Ultrafast Intrachain Photoexcitation of Polymeric Semiconductors

T. Virgili,[1] D. Marinotto,[2] C. Manzoni,[2] G. Cerullo,[2] and G. Lanzani[2]
[1]*IFN-CNR, Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy*
[2]*ULTRAS-INFM, Dipartimento di Fisica, Politecnico di Milano, 20133 Milano, Italy*
(Received 12 July 2004; published 22 March 2005)

We report on excited state dynamics in isolated poly(9,9-dioctylfluorene) chains obtained by embedding the polymer in an inert plastic matrix. Early events (<300 fs) of intrachain photophysics are detected by pump-probe spectroscopy using tunable UV 25-fs pump pulses and sub-10-fs visible probe pulses. We show that higher-lying optical states, reached by multiphoton transitions, give rise to on-chain charge separation on the ultrafast time scale. The intrachain charge pair decays geminately within 500 fs to the lowest singlet state. Characteristic time scales for internal conversion and intramolecular vibrational redistribution are also determined.

DOI: 10.1103/PhysRevLett.94.117402 PACS numbers: 78.55.Kz, 78.30.Jw, 78.47.+p

A conjugated polymer (CP) chain is a natural quantum wire whereby π electrons experience extremely small lateral confinement, which can in principle behave as a functional unit in a molecular scale device. For this reason it is very interesting to study intrachain physics [1] and, in particular, the possibility of supporting quasiparticles in the 1D space [2]. The observation of intrachain charge photogeneration (CPG) is crucial for demonstrating the semiconductor character of a conjugated chain.

There are at present a few clear points about CPG in conjugated polymers. The first one is that higher-lying excited states play an important role in charge dissociation, consistent with the phenomenon of ‘‘autoionizatiòn’’ [3] invoked for molecular crystals. This is proved by photoconductivity [4] and pump-probe [5] and pump-push-probe experiments [6]. This evidence excludes the presence of bandlike conduction states near the absorption edge. Dissociation of higher-lying excited states can also explain CPG following band gap excitation with ultrashort pulses, when multiphoton transitions are present [7]. The second point is that high order in conjugated polymer films, with enhanced π-π overlap, favors interchain charge separation, as in polythiophene [8] and polyfluorene [9] films. In this case, the oppositely charged, strongly bound polarons dwell on different chains and decay geminately. Their excitation is linear in pump intensity and occurs within 200–300 fs. The last point is that an electric field on the order of 1 MV/cm can dissociate neutral states with an efficiency of a few percent, either instantaneously (during excitation), as in polyfluorene [10], or later in time, as in ladder-type polymers [11]. This observation indicates that the energy required to ionize a neutral state is quite large, 0.5–1 eV, suggesting that the neutral singlet state is the lowest excitation of the system, and charge separation is a secondary effect. The experiments so far reported display a rich phenomenology, but they cannot distinguish between intrachain and interchain effects. A theory on intrachain separation has been developed [12], notably not involving higher-lying states, and this mechanism is sometimes invoked to explain experimental results [13], yet no solid evidence has so far been reported.

In this Letter, we present a clear-cut experiment demonstrating intrachain charge separation in a conjugated polymer. CPG is studied in poly(9,9-dioctylfluorene) (PFO) by the pump-probe technique with two characteristics: first, the time resolution of the measurement is pushed down to 25 fs, an order of magnitude lower than normally used in time-resolved experiments with CPs; second, we probe ‘‘isolated’’ PFO chains, embedded in an inert matrix, thus revealing, by comparison with the aggregate chain response, the true intrachain behavior. We show that intrachain charge separation can indeed take place, and that such confined pairs decay in about 500 fs.

