

# Photoinduced on-chain charge-separation and ultrafast recombination in a sugar-coated insulated molecular wire

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Transient absorption three-beam pump-push-probe experiments demonstrate that cyclodextrin-encapsulation of conjugated polymer chains prevents interchain effects, such as energy migration and charge hopping. In the unencapsulated polymer, transient population of high-lying singlet states leads to interchain ionization, generating long-lived charge-separated species. Supramolecular encapsulation prevents this process; with high-lying singlets undergoing on-chain ionization, followed by very rapid charge recombination. Threading is an efficient way to control charge recombination and to obtain a material suitable for photonic applications, where the push effect can be implemented for all-optical ultrafast switching.

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## I. INTRODUCTION

Polymer semiconductors are usually introduced as bundles of loosely bound chains of conjugated carbon atoms.<sup>1</sup> Interchain interactions, however, are far from negligible in their photophysics and separating inter- from intrachain contributions is an important issue which to date, has yet to be solved.<sup>2,3</sup> The topic has both basic and applied relevance. An isolated polymer chain is a natural quantum wire with extreme confinement, which should display all the features expected for the physics of a one dimensional  $\pi$ -electron system. In addition it is a good test-bench for theory, which by and large deals with the isolated chain. In technological applications such as organic light emitting diodes (OLED),<sup>4-6</sup> amplifiers, and lasers,<sup>7-9</sup> aggregation can be detrimental to quantum efficiency. The control of chain separation, preventing chain aggregation, may enable high yield solid-state emitters.

Most of the existing experimental results dealing with polymer photophysics have been obtained from solid-state samples with substantial chain aggregation, and depend on the complex intrachain and interchain properties.<sup>10</sup> Strategies for chain isolation include dissolving in solvents, dispersing in solid matrices or deposition of isolated chromophores on solid substrates. All such approaches have limited interest for application, can be cumbersome and they are not always successful. For instance phase separation in solid matrices can be hard to avoid<sup>11</sup> and in solution, coiling of a single chain may lead to solid-state effects.<sup>12</sup> Supramolecular chemistry is by contrast a reliable tool for controlling chain interactions.<sup>12-15</sup> It allows good interchain separation even in densely packed solid-state samples, thus preserving important characteristics of the material for applications, and sometime introducing new functionalities. For instance, all-optical switching has been recently demonstrated in polymer photonic devices, highlighting the effect of chain-separation for ultrafast nonlinear response.<sup>16</sup>

Here, we report studies on the ultrafast photophysics of conjugated polymers threaded through sugar macrocycles. The surrounding structure provides full separation of long conjugated segments, leaving only small fractions in the chain exposed to possible interactions with other neighboring chains. The resulting optical properties bear the clear signature of this modification. Our investigation is focused on charge photogeneration in the isolated chain, by applying the pump-probe technique which is best suited for detecting non-radiative processes, such as relaxation and recombination. In the following we will present results obtained in threaded and nonthreaded chains for comparison and show the peculiar intrachain phenomena that are highlighted by the chain separation. A modified version of the pump-probe experiment, in which a second pulse (“push”) excites the sample, is also carried out, in order to elucidate details of the internal-conversion process, to explore the intrachain charge generation and recombination dynamics and to reliably assign the transient spectral features. In addition, these experiments demonstrate all-optical modulation gain in the sample.

## II. EXPERIMENTAL DETAILS

The chemical structure of the conjugated polyrotaxane poly(4,4'-diphenylene vinylene) through  $\beta$ -cyclodextrin (PDV.Li  $\subset$   $\beta$ -CD) and reference polymer PDV.Li are shown in Fig. 1(a). The synthesis of these materials has been described elsewhere.<sup>17,18</sup> Both PDV.Li and PDV.Li  $\subset$   $\beta$ -CD have a number-average degree of polymerization of  $n=10$  (Refs. 13 and 18); the polyrotaxane chains have an average threading ratio of 1.4 cyclodextrins per unsubstituted stilbene unit. Both films were prepared by the drop-cast technique from the aqueous solution (10 mg/mL) on the spectrosil® substrates resulting in a film thickness of  $\sim 100$  nm (profilometer KLA-Tencor, Alpha-Step® IQ). The PL spectra were recorded using a spectrofluorimeter SPEX; all the spectra

