 eV, and 1.71 eV, which are ascribed to the 0–0, 0–1, and 0–2 transitions, respectively.

Selections of transient absorption spectra of the aggregated phase of MEH-PPV at 140 K and different population times T are shown for excitation at 2.10 eV (Fig. 1(b)) and 2.03 eV (Fig. 1(c)). No significant difference in the dynamics is observed by lowering the temperature to 120 K (Fig. S3 in the supplementary material). As it is the purpose of this study to selectively investigate the dynamics in the aggregated phase, we did not excite the sample at energies higher than 2.1 eV, where absorption from a fraction of the sample in the coiled phase may still be present. For both excitation energies, the transient signals are dominated by three major negative bands at ≈2.27 eV, ≈2.08 eV, and ≈1.88 eV. A fourth small negative band at ≈1.72 eV is evident upon 2.10 eV excitation; upon 2.03 eV excitation, the noise in this spectral region is comparable with the expected magnitude of such a feature. By comparing the shape and energy position of the observed bands with the inverted static absorption and emission (see Fig. 1(a)), we can ascribe the negative feature at 2.27 eV to the ground-state bleach of the vibronic 0–1 transition and we will refer to this band as B₀₁ in the following. The band at 2.08 eV (B₀₀ in the following) contains contributions from both the ground-state bleach and the stimulated emission (SE) of the 0–0 transition, while the negative bands at ≈1.88 eV (SE₀₁) and ≈1.72 eV (SE₀₂) arise from SE from the 0–1 and 0–2 vibronic transitions, respectively. No clear signatures of excited-state absorption (positive ΔOD signals) are observed in the entire investigated spectral range.

Interestingly, the ground-state bleach signal in the 2.10–2.50 eV region does not resemble the steady-state absorption, but it appears as the mirror image of the stimulated emission. Since no signatures of excited-state absorption are detected in this spectral region, the discrepancy between bleach and steady-state absorption must be ascribed to the fact that only a fraction of the steady-state absorption stems from the states absorbing at 2.10 eV, i.e., from the aggregated phase. Although a precise determination of the fraction of MEH-PPV in the planarized conformation is still pending, the formation of the planarized chromophores is expected to affect only a fraction of the sample. In fact, in conjugated polymers typically between 40% and 60% of the polymer chains can form planarized chromophores. Thus, we assign the steady-state absorption above 2.10 eV that is not reflected in a transient bleach signal to the contribution from the coiled phase.

For both excitation energies, the transient absorption signal decays non-exponentially and completely recovers in less than 1 ns (Fig. S4 in the supplementary material). The most pronounced difference between the evolution of the transient signals at the two excitation energies is observed in the sub-10 ps dynamics. Upon excitation at 2.10 eV, all the bands show a shift to lower energies, most pronounced in the SE (Fig. 1(b)). The amplitude of this shift is almost completely suppressed when the excitation is tuned to the lowest edge of the aggregated-phase absorption at 2.03 eV (Fig. 1(c)).

In general, broadband transient absorption data can be described globally by assuming kinetic models with rates that are independent from the detection wavenumber. Such global description allows identifying the spectral features associated with different processes through their time evolution. However, when the transient spectra show pronounced spectral shifts on time scales comparable with the population relaxation (such as in Fig. 1(b)), the results from such a global analysis can be difficult to interpret.

Here, we follow a different approach. Since the transient absorption signals are dominated by well-separated bleach and SE bands, an analysis of the spectral moments of these bands can be performed to disentangle different molecular processes. We define the spectral moments M₀⁽¹⁾ and M₁⁽¹⁾ of
the three major bands $i$ ($i = B_{01}, B_{00}$ and SE$_{01}$) according to

$$M_0^{(i)}(T) = \sum_{\nu=\nu_{1}^{(i)}}^{\nu_{2}^{(i)}} I(\nu,T) \cdot \Delta\nu,$$

$$(1a)$$

$$M_1^{(i)}(T) = \frac{1}{M_0^{(i)}(T)} \sum_{\nu=\nu_{1}^{(i)}}^{\nu_{2}^{(i)}} \nu \cdot I(\nu,T) \cdot \Delta\nu,$$

$$(1b)$$

where $I(\nu,T)$ is the absorbance change at frequency $\nu$ and population time $T$, $\nu_{1}^{(i)}$ and $\nu_{2}^{(i)}$ are the frequency summation limits for each band $i$, and $\Delta\nu$ is the frequency interval between data points. As long as bands are not overlapping, the band integrals $M_0^{(i)}$ (zero-order moments) are not sensitive to variations in the shape or position of the bands, but probe exclusively the population dynamics. The first spectral moments $M_1^{(i)}(T)$ correspond to the average spectral positions of the bands and allow us to directly monitor band shifts.