In our experimental setup [14], a Ti:sapphire laser (780 nm, 150 fs, 500 μJ, 1 kHz) drives two noncollinear visible optical parametric amplifiers (NOPAs). The first NOPA generates transform-limited visible pulses with 15–20-fs duration, which are frequency up-converted to the UV by sum-frequency generation with 780 nm light in a 50-μm-thick beta-barium-borate crystal. The UV pulses are compressed to 20–25-fs duration by fused silica prisms and used as pump. The second NOPA generates ultrabroadband pulses spanning the 500–700-nm wavelength range, compressed to sub-10-fs duration by chirped mirrors and used as a probe. The pulses from the NOPAs are synchronized by a delay line and focused on the sample using reflective optics, in a noncollinear pump-probe configuration. Time-resolved measurements at specific wavelengths are obtained by spectrally filtering the probe beam after the sample and combining differential detection with lock-in amplification. A more conventional setup was used for pump-probe experiments with 150-fs time resolution, as in [15]. Here excitation pulses at 390 nm are obtained by second harmonics, and a broadband probe in the visible and near-infrared spectral ranges is obtained by the white-light supercontinuum generated in a thin sapphire plate.

The samples used consist of films drop cast on a thin quartz slide from a toluene solution of 10% PFO doped in a polymethylmetacrylate (PMMA) matrix (50 mg/ml); the film thickness is around 500 nm. We obtained highly inhomogeneous films, due to efficient phase separation [16], which show colored regions (consisting mostly of PFO) and whitish regions; the size of these regions is of the order of hundreds of microns, so that they can easily be selectively excited by our focused laser spots. For comparison, we also used spin-coated PFO films with thickness of ≈100 nm.

Figure 1(a) shows the differential transmission ($\Delta T/T$) spectrum of a spin-coated PFO film, using 390-nm, 150-fs pump pulses, for a 2-ps pump-probe delay; the results are consistent with those reported in the literature. Based on previous work [7,17], we assign the photoinduced absorption (PA) at 560 nm to charged states absorption, and the PA at longer wavelengths to singlet-singlet transitions. The colored regions of the PFO-doped PMMA film display, under photoexcitation, a $\Delta T/T$ spectrum similar to the one from a spin-coated PFO film. This perfect match with data from solid-state samples suggests that the colored regions contain either clusters of chains or (unlikely) coiled chains, in which intersegment interaction can take place.

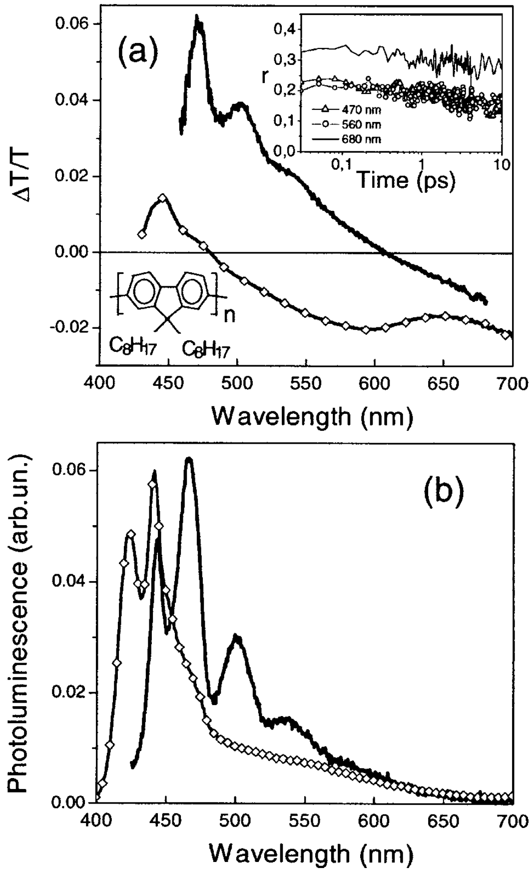

FIG. 1. (a) $\Delta T/T$ spectrum at probe delay of 2 ps for the whitish region in the PFO-doped PMMA film (solid line) and for a spin-coated PFO film (open diamonds + line). In the inset, polarization anisotropy decay at 470 nm (open triangles + line), at 560 nm (open circles + line), and at 680 nm (solid line) for the PFO-doped PMMA film (whitish regions). The chemical structure of PFO is also shown. (b) Photoluminescence spectra from the whitish region in the PFO-doped PMMA film (solid line) and from a spin-coated PFO film (open diamonds + line).