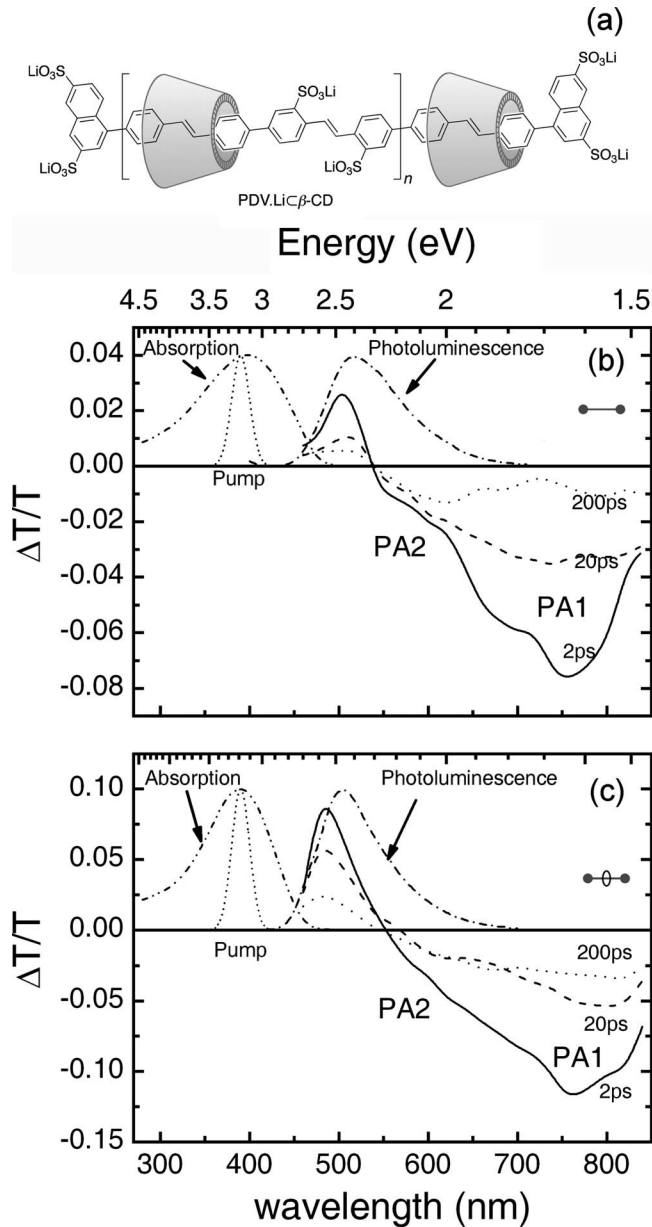


FIG. 1. (a) Chemical structure of PDV.LiC $\beta$ -CD, where the cone represents the  $\beta$ -cyclodextrin macrocycle; PDV.Li has an identical structure except without these threaded  $\beta$ -CD units. Transient transmission spectra of (b) PDV.Li and (c) PDV.LiC $\beta$ -CD at different time delay: 2 ps (solid line), 20 ps (dashed line), and 200 ps (dotted line). For a comparison are shown normalized: absorption (dot dash line) and PL (dash dot line) spectra and pump pulse (short dot line).

were corrected for the overall spectral response. Absorption spectra were recorded using a spectrophotometer (Perkin Elmer). During the pump-probe experiment, the samples were kept under dynamic vacuum ( $\sim 0.3$  Pa) at room temperature. The pump-probe and pump-push-probe experiments were performed using the standard setup for time-resolved measurements.<sup>19,20</sup> In the pump-probe experiment the first pulse, named the “pump” (180 fs, 390 nm, 500 Hz, 1.05 mJ/cm<sup>2</sup>), excites the sample and the second, broadband, and delayed pulse, named the “probe,” monitors the

system evolution after the excitation. After the sample, the probe beam passes through interference filters of 10 nm bandwidth and then focused onto a silicon photodiode. The  $\Delta T/T$  spectra were obtained point-by-point (every 10 nm) with a lock-in amplifier at fixed time delay, while the dynamics were recorded at fixed wavelength. The pump-pulse induces a transmission change  $\Delta T = (T_{\text{on}} - T_{\text{off}})$ , which is detected by the photodiode connected to the lock-in amplifier. The lock-in is referenced at the pump beam modulation frequency that is achieved by a mechanical chopper removing every second pulse. The pump-probe signal is the normalized transmission change,  $\Delta T/T = (T_{\text{on}} - T_{\text{off}})/T_{\text{off}}$ , which is proportional, in the small signal approximation, to the change in absorbance,  $\Delta A$ .

A second set of experiments was performed using two excitation pulses: again the pump pulse at 390 nm, and a second one, named the “push,” at 780 nm (150 fs, 1 kHz, 26 mJ/cm<sup>2</sup>). After these two excitations, the broadband probe pulse is used as before. We keep a fixed delay between the pump and the push pulse, in order to study the dynamics of the state formed upon the re-excitation by the push. The push pulse (at 780 nm) comes 1.2 ps after the pump pulse (at 390 nm) and brings the population from the first-excited state ( $S_1$ ) to higher lying singlet state of even parity ( $S_n$ ), from which a decay path to charged (doublet states) exists.<sup>20,21</sup> Note, that the push pulse wavelength is in the transmission region of the sample, and cannot excite the samples by a linear absorption. In principle, multiphoton transitions could take place, but their effect would be clearly distinguished.