Figures 2(a) and 2(b) depict $M_0^{(i)}(T)$ for 2.10 eV and 2.03 eV excitation, respectively (symbols). At both excitation energies, the temporal evolution of the band integrals appears as a non-exponential decay. A priori, due to the wide distribution of polymer lengths and possible conformations in our sample, the measured temporal evolution could arise either (I) from a broad distribution of rates or (II) from several distinct kinetic processes. We will now proceed to analyze the observed population dynamics both via model I and model II and provide arguments for both of them. However, we stress that the main conclusion of our work, i.e., the characterization of the dynamics of exciton relaxation and transport within the aggregated phase, will be based on the band-shift analysis that is completely independent from the choice of the population-kinetics model.

Kinetics in case I can be modelled with a stretched exponential function according to $M_0^{(i)}(T) = A \cdot e^{-(T/\tau)^{\beta}}$ with amplitude $A$, characteristic time $\tau$, and distribution width $\beta$. This stretched exponential form is also known as Kohlrausch-Williams-Watts (KWW) function. A number of theoretical treatments have shown that the stretched exponential is recovered when modelling independent, parallel single-step processes on one hand yet, on the other hand, also for sequential, multistep processes on disordered structures. In particular, energy-dispersive hopping in disordered organic semiconductors is characterized by a KWW-like behaviour. In that case, the double logarithmic plot $\ln(I(T=0)/I(T))$ of the signal intensity $I$ versus the time $T$ typically shows two regimes (see Fig. S5 in the supplementary material). For short times, a slope $\beta$ of unity—equivalent to an exponential decay—indicates vanishing dispersion. This is commonly interpreted

**FIG. 2.** Spectral moments of the three major bands observed in the transient absorption experiments as a function of the population time $T$: integrated intensity $M_0^{(i)}$ (Eq. (1a)) of the three major bands for excitation at (a) 2.10 eV and (b) 2.03 eV and their average spectral position $M_1^{(i)}$ (Eq. (1b)) upon excitation at (c) 2.10 eV and (d) 2.03 eV. Consistent with the results of the maximum entropy method analysis, the temporal dependence of the spectral moments is fitted by a multi-exponential kinetics (dashed lines).
to designate energetic relaxation by jumps to lower energy nearest neighbors. Subsequently, lower energy sites immediately adjacent to an excitation are no further available. Thus, at longer times, jumps to non-nearest neighbours prevail and the slope \( \beta \) acquires a value near 0.5. Note that values of \( \beta = 1/2 \) and \( \beta = 1/3 \) are expected for Förster transfer from a random ensemble of donors to a dilute array of acceptors in a 3D and 2D case, respectively.

In case II, a multiexponential fit function

\[
M^{(ii)}_0(T) = \sum_{j=1}^{4} A_j \cdot e^{-T/\tau_j},
\]

with amplitudes \( A_j \) and characteristic times \( \tau_j \), is suitable. Both models are approximately consistent with our experimental data (Fig. S6 in the supplementary material\(^{80}\)). In order to attempt a discrimination without initial bias, the maximum entropy method (MEM) is employed, via the open-source program MemExp,\(^{48,49}\) to simulated data for models I and II and to the experimental data (Fig. S7 in the supplementary material\(^{80}\)) shows exemplary results for \( M^{(Bo)}_0 \). The MEM analysis of the experimental data contains four distinct time scale peaks (Figs. S4, S7, and S8\(^{80}\)) and thus more clearly resembles model II rather than model I. Thus, we further discuss our results in terms of a multi-

The temporal evolution of the average spectral position \( M^{(ii)}_0(T) \) of the three major bands is plotted in Figs. 2(c) and 2(d) for excitation at 2.10 eV and 2.03 eV, respectively, and fit results are again reported in Table I. Upon excitation at 2.10 eV, all bands show a red-shift which is completed within the first 15 ps. The bleach band (Bo) shifts mono-exponentially towards lower wavenumbers on a 4 ps time scale (see also the \( \tau_2 \) values in Table I). A red-shift with similar time constants is observed also in the average spectral position of bands Bo and SEo, preceded by an additional fast (\( \tau_1 \approx 200 \sim 250 \) fs) red-shift. Noteworthy, the amplitude of the \( \approx 4 \) ps red-shift is virtually identical \( (42 \pm 3 \) cm\(^{-1}\)) for the Bo and SEo bands.