The whitish regions of the PFO-doped PMMA film display dramatically different behavior with respect to the colored ones, showing more structured photoluminescence spectra [Fig. 1(b)] and a broad stimulated emission (SE) band [Fig. 1(a), solid line]. Such a broad SE band has never been detected in PFO. In the whitish regions, we observe the following features: (i) nearly perfect match between photoluminescence and SE, which is not masked by the PA of the charged states; (ii) absence of bimolecular effects upon changing pump intensity, at odds with bulk samples displaying strongly intensity dependent dynamics; (iii) long-lived $\Delta T/T$ anisotropy [18] [inset of Fig. 1(a)] in contrast with the fast decay observed in bulk samples. These observations evidence the lack of interchain coupling and suggest one to assign the whitish regions to isolated PFO chains, probably in β-phase conformation [19], i.e., planar isolated chains embedded in PMMA. $\Delta T/T$ kinetic traces at selected probe wavelengths point out the different behavior of the two regions. In Fig. 2(a) we show that in the colored region (corresponding to the PFO film) PA at 560 nm and at 680 nm have different kinetics. The longer-lived component, evident after 1 ps at 560 nm, is ascribed to charged states contribution. On the contrary, in the whitish region of the sample (where polymer chains are isolated), SE at 560 nm and PA at 680 nm have almost identical kinetics [see Fig. 2(b)], both ascribed to singlet population decay; no charged states are observed.

We now discuss pump-probe experiments performed with 25-fs time resolution. Figure 3 shows the $\Delta T/T$ spectra of PFO isolated chains after excitation with pulses at 325 nm (3.8 eV) and photon flux of 4×10^{14} cm^{-2}. The $\Delta T/T$ spectrum at 20-fs pump-probe delay shows a broad PA band below 520 nm, peaking at 580 nm and growing again towards the red edge of the pulse spectrum. The overall spectrum evolves in time, and it turns to the line shape observed using longer pulses after 300 fs. The $\Delta T/T$ spectrum at 20 fs delay is understood as a superposition of PA and SE, originating from two different contributions: a nascent singlet population, with the expected positive spectral signatures, and a second species, formed within the pulse duration, absorbing in the 500–600-nm spectral region. The same dynamics, i.e., SE buildup in the emission region and a partial decay in the singlet PA region, is detected by measuring $\Delta T/T$ time traces at selected probe wavelengths (see Fig. 4). Based on spectral location and line shape of the short-lived PA band, matching very well with that of polarons in PFO, we assign it to geminate charge pairs (often named polaron pairs). Upon geminate recombination, their PA decays and the underlying SE band reappears. Our findings imply that charge separation can indeed take place on a single polymer chain. We find that the generation efficiency of intrachain pairs is highly nonlinear, as demonstrated by the dependence on the excitation density, shown in Fig. 4(a) for a 560-nm probe

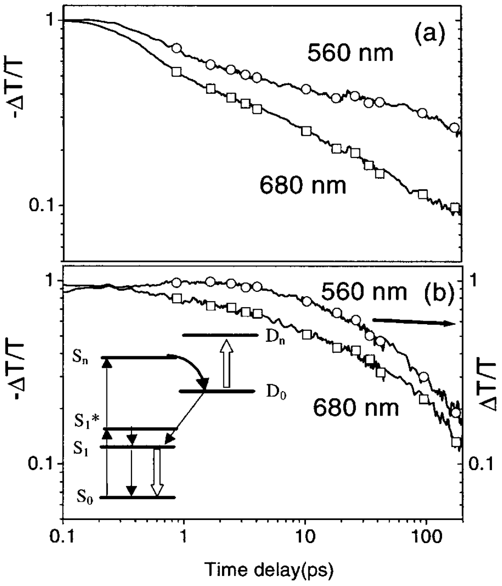

FIG. 2. (a) Normalized pump-probe kinetics at 560 nm (open circles) and at 680 nm (open squares) for the spin-coated PFO film. (b) Normalized pump-probe kinetics at 560 nm (open circles) and at 680 nm (open squares) for the PFO-doped PMMA film (whitish regions). A schematic diagram of the model used for the fitting is shown.

wavelength, corresponding to the maximum of the PA band. By reducing the pump photon flux, $\Delta T/T$ becomes positive, but still shows buildup kinetics. We think that, at lower intensity, the process of PA and SE competition still takes place, but with lower relative amplitude of the PA, proving that the CPG yield depends superlinearly on intensity.