### III. RESULTS

#### A. Absorption, photoluminescence, optical pump-probe spectra

In the following, we propose an assignment of the common features observed in the excited-state transmission spectra of PDV.Li and its rotaxinated analogs. The discussion leads to the identification of the elementary species generated by the optical excitation and of their dynamics.

The normalized absorption and photoluminescence (PL) spectra for both naked PDV.Li and threaded polymer PDV.LiC $\beta$ -CD are shown in Figs. 1(b) and 1(c). From these spectra we can make two observations. First, the rotaxinated polymer displays a sharper absorption and PL spectra than the unthreaded one. Second, the PL spectrum of the threaded polymer is blueshifted relative to naked polymer by about 20 nm (0.1 eV).<sup>22</sup> Such behavior demonstrates reduced inhomogeneous broadening and/or reduced spectral migration in the threaded sample, which can be rationalized by reduction in the intermolecular interaction and reduction in the conformational flexibility in the excited state.<sup>15</sup> Results reported later help to distinguish these two effects. The phonon replica for both polymers in the PL spectra cannot be resolved and gives rise to the asymmetric tail toward low energy (see Ref. 23, Fig. 5). In the film of the naked polymer, PL comes from low energy sites of the inhomogeneous distribution following spectral relaxation. The emitting chains are a narrow subset of the whole ensemble. As a consequence, PL line shape is not strongly affected by chain isolation in contrast to absorp-

tion. The spectral changes in the emission and absorption spectra can be a result of the three effects: solvatochromism, conformational effects, and aggregation.<sup>15</sup> Often spectral changes are a combination of all three of these effects and reduced aggregation affects the electronic interchain coupling resulting in quantum confinement of the wave function.<sup>13,24</sup>

The differential transmission spectra ( $\Delta T/T$ ) for PDV.Li and PDV.Li $\subset\beta$ -CD are shown in Figs. 1(b) and 1(c), respectively, for different pump-probe delays from 2 to 200 ps. The samples were excited on the maximum of the ground-state absorption (pump  $-3.2$  eV), and probed on the red tail, so that the photobleaching (PB) falls outside the detection range. The structure of the spectra appears to be complex, with several distinct bands displaying markedly different temporal dynamics. We observe one positive band and a large, structured negative band. The positive  $\Delta T/T$  signal at high energies appears at the same spectral position as the PL, and can be attributed to stimulated emission (SE) due to the singlet-singlet transition ( $S_1^{th} \rightarrow S_0$ ).<sup>25</sup> Enlargement of the gain spectral region by about 0.1 eV is observed upon threading the chain of PDV.Li with  $\beta$ -CD.

The origin of the negative photoinduced absorption (PA) band, below 2.35 eV for unthreaded polymers, and 2.26 eV for the rotaxinated one, can be understood by observing the dynamics shown in Fig. 2. In the PDV.Li sample, the temporal evolution of the spectra displays a change in shape. The PA decays almost to zero in 200 ps in the 1.7 eV region, while it is almost constant close to 2.0 eV. Consequently, we identify two features, namely, PA1 at 1.7 eV and PA2 at  $\sim 2.0$  eV. For the threaded polymer chain [Fig. 1(c)], one can observe that the decay of PA1 and PA2 bands is clearly correlated with the decay of a positive band (SE) peaking at 2.5 eV which indicates the presence of only one species singlets. Based on these results we can assume that threading of the polymer chain prevents interchain interactions and formation of long-lived charge-separated states.

**B. Optical pump-probe dynamics**

Figures 2 and 3 compare normalized dynamics traces taken in the SE, PA1, and PA2 bands. In Fig. 2 we show  $\Delta T/T$  dynamics at selected probe energies for PA1 (1.5 eV) and PA2 (2.0 eV) bands for a pure [Fig. 2(b)] and a threaded polymer chain [Fig. 2(c)]. Both theoretical curves are shown as black lines. For both samples, an initial fast decay is observed, which is attributed to bimolecular  $S_1$  annihilation as a consequence of the high excitation density.<sup>26</sup> Indeed for very low pump intensity, the fast initial decay is absent (see Ref. 23, Fig. 6).

For the unthreaded polymer chain [Fig. 2(b)] a significant difference between 1.5 eV (PA1) and 2.0 eV (PA2) dynamics is observed. The initial decay, common for PA1 and PA2 in the first 5 ps, is due to the fact that the two bands overlap one another. The initial decay of PA1 and PA2 has the common origin in higher lying singlet excited states. The long-lived component of PA2 is due to the charge-separated state.