The sub-300 fs shift appears exclusively in bands containing contributions from SE, thus we ascribe it to processes occurring in the excited state. The lack of such contribution in the Bo band is a further indication that no significant excited-state absorption is contributing to the signal in this spectral region.

Upon excitation at 2.03 eV (Fig. 2(d)), no spectral evolution is observed in the three bands, except for a very small initial red-shift on a sub-500 fs time scale in the SEo band.

### B. Coherent 2D spectroscopy

Coherent electronic 2D spectroscopy can be seen as an extension of transient absorption spectroscopy, where the time-dependent molecular signal is measured as a function of both the excitation and detection frequency. In coherent 2D spectroscopy, the molecular response to the interaction with three electromagnetic fields is measured as a function of three time delays. For each fixed population time \( T \) (between the second and third pulse), Fourier transformation of the emitted signal with respect to the time delay \( \tau \) between the first two pulses, and \( t \) between the third pulse and the signal, yields the excitation and detection axes, respectively. Since the 2D signal and its time evolution allow mapping of electronic couplings and correlations between initial and final electronic states during molecular relaxation, respectively, coherent 2D spectroscopy is particularly suitable to characterize processes of energy transfer in complex systems.\(^{50-52}\) In the following, we apply coherent 2D spectroscopy to discriminate between band shifts and homogeneous broadening in the temporal evolution of the aggregated-phase signal of MEH-PPV, as well as to observe exciton dynamics and energy transfer at several excitation energies with high frequency resolution.

Figures 3(a)-3(d) show a selection of 2D spectra of MEH-PPV in the aggregated phase for four different population times \( T \). Data are acquired at 140 K with the excitation pulses shown in Fig. 1(a) (black dotted), thus the lowest transition band of the aggregated phase is selectively investigated. At all population times, the 2D spectra are dominated by a single feature, containing contributions from the bleach and SE of the \( 0 \rightarrow 1 \) transition (see also Fig. 1(b)). No clear signatures of excited-state absorption are detected.

### TABLE I. Characteristic time constants obtained from a multi-exponential global fit of the integrated signals

<table>
<thead>
<tr>
<th>Excitation energy</th>
<th>Temperature</th>
<th>( \tau_1 ) (fs)</th>
<th>( \tau_2 ) (ps)</th>
<th>( \tau_3 ) (ps)</th>
<th>( \tau_4 ) (ps)</th>
<th>( \tau_5 ) (fs)</th>
<th>( \tau_6 ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.10 eV</td>
<td>120 K</td>
<td>220 ± 50</td>
<td>2.6 ± 0.2</td>
<td>41 ± 4</td>
<td>320 ± 20</td>
<td>3.9 ± 0.8</td>
<td>2.9 ± 0.5</td>
</tr>
<tr>
<td>2.10 eV</td>
<td>140 K</td>
<td>290 ± 40</td>
<td>2.5 ± 0.3</td>
<td>32 ± 3</td>
<td>312 ± 11</td>
<td>4.8 ± 0.8</td>
<td>3.6 ± 0.6</td>
</tr>
<tr>
<td>2.03 eV</td>
<td>120 K</td>
<td>240 ± 60</td>
<td>5 ± 2</td>
<td>41 ± 8</td>
<td>380 ± 50</td>
<td>400 ± 200</td>
<td>400 ± 200</td>
</tr>
<tr>
<td>2.03 eV</td>
<td>140 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

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FIG. 3. Selection of experimentally retrieved (normalized) 2D spectra of MEH-PPV at different population times $T$: (a) 0 fs, (b) 60 fs, (c) 400 fs, and (d) 5000 fs. Contour lines display signal levels from 5% (light pink) to 95% (dark red) in steps of 10%. The dashed horizontal line marks the $T = 0$ average spectral position of the 2D signal at $\tilde{\nu}_r = 1.6987 \times 10^4$ cm$^{-1}$, while the black arrow indicates the shift of the 2D signal towards lower detection wavenumbers as a function of the population time $T$. (e) Spectral evolution of the signal along the detection axis for excitation at $\tilde{\nu}_r = 1.6987 \times 10^4$ cm$^{-1}$ (orange vertical dashed line in panel (a)). (f) Temporal evolution of the first moment (i.e., average spectral position) of the signal along the detection axis (symbols) for the different excitation wavenumbers shown by the vertical lines in panel (a). Overlayed solid lines show the best individual bi-exponential fit of each trace.