An alternative explanation to the SE buildup could be vibronic relaxation from a higher-lying excited state reached by the pump photons. To test this hypothesis, we tuned the pump wavelength to 360 nm (3.45 eV) [Fig. 4(b)]; we found no appreciable change in the dynamics, indicating that excess energy does not play a crucial role in the SE buildup phenomenon and thus arguing against hot state relaxation. However, thermalization is expected to occur following excitation. This is indeed observed at 680 nm [Fig. 4(c)], where pure singlet state dynamics is measured. There is a partial decay in the first 500 fs, which we assign to vibrational relaxation from the state reached by one-photon excitation, located about 0.8 eV above the optical gap.

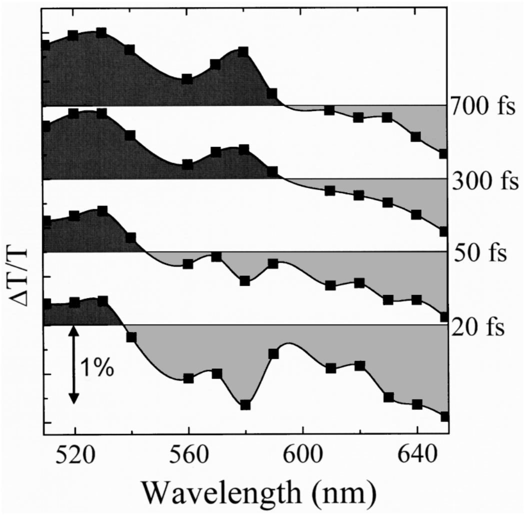

FIG. 3. $\Delta T/T$ spectra at different probe delays for the PFO-doped PMMA film (whitish regions).

The rate equation model used for fitting the data is sketched in the inset of Fig. 2(b). In order to reproduce nonlinear dependence on pump intensity, we assume that ionization takes place from an higher-lying excited state reached by sequential excitation [7]. This mechanism involves the absorption of two photons by the same PFO molecule, so it displays a nonlinear intensity dependence. The time constant of intramolecular vibrational relaxation (IVR) from S_1^* to S_1 (k_{IVR}) is 120–130 fs, as determined by fitting the singlet dynamics, for instance at 680 nm [see

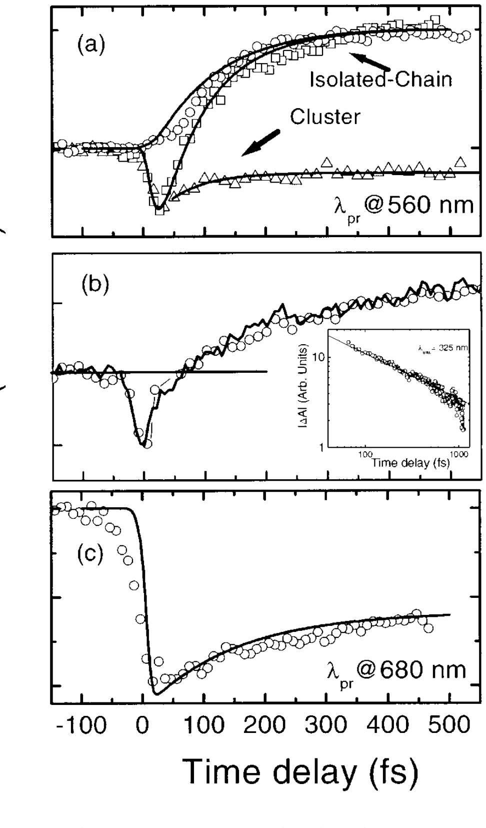

FIG. 4. Normalized pump-probe kinetics for the PFO-doped PMMA film (whitish regions) are shown. (a) At 560 nm at different excitation densities: 4×10^{14} cm^{-2} (open squares) and 6×10^{13} cm^{-2} (open circles). Normalized pump-probe kinetic for the colored region (open triangles) is also shown. (b) At 560 nm for two different pump wavelengths: 360 nm (open circles + line) and 325 nm (solid line); in the inset $|\Delta A|$ (absolute value of absorption) at 560 nm (open circles) on a log-log scale. (c) At 680 nm. Fits to the data are shown by solid lines.