In particular at 2.0 eV (mainly PA2) we observe a long-lived,  $>5$  ps, component. On the contrary, for the threaded

parameter	value	(a)
decay times (ps)		
$\tau_{1\rightarrow1}$	0.1	
$\tau_{D1}$	1/0.5 <sup>(*)</sup>	
$\tau_{D2}^{(*)}$	-/600 <sup>(*)</sup>	
$\tau_{n1}$	0.05	
$\tau_{m1}$	0.04	
$\tau_{nD}$	0.15	
$\tau_{mD}$	0.15	
cross section <sup>(**)</sup> (cm <sup>2</sup> )		
$\sigma_{1\rightarrow m}$	$4 \times 10^{-15}$	
$\sigma_{1n}$	$1 \times 10^{-15}$	
$\beta$	$1 \times 10^{-29}$	

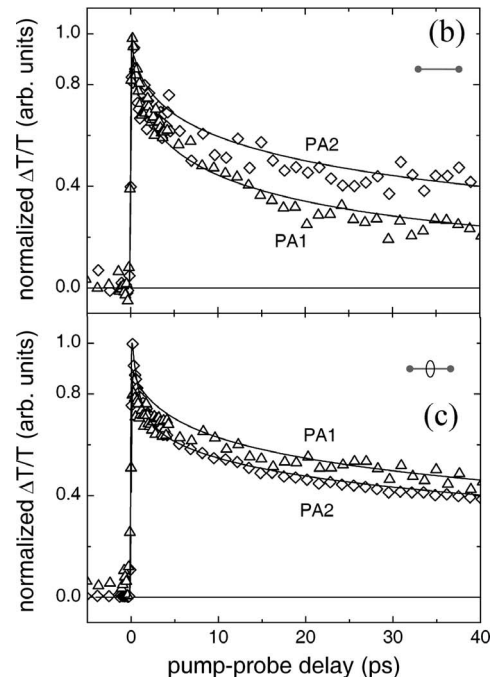
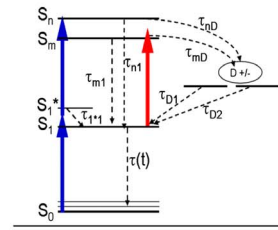


FIG. 2. (Color online) (a) Kinetics model, decay times parameters and cross section used in the numerical simulation. (<sup>\*</sup>  $\tau_{D2}$  is the time constant for the long-lived charges, which are present in the non isolated chain. For the pure polymer the decay of the charges is due to the intra- and interchain recombination. <sup>\*\*</sup>Note, that cross sections are normalized.)  $\Delta T/T$  dynamics of (b) PDV.Li and (c) PDV.Li $\subset\beta$ -CD film at the different photon energies: 2.0 eV (open squares) and 1.5 eV (open triangles), energies correspond to PA2 and PA1, respectively.

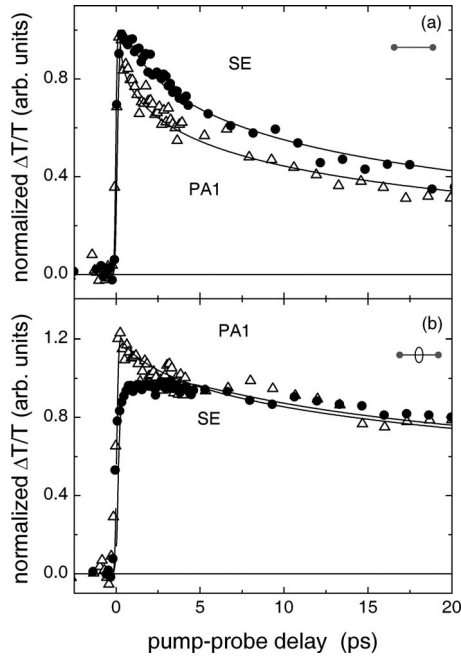


FIG. 3.  $\Delta T/T$  dynamics of (a) PDV.Li and (b) PDV.Li/ $\beta$ -CD film at the different photon energies: 2.5 eV (filled circles) and 1.5 eV (open triangles), energies correspond to SE and PA1, respectively.

polymer chain, Fig. 2(c), both dynamics at 1.5 and 2.0 eV, decay in similar way, suggesting that there is only one state.

Dynamics traces for a PA1 and SE bands are shown in Fig. 3 for a pure polymer (upper panel) and threaded one (lower panel). The decay of traces for both samples is clearly related. This suggests the assignment of both bands to optical transitions from the vibrationally relaxed lowest excited singlet state.<sup>27,28</sup>

On more detailed inspection, we do observe some indication of more complex dynamics in the threaded polymer. There is a build-up of the SE signal at 2.5 eV, Fig. 3(b), which is attributed to the overlap with a fast decaying PA.<sup>29</sup> This can be an indication of *intrachain charge generation*, followed by ultrafast geminate recombination, suggesting that there is a spectral overlap between SE and the photoinduced absorption band due to charges.<sup>30</sup> The generation mechanism can be assigned to multiphoton transitions,<sup>30,31</sup> reaching higher lying states which later dissociate.<sup>32</sup> There is evidence that high-lying states have significant rate of charge separation.<sup>29,30,33–35</sup>