The most prominent features in these spectra are the initial elongation of the signal along the $(\sim \tilde{\nu}_r = \tilde{\nu}_i)$ diagonal, which disappears on a time scale of $<100$ fs, and the continuous red-shift of the 2D signal along the detection axis $\tilde{\nu}_r$ (see the horizontal dashed line and solid arrow in Figs. 3(a)-3(d)).

The temporal evolution of the 2D signal can be inspected by performing a global analysis and constructing two-dimensional decay-associated spectra (2D-DAS).

The 2D-DAS are not required for further analysis but are reported in Fig. S9 and discussed in Sec. S3 of the supplementary material. The 2D-DAS are not required for further analysis but are reported in Fig. S9 and discussed in Sec. S3 of the supplementary material.

The analysis of the transient absorption data at different excitation energies revealed complex population dynamics. The 2D experiment identified an additional ultrafast (sub-30 fs) component, shorter than our instrumental response function.
(see Fig. S9a in the supplementary material\textsuperscript{80}). This component accounts for an ultrafast loss of memory in the system, visible as the disappearance of the diagonal elongation in the 2D spectra within the first 100 fs; the non-resonant response of the solvent is also expected to contribute to this signal. An ultrafast ($\lesssim 25$ fs) component was observed with three-pulse photon echo peak shift (3PEPS)\textsuperscript{31,56,57} on MEH-PPV at room temperature and ascribed to ultrafast exciton localization. The ultrafast depolarization of the anisotropy, proceeding on a similar time scale, has been explained in terms of several competing molecular processes, including exciton relaxation within a manifold of delocalized states and exciton localization.\textsuperscript{14,58} As such processes lead to a loss of the initial memory in the system, we tentatively ascribe the $<30$ fs component observed in the 2D experiment to the initial exciton relaxation and localization.

Non-exponential kinetics have been repeatedly observed in solutions, films, and isolated molecules of MEH-PPV.\textsuperscript{22,24,26,27,30,59,60} It was suggested that photoluminescence decay in isolated chains is mono-exponential with characteristic time scales between 0.4 and 1.2 ns, while non-exponential relaxation was observed in presence of aggregation,\textsuperscript{24,27} in films,\textsuperscript{17,61,62} and in collapsed MEH-PPV chains.\textsuperscript{23,63} All the aforementioned configurations are characterized by a strong reduction in the photoluminescence quantum yield, which is ascribed to the formation of non-emissive interchain species.\textsuperscript{16,24,64-66} These species, absorbing above 600 nm, were assigned alternately to excimers, aggregates, polaron, or polaron pairs, which are formed either via direct photoexcitation or via quenching of the singlet excitons.\textsuperscript{16,18,58,59,63,67,68}

In none of our experiments on the aggregated phase of MEH-PPV do we detect clear signatures of excited-state absorption signals, neither in the transient spectra nor in the temporal evolution of the signals (Figs. 1(b)-1(c) and Fig. S3 in the supplementary material\textsuperscript{80}). This is somewhat surprising, because excited-state absorption to the two-exciton state should appear at energies close to the one-exciton absorption. Deviations from this behavior can be expected in presence of strong electron correlations such as in polycenes. We cannot exclude that some excited-state absorption from the one-exciton states overlaps with the signal at certain wavenumbers (but not with the band $B_0$, see Sec. III A); however, if present, these contributions are not dominant. The 2D signal at $T = 0$ peaks below the diagonal, and this feature could arise from excited-state absorption contributions above the diagonal or from an instantaneous Stokes shift or relaxation process occurring within our time resolution. Although we cannot unambiguously discriminate between the two interpretations, we note that some instantaneous relaxation is expected because of the ultrafast exciton localization process. Two-dimensional double-quantum coherence spectroscopy\textsuperscript{69} could provide a direct way to measure the energy position of the two-exciton states in this system, as well as their correlations with the one-exciton states. Instead, we can exclude the presence of long-lived ($>1$ ns) excited species formed upon direct photoexcitation, which are suggested to relax by re-population of the emissive singlet exciton state in MEH-PPV films. To the best of our knowledge, such excited species were observed exclusively when the excitation energy was tuned above 2.14 eV,\textsuperscript{16,17,24,59,63,67,68} where the coiled phase absorbs. Thus, we suggest that these long-lived species are not generated in significant amounts at the excitation energies of our pulses.

In Sec. III A, we have reported the results of a multi-exponential analysis of the $M_0(\tau)$ for the three major bands observed in the transient absorption experiments. An alternative model which describes the data as a linear combination of a single exponential and a stretched exponential decay is additionally presented in the supplementary material (Table S1).\textsuperscript{80} While our data cannot distinguish unambiguously between the two models, both models result in a similar interpretation for the population dynamics in the aggregated phase of MEH-PPV.

For the following discussion, we distinguish between two kinetic regimes: a “slow regime” comprising processes occurring with characteristic time scales of tens to hundreds of ps and a “fast regime” describing processes faster than 10 ps. The processes occurring in the “slow regime” result in a complete recovery of the transient absorption signal at all detection wavenumbers (i.e., a recovery of the thermalized electronic ground state). As energy transfer between excitonic states occurs on sub-10 ps time scales (see also the detailed discussion in Sec. IV B), we ascribe the population decay in the “slow regime” to the $S_1 \rightarrow S_0$ relaxation of the exciton states at the bottom of the density of states. According to the multi-exponential model, two distributed kinetics account for exciton relaxation in the “slow regime,” with average time scales of $\approx 40$ ps and $\approx 320$ ps. Upon 2.10 eV excitation and at 140 K, the $\approx 40$ ps and $\approx 320$ ps components account for a 25% and 43% decay of the excited population, respectively. By lowering the temperature to 120 K, about 38% of the total population decay takes place on 40 ps, while the percentage of excitons relaxing on the long time scale decreases to 32%. The presence of two relaxation processes, with virtually the same time scales as observed here, was previously reported for MEH-PPV aggregates in solution, where interchain interactions are likely to play a role in the photophysics.\textsuperscript{70} Motivated by the simultaneous decay of an excited-state absorption and the bleach signal, Rothberg and co-workers\textsuperscript{70} ascribed the faster process to the non-radiative decay of polaron pairs, and this interpretation additionally explained the low photoluminescence quantum yield of their sample. In our experiment, the $\approx 40$ ps component appears as a simultaneous decay of the bleach and SE signals. Thus, it cannot be explained by the (non-radiative) decay of non-emissive states like polaron pairs, which would not cause a decay of the SE. It has been suggested that the geminate recombination of polaron pairs may result in a delayed population of the emissive singlet exciton states.\textsuperscript{74,66} Such a process has been invoked to explain the long-lived emission tail in MEH-PPV films; however, it can also not explain our experimental observations as it would result in an increase (and not a decrease) of the SE signal and it would not affect the bleach. Instead, we suggest that the 40 ps component might be related to energy transfer proceeding from the lowest-energy exciton states of the aggregated phase to defect sites, while the 320 ps kinetics could map the (radiative and intrinsic non-radiative) relaxation of chromophores that are not in proximity of defect sites, and thus are not quenched by such energy transfer process.
In the same way as when interpreting the data in a multi-
exponential way, when describing the dynamics in the “slow
regime” as a single stretched exponential, i.e., by assuming that
the exciton relaxation has a very broad ($\beta \approx 0.48$) distribution
of rates, the slow (>10 ps) kinetics is considered to describe the
$S_1 \rightarrow S_0$ relaxation. However, in contrast to the multi-
exponential decay, the approximate $\exp\left(-\frac{t}{\tau}\right)^{0.5}$ dependence can be interpreted to indicate dispersive energy transfer, e.g., by dipole-dipole coupling, to lower-energy sites where the excitation is immediately quenched. The spatial distribution of such defect sites would lead to a concomitant distribution of transfer rates and thus to the stretched-exponential decay observed in the signals from stimulated emission and ground-state bleach. In the structurally closely related alkoxy-PPV-derivative OC1C10-PPV, a density of electron traps with depth 0.7 eV on the order of $10^{23} m^{-3}$ was determined. These electron traps have been shown to be omnipresent at about the same density in $\pi$-conjugated polymers as they are likely to arise from some kind of water-oxygen complex. It has been suggested that they also function as exciton traps and in this way limit the exciton diffusion length.