Based on existing literature on similar polymers, the PA2 band in the neat polymer is assigned to absorption of the correlated charge pair.<sup>36–40</sup> On the other hand, looking at time evolution of all dynamics at 1.5, 2.0, and 2.5 eV [Figs. 2(b) and 3(b)] for the threaded polymer, both PA (PA1 and PA2) bands can be assigned to singlet-singlet absorption, i.e., there is no charge contribution in PA2 band. In addition, for the pure polymer, the signal at 2.5 eV (SE band) changes sign after 150 ps (see Ref. 23, Fig. 7). This indicates, that there is a spectral overlap of the SE and PA.<sup>41</sup> For the threaded polymer chain however [Fig. 3(b)], the decay traces for SE and PA1 are all similar also on the long time scale, and therefore arise from the same species.<sup>36,38</sup> The small dif-

ference in the decay traces for PA and SE highlight the different cross sections of the two transitions (PA and SE). From these measurements we confirm that threading of a polymeric chain prevents formation of *long-lived charges* by detecting charged states in the neat polymer but not in the threaded one.

To summarize, the PA2 band due to the absorption of the charged state also exists in the threaded chain but with a much shorter lifetime (sub-ps) due to the one-dimensional confinement of the nascent charge pair. Pump-push-probe experiments, reported below, provide further support for this model.

### C. Pump-push-probe dynamics, modeling

The effect of the push pulse (780 nm) on the pump-probe dynamics for pure and threaded polymer chain is shown in Fig. 4. For both polymers we plot traces at 2.5 eV (SE) and 2.0 eV (PA2). In the pure polymer, the push pulse, which is resonant with the singlet-singlet transition, reduces SE by about 80% at 2.5 eV [Fig. 4(a)] and enhances PA by about 40% at 2.0 eV [Fig. 4(b)], which suggests a different origin of the two transitions. After push re-excitation, there is a very fast recovery at 2.5 eV, followed by a slower decay: some 15–20 % of the change can still be observed after 10 ps (see Ref. 23 for dynamics on a long time scale).

Kinetics for the rotaxinated chain are shown in Figs. 4(c) and 4(d). There is a similar initial change, but unique and smoother kinetics of recovery at 2.5 eV [Fig. 4(c)] with *sub-ps time constant*, which leads to almost *full recovery* within 2 ps. Interestingly, at 2.0 eV [Fig. 4(d)] we see competition of two effects on the very short time scale (within 300 fs from peak to peak) with a decrease and later enhancement of the PA signal. The total recovery is again within 2 ps. This behavior can be understood if we assume that two states can contribute at the photoinduced absorption band at this energy. First, we observe singlet population depletion (less PA) due to push absorption. This effect can only be observed in the threaded chain where pump-induced charge generation is hampered. Second, the formation of new charge carriers confined on the chain is observed, which is induced by the push pulse. The absorption of the charges overwhelms the depletion contribution, and there is an overall larger PA. Geminate recombination causes ultrafast and full recovery back to the initial condition, with no evident leakage (Vavilov rule is respected here<sup>42</sup>). It is thus demonstrated that threading of the chain leads to full and ultrafast recovery of SE.

We use a dynamics model [shown in Fig. 2(a)] based on rate equations to simulate our results. The model considers six states, namely, the ground state  $S_0$ , the vibrationally excited singlet state  $S_1^*$ , (reached by the pump), the relaxed singlet state  $S_1$ , the two higher lying states  $S_n$  and  $S_m$ , and the charge state (doublets)  $D$ . Charge generation occurs both from the  $S_n$  and  $S_m$  states during the pump pulse via sequential re-excitation. Since the relaxation processes occur without migration of an exciton on the chain a distribution of decay time constants is expected. Observed decay is nonexponential and thus the stretched-exponential decay law was

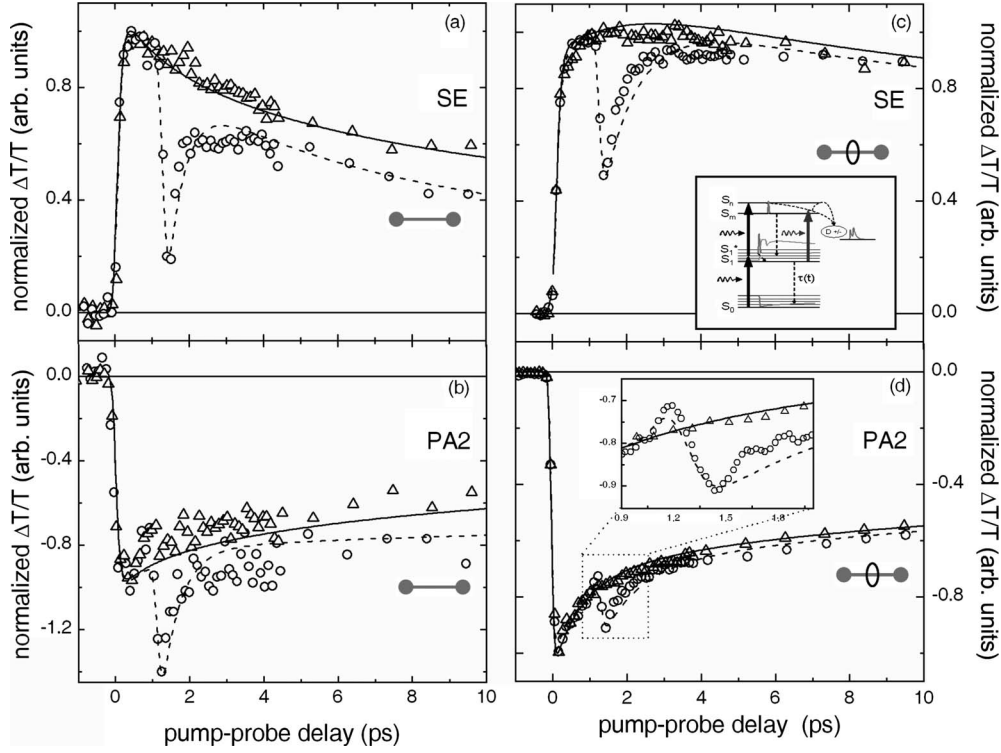


FIG. 4. Transient transmission dynamics of PDV.Li at (a) and (b) and of PDV.LiC- $\beta$ -CD at (c) and (d) are present. The panels (a) and (c) at 2.5 eV and (b) and (d) at 2.0 eV, respectively. The traces with (open circles) and without (open triangles) re-excitation 1.2 ps after pump pulse are shown. The lines represent a numerical simulation, solid without and dash with re-excitation. In (c) we show scheme energy levels with evolution of population in time after excitation and re-excitation with the second pulse. In (d) is shown in zoom the switching zone.

applied to a dynamics model.<sup>43</sup> Below we show the set of rate equations used for numerical simulation.

$$\frac{dS_0}{dt} = -[1 + \beta]g^2(t, \tau)S_0 + at^{m-1}S_1 - g(t, \tau)S_0, \quad (1a)$$

$$\frac{dS_1}{dt} = -at^{m-1}S_1 + \frac{1}{\tau_{1*}}S_{1*} + \frac{1}{\tau_{D1}}D + \frac{1}{\tau_{n1}}S_n + \frac{1}{\tau_{m1}}S_m - \frac{e(t, \tau)\sigma_{1n}(S_1 - S_n)}{\sigma_{1n}}, \quad (1b)$$

$$\frac{dS_{1*}}{dt} = g(t, \tau)S_0 - \frac{1}{\tau_{1*}}S_{1*} - \frac{e(t, \tau)\sigma_{1*m}(S_{1*} - S_m)}{\sigma_{1n}}, \quad (1c)$$

$$\frac{dS_n}{dt} = -\left(\frac{1}{\tau_{nD}} + \frac{1}{\tau_{n1}}\right)S_n + \frac{e(t, \tau)\sigma_{1n}(S_1 - S_n)}{\sigma_{1n}}, \quad (1d)$$

$$\frac{dS_m}{dt} = \frac{e(t, \tau)\sigma_{1*m}(S_{1*} - S_m)}{\sigma_{1n}} - \left(\frac{1}{\tau_{m1}} + \frac{1}{\tau_{mD}}\right)S_m, \quad (1e)$$

$$\frac{dD}{dt} = \beta g^2(t, \tau) - \frac{1}{\tau_{D1}}D + \frac{1}{\tau_{nD}}S_n + \frac{1}{\tau_{mD}}S_m, \quad (1f)$$

$\sigma_{ij}$  represents the absorption and emission cross section between  $i$  and  $j$  states,  $\tau_{ij}$  is the decay time from level  $i$  to  $j$ ,  $\beta$

is an effective two photon or two step cross section,  $a$  is parameter linked with decay rate,<sup>44</sup>  $dS_i/dt$  and  $dD/dt$  represent the population of the corresponding states, and  $g$  and  $e$  represent pump and push rate, respectively.

The table shown in Fig. 2(a) summarizes the best-fit parameters obtained from the numerical calculations and shows schematically the kinetic model. Their time evolution in the pump-push-probe experiment is depicted in Fig. 4 and for pump-probe experiment in Figs. 2 and 3. The model is in good agreement with experimental data.