A significant fraction of the excited population relaxes to the ground electronic state on time scales faster than 10 ps, as shown by the simultaneous decrease of both SE and bleach signals. As shown in Figs. 2(c)-2(d) and Table I, the band-shift evolution, which probes exciton relaxation and transfer (see also the discussion in Sec. IV B), is also limited to the “fast regime.” We tentatively ascribe the population decay in the “fast regime” to non-radiative internal conversion processes mediated by the presence of defects in the aggregated phase. According to this interpretation, exciton relaxation and transfer can result in the population of defect states that efficiently quench the excited population. Such interpretation is consistent with the decrease of emission quantum yield reported for MEH-PPV films and aggregates as compared to single solvated chains.

**B. Energy transport and relaxation**

Turning now to the temporal evolution of the spectral average position of the transient bleach and stimulated emission bands, the analysis of the transient absorption data allowed us to distinguish two processes occurring on ~200 fs and ~4 ps time scales. The former appears as a red-shift of only the SE signals, while the latter can be detected in both the ground-state bleach and the SE bands and is absent when exciting at the onset of the absorption (2.03 eV).

Let us consider the slow (~4 ps) shift first. A spectral shift of the ground-state bleach can arise from spectral diffusion in the electronic ground state or from Förster energy transfer from higher-energy to lower-energy excitons located at different sites in the aggregate (exciton hopping). We now discuss both putative explanations before illustrating how to differentiate them.

Spectral diffusion in the ground state is observed in presence of an inhomogeneous distribution of transition energies. Photoexcitation with spectra narrower than the inhomogeneous spectral width selects a sub-ensemble of chromophores with their electronic transition matching the energy of the excitation pulse. The hole generated in the ground-state distribution by such photoselection is refilled prior to the excited-state relaxation due to environment-induced fluctuations in the transition energy of non-photoexcited chromophores. Depending on whether the excitation pulse selects a sub-ensemble of chromophores in the center of the transition energy distribution (i.e., in the middle of the absorption band) or at one edge of it, this process will appear as a broadening or as a shift of the bleach band, respectively.

As the second possible explanation, (Förster) energy transfer within the exciton density of states also results in a shift of both absorption and emission towards lower energies as the energy flows from higher-energy to lower-energy exciton states located on different segments of the polymer. Förster energy transfer occurs between excitonic states with little or no orbital overlap by dipole-dipole coupling. Since the donor and acceptor excitons do not share a common ground state, relaxation of the excitons absorbing at higher energies results in the recovery of the high-energy tail of the ground-state bleach, while the simultaneous excitation of lower-energy exciton states causes an increase of the low-energy side of the bleach signal.

Coherent 2D spectroscopy can discriminate very clearly between the aforementioned two processes as follows. Spectral diffusion by homogeneous broadening in the ground state appears as a loss of the memory of the initial excitation (i.e., loss of the diagonal elongation), while the 2D signal broadens symmetrically and becomes round. In our data, none of these features is observed on time scales longer than 100 fs. Instead, on a 4 ps time scale, the signal intensity shifts asymmetrically towards the cross-peak below the diagonal, and this signifies excitonic energy transfer. Indeed, a 2D spectrum correlates the initially photoexcited states (along $\nu_r$) with the signal arising from the states populated after waiting time $T$. Thus in 2D spectroscopy, energy transfer appears as a rise of the cross peaks between the initial high-energy states (along $\nu_r$) and the final lower-energy states (along $\nu_s$). When, as in the case of MEH-PPV, the high exciton density prevents us to distinguish the single exciton states (and thus the single cross peaks), the energy flow through these states appears as a red-shift of the 2D signal along the detection axis. Consistent with our interpretation, the amplitude of red-shift increases when moving the excitation to higher wavenumbers, because higher-energy excitonic states are accessed (see also Fig. 3(f)).

Two-dimensional spectroscopy further allows us to observe the dynamics of energy transfer as a function of the excitation wavenumber $\nu_r$. The amplitude of the ~4.5 ps red-shift observed in the 2D experiment is obtained from the global analysis of $M_1(\nu_r, T)$ and is plotted in Fig. 4 as a function of $\nu_r$. Since the bleach and SE components of the signal shift simultaneously and with the same amplitude (as it is well resolved by the analysis of the first moments of the transient absorption bands $B_{01}$ and $S_{01}$ upon 2.10 eV excitation), the amplitude of the shift at each $\nu_r$ reflects the amount of energy relaxation. No shift of the signal is observed, within our signal-to-noise ratio, for $\nu_r < 1.6750 \times 10^4 cm^{-1}$, except for a small ultrafast component (~40 fs blue-shift) ascribed to the initial loss of the diagonal elongation. Accordingly,
we conclude that the position of the 0–0 transition for the lowest exciton states in the aggregated phase of MEH-PPV is \( \tilde{\nu} = (16750 \pm 50) \text{ cm}^{-1} \), where the confidence value of 50 cm\(^{-1}\) is given by the wavenumber separation between consecutive \( \tilde{\nu} \) points in Fig. 4.

Noteworthy, despite the fact that \( M_{1}(\tilde{\nu}, T) \) reaches the same asymptotic value for each \( \tilde{\nu} \), (Fig. 3(f)), the \( \approx 4.5 \text{ ps} \) red-shift (Fig. 4) accounts only for a small fraction of the energy relaxation (\( \approx 55 \text{ cm}^{-1} \) at \( \tilde{\nu} = 1.7224 \times 10^4 \text{ cm}^{-1} \) instead of the expected \( \approx 400 \text{ cm}^{-1} \)). This indicates that most of the energy relaxation occurs on time scales much faster than 4.5 ps and populates the low-energy exciton states, at most \( \approx 55 \text{ cm}^{-1} \) higher in energy than the lowest energy states of the aggregated phase. Thus, Förster energy transfer occurs between states at the bottom of the density of states.

The typical intrachain energy transport in the blue phase of MEH-PPV is on the order of \( \approx 250 \text{ ps} \), while much faster energy transport is observed in films and ascribed to interchain exciton hopping.\(^{12,15,16,74} \) The short average time scale observed in our work indicates strongly, by comparison, that energy transfer in the aggregated phase has mostly an interchain character. The dominant interchain character of energy hopping in the aggregated phase is not surprising, due to the higher percentage of chromophores with interchain neighbors in the ordered aggregated structure as compared to the solvated molecules at room temperature. Additionally, the average value of \( \approx 4 \text{ ps} \) for energy transfer in the aggregated phase of MEH-PPV compares well with the observation by Basché and coworkers,\(^{26} \) who reported a 3.9 ps average energy transfer time between red-emitting chromophores in packed chain regions of single MEH-PPV molecules. Thus, it is likely that the molecular organization of MEH-PPV in packed chain regions is locally ordered and resembles that of the low-temperature aggregate.

It would be meaningful to compare the average time scale for Förster-like energy transfer in the aggregated phase and in the coiled phase. However, we are not aware of a precise estimation of either the excitation-dependent or the average time constants for interchain exciton energy transfer in the coiled phase of MEH-PPV. Energy transport in both room-temperature and low-temperature films of MEH-PPV is found to occur on a few-ps time scale with a rate that increases with increasing excitation energy,\(^{16,75} \) however, it is not clear how these value relate with the energy migration between blue and red sites of MEH-PPV, which are believed to co-exist in films.

We noted before that both our transient absorption and 2D experiments show an additional ultrafast (\( \approx 200 \text{ fs} \)) red-shift of the transient signal, which is observed exclusively in the SE bands and whose amplitude increases at higher excitation energies. The \( \approx 200 \text{ fs} \) shift amplitude is plotted in Fig. S10 of the supplementary material\(^{80} \) as a function of the excitation wavenumber; however, the interpretation of these data is complicated by the presence of overlapping contributions. Several processes can cause a red-shift of the SE, and in general, it is not trivial to distinguish whether such a red-shift arises from exciton relaxation, vibrational relaxation, or conformational dynamics in the excited state. As the \( \approx 200 \text{ fs} \) shift is observed exclusively in the SE signal, we can exclude that it originates from Förster electronic energy transfer between states located on different segments of the polymer, which would result also in a red-shift of the bleach signal.

A decay in the transient grating and 3PEPS signals of the room-temperature phase of MEH-PPV on similar time scales (\( \approx 200 – 400 \text{ fs} \)) was reported\(^{31,56} \) and ascribed to excitation relaxation. The sub-ps red-shift of the emission observed in several PPV-based polymers at room temperature was also ascribed to exciton relaxation. Indeed, being absent in small oligomers, this red-shift cannot be accounted for exclusively by vibrational relaxation or solvation dynamics.\(^{76,77} \) A similar argument has also been used to exclude that the aforementioned red-shift is primarily due to conformational dynamics and planarization in the excited state. Conformational dynamics in the excited state are believed to play an important role in the relaxation of photoexcited polymers. In particular, ultrafast structural relaxation on a time scale comparable with the period of high-frequency vibrational modes is believed to