#### IV. CONCLUSION

In conclusion, sugar encapsulation of conjugated chains leads to effective reduction of interchain effects, which include energy migration and charge hopping. Pump-push-probe experiments confirm the emerging picture for charge photogeneration in polymer semiconductors pointing out the role of singlet states well above the optical gap. The Vavilov-Kasha rule is usually only partially fulfilled in solid-state samples, where Vavilov prediction (quantum efficiency of PL independent on photon energy excitation) is not respected. At high energy new decay paths are available, changing the yield of  $S_1$  states. Here, using threaded polymer chains, we showed that this behavior can be restored in solid-state samples. The initial charge generation process is the on-chain ionization of a higher lying singlet state. In the threaded chain the nascent charge pair recombine quickly to  $S_1$ , restor-

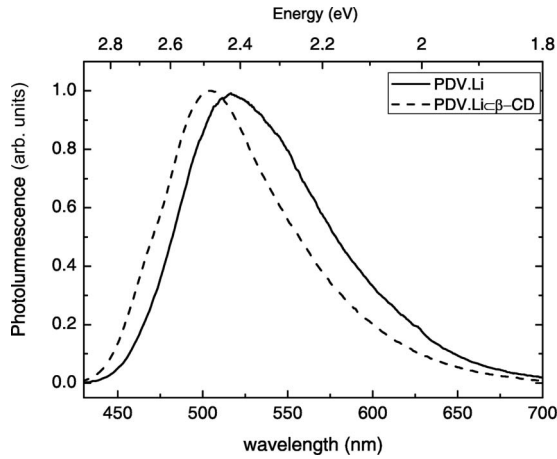


FIG. 5. The PL spectra for a naked (solid line) and threaded (dashed line) PDV.Li chain.

ing the original situation. In the aggregated chains, a fraction of the nascent charges hop to a neighboring chains leading to stable and long-lived charge-separated species. Threading is demonstrated to be an efficient way to control charge recombination and to obtain a material suitable for photonic applications, where the push effect can be implemented for all optical ultrafast switching.<sup>16,45</sup> Polyrotaxane formation can be used to enhance the luminescence behavior of a wide range of conjugated polymers, including polyfluorenes and polyparaphenylenevinyls.<sup>13,18</sup> The results presented here indicate a new applicable strategy for the synthesis of a new class of active materials suitable for optically-pumped organic laser<sup>46,47</sup> and for electrically or hybrid driven laser.<sup>48</sup>

## ACKNOWLEDGMENTS

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## APPENDIX

### 1. Photoluminescence spectra

Figure 5 shows the neat polymer film where PL comes from low energy sites of the inhomogeneous distribution, following spectral relaxation. The emitting chains are a subset of the whole ensemble and have narrower spectra. As a consequence, the PL line shape is not strongly affected by chain isolation, in stark contrast with absorption a slight difference is however displayed.

### 2. Pump-probe spectra

Figure 6 gives a support explanation for an initial fast decay present in the differential transmission dynamics. The initial fast decay is assigned to biexcitonic  $S_1$  annihilation as a consequence of the high excitation density. Indeed for very low pump intensity the fast decay is absent.

Below the differential transmission dynamics on the long time scale for both sample are presented. Figure 7 shows the decay traces taken at 2.5 eV (SE) and 1.5 eV (PA1). There is

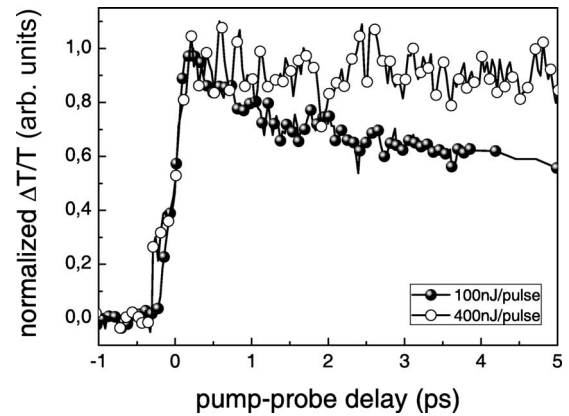


FIG. 6. Normalized  $\Delta T/T$  dynamics for PA1 of PDV.Li film at the different pump intensities: 100nJ/pulse (black) and 400nJ/pulse (white).

an evident difference between the kinetics decay at 2.5 eV (SE band) and at 1.5 eV (PA1 band) taken for the pure (Fig. 7, upper panel) and the threaded polymer chain (Fig. 7, lower panel). The difference in the decay for the naked polymer is mainly due to the charge photo-induced absorption band (PA2), which spectrally overlaps with the SE band. On the