![FIG. 4. Amplitude of the \( \approx 4.5 \text{ ps} \) red-shift along the detection axis observed in the 2D experiment as a function of the excitation wavenumber \( \tilde{\nu} \), obtained from the bi-exponential global fit of the \( M_{1}(\tilde{\nu}, T) \). Error bars are \( \pm \sigma \). The data are phenomenologically described by a linear fit (red line) with slope of 0.113 \pm 0.002.](image)

![FIG. 5. Schematic view of the photophysics of the aggregated phase of MEH-PPV. The delocalized exciton states initially photoexcited (upper frame) localize on an ultrafast (\( < 30 \text{ fs} \)) time scale on smaller domains on the aggregate chains (lower frame). Within the following \( \approx 200 – 250 \text{ fs} \), exciton relaxation within these smaller domains occurs and leads to the population of the exciton states at the bottom of the density of states. On a \( \approx 4 \text{ ps} \) time scale, Förster energy transfer leads to migration of the exciton towards the lowest energy states of the aggregated phase, from which energy transfer to defect states and radiative relaxation take place.](image)
be responsible for the ultrafast exciton localization in MEH-PPV. In contrast, torsional relaxation and excited-state planarization are expected to take place on a time scale of a few ps or longer in MEH-PPV at room temperature and in solution. In an aggregated state and at low temperature, we expect such conformational changes to be even slower.

In agreement with all these observations, we argue that the \( \approx 200 \) fs shift arises mostly from exciton relaxation within a manifold of electronic states sharing the same ground state (otherwise the bleach would shift as well). This assignment is further supported by the fact that, as discussed above, on a ps time scale, the exciton population is already relaxed to exciton states at the bottom of the density of states, from which Förster energy transfer takes place.

V. SUMMARY AND CONCLUSIONS

Summarizing, the combination of broadband transient absorption and coherent 2D spectroscopy experiments allows us to propose the relaxation pathways shown in Fig. 5 for the aggregated phase of MEH-PPV at low temperatures.

The initially delocalized photoexcited exciton states localize on a sub-30 fs time scale on smaller conjugated domains of the polymer chains (spectroscopic units in the following). Depending on the excitation frequency and owing to the energetic disorder within the aggregate, different spectroscopic units can be accessed. Exciton relaxation within the manifold of states sharing the same ground state occurs on a time scale of \( \approx 200 \) fs, simultaneous with cooling. This mechanism can be regarded as a relaxation process occurring within each spectroscopic unit and leads to the ultrafast population of the lowest excitonic states belonging to that spectroscopic unit. Our 2D measurements reveal that in the frequency range accessed by our pulses, the average energy of the exciton states populated after the \( \approx 200 \) fs relaxation is at most \( \approx 55 \) cm\(^{-1}\) higher than the lowest exciton states of the aggregate. It would be interesting to compare this value with the theoretical inhomogeneous width of the lowest-exciton density of states in the aggregated phase that can be accessed by our excitation pulses, as a function of the energetic disorder and the excitonic density of states within the single spectroscopic units.

Diffusion of the relaxed excitons occurs on a longer (\( \approx 4 \) ps) time scale via interchain Förster energy transfer. As no further signatures of energy transfer within the aggregated-phase are detected on longer time scales, we conclude that the \( \approx 4 \) ps exciton diffusion localizes efficiently the excitons in the energetic states at the bottom of the aggregated-phase density of states. From these states, further exciton transfer towards defect sites, as well as population relaxation, occurs with a broad distribution of rates on time scales \( > 10 \) ps.

Noteworthy, despite chain planarization in the excited state is expected in polymers, we do not see clear signatures of such a process in our data. The MEH-PPV aggregated phase compares better to a bulk polymer than to solvated chains, thus conformational effects are expected on time scales longer than 10 ps. It is possible that due to the already highly planar structure of the aggregated phase, the effects of conformational changes on the emission spectra are too small to be detected in our experiments. Experiments monitoring the aggregated-phase emission with a higher spectral resolution could give an answer to this question.

Coherent 2D spectroscopy is a particularly suited technique to observe the energetic relaxation as a function of the excitation energy in complex systems. By combining coherent 2D spectroscopy and transient absorption, we have characterized the energy relaxation in the aggregated low-temperature phase of MEH-PPV. In particular, we showed that most exciton relaxation is ultrafast with little spatial energy displacement, and that 95% of excitons are localized in the low-energy exciton states within the first \( \approx 12 \) ps after excitation.

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