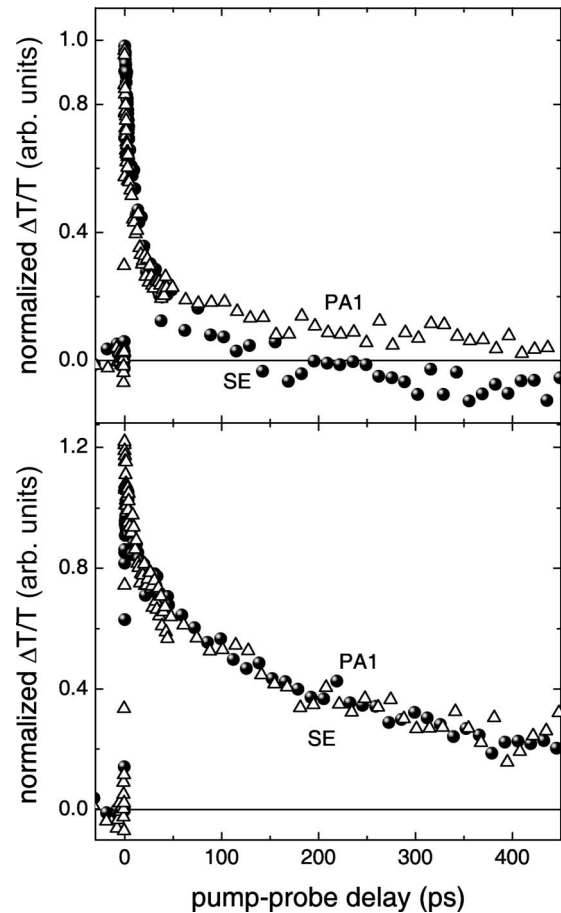


FIG. 7.  $\Delta T/T$  dynamics of PDV.Li (upper panel) and PDV.Li  $\subset$   $\beta$ -CD (lower panel) film at the different photon energies: 2.5 eV (filled circles) and 1.5 eV (open triangles), energies correspond to SE and PA1 on the long time scale, respectively.

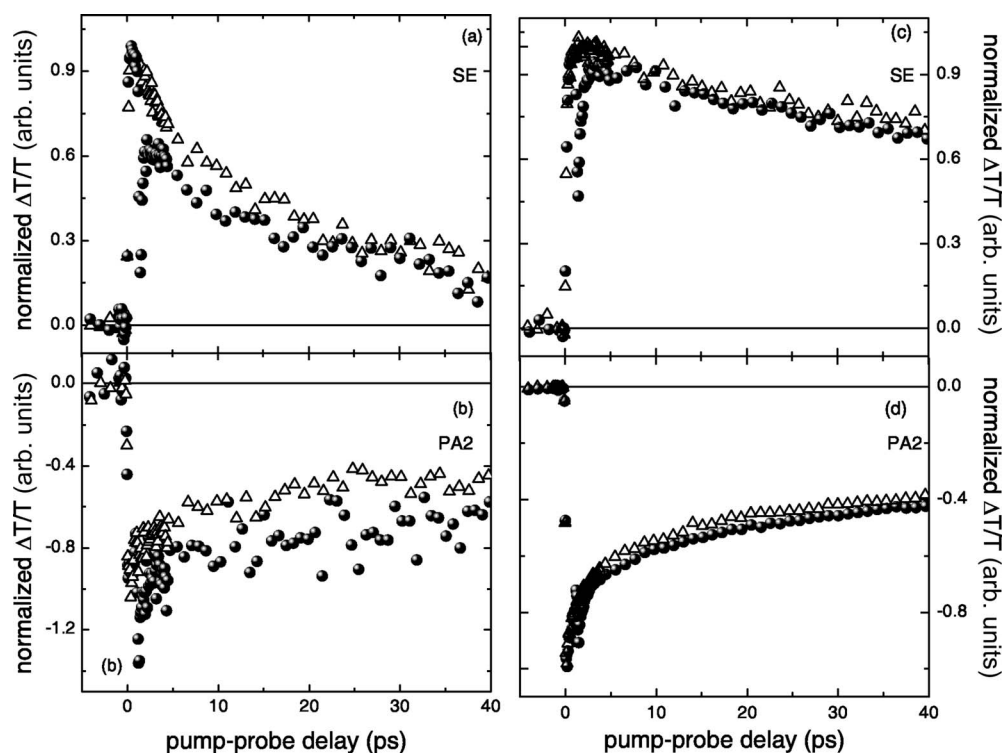


FIG. 8. Transient transmission dynamics of PDV.Li at (a) and (b) and of PDV.Li- $\beta$ -CD at (c) and (d) are present. The panels (a) and (c) at 2.5 eV while (b) and (d) at 2.0 eV, respectively. The traces with (filled circles) and without (open triangles) re-excitation 1.2 ps after pump pulse are shown.

other hand, there is no evidence for such a contribution in the threaded chain. Both dynamics have correlated decays which correspond to singlet-singlet transitions.

In Fig. 8 the time evolution of the decay after re-excitation with the second pulse, called “push” on the long

time scale are shown. Figures 8(c) and 8(d) show that there is full recovery for a threaded chain, while for a pure polymer chain [Figs. 8(a) and 8(b)] there is a part of the population assigned to charge state, that do not recombine. The full recovery is not observed even after tens of ps.

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