Fig. 4(c)]. PA extinction and SE recovery are partially due to IVR, but the main cause is intrachain geminate polaron recombination, which contributes twice: charge population depletion and singlet population filling. It is assumed that intrachain polaron pairs recombine to the first excited singlet state, S_1, with a biexponential kinetics, with time constants of 60 fs and 500 fs. Interestingly, the observed dynamics can be reproduced by a $t^{-1/2}$ power law, as predicted for geminate recombination after one-dimensional random walk in confined segments [experimental data on a log-log scale are shown in the inset of Fig. 4(b) together with a linear fit with slope $-1/2$] [20]. At longer times, the kinetics deviates from that, as predicted by theory, becoming exponential. We neglect the possibility of intersegment separation, within the same chain, because it would generate a long-lived charge population and an incomplete recovery to S_1. The efficiency of S_n dissociation (i.e., the number of charge pairs formed following S_n population) obtained from our model is around 80%. Dissociation is in competition with $S_n \rightarrow S_1$ internal conversion, modeled by a rate of 50^{-1} fs^{-1}, according to recent measurements of higher excited state lifetime [21]. S_n can be considered either a charge transferlike state, as proposed in Ref. [22], or an electron-hole continuum found in correlated models for electronic structure [23]. Two different CPG mechanisms are present in CPs: intrachain charges are formed by high-lying singlet fission within the 1D space; they exist for a brief time interval and geminately decay under mutual Coulomb attraction. Interchain charges are formed by electron transfer, through π overlap between adjacent conjugated strands, and live longer. For close chains the overall energy of the interacting Coulomb pair is low enough for dissociation to occur even from the lowest optical state, thus explaining the observed linear intensity dependence. The two mechanisms are not, however, completely separated. In the solid state, intrachain charge generation can be the first step towards long-lived interchains charges; this process will have small efficiency given the high charge recombination rate, yet not negligible.

The plot in Fig. 4(a) also contains the PA measured at 560 nm in the colored region. In this case, a long-lived PA signal is observed, with a fast initial decay to a plateau. This fast partial recovery is perfectly reproduced by the biexponential decay with 60- and 500-fs time constant, i.e., the lifetime of the intrachain pair. Intrachain charge generation is taking place even in the solid state, following optical excitation with short pulses. In this case, however, the fraction of pairs undergoing geminate recombination (notably with the same dynamics as in isolated chains) may not be 1, because of interchain hopping. The fit in Fig. 4(a) includes the contribution of both interchain and intrachain charges, with a relative weight of 1:1.

In conclusion, by studying isolated PFO chains excited by 25-fs UV pulses, we present the first experimental evidence of intrachain generation and recombination of charges in a π-conjugated chain. We find that on-chain charge generation does not take place from the lowest excited state S_1 but rather upon higher-lying optical state excitation. The conjugation length of a single segment on the chain is large enough to support a charge separated state, with a lifetime of about 500 fs. We identify the same process in the condensed phase, yet in this case geminate recombination is not complete and other mechanisms are active, resulting in a longer-lived charge population.

[1] J. G. Müller *et al.*, Phys. Rev. Lett. **91**, 267403 (2003); R. Lécuiller *et al.*, Phys. Rev. Lett. **80**, 4068 (1998).

[2] P. Tavan and K. Schulten, Phys. Rev. B **36**, 4337 (1987).

[3] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers* (Oxford University Press, New York, 1999).

[4] A. Köhler *et al.*, Nature (London) **392**, 903 (1998); C. Zenz *et al.*, Chem. Phys. Lett. **341**, 63 (2001).

[5] C. Silva *et al.*, Phys. Rev. B **64**, 125211 (2001).

[6] C. Gadermaier *et al.*, Phys. Rev. Lett. **89**, 117402 (2002); S. Frolov *et al.*, Phys. Rev. Lett. **85**, 2196 (2000).

[7] M. A. Stevens *et al.*, Phys. Rev. B **63**, 165213 (2001).

[8] O. J. Korovyanko *et al.*, Phys. Rev. B **64**, 235122 (2001).

[9] O. J. Korovyanko and Z. V. Vardeny, Chem. Phys. Lett. **356**, 361 (2002).

[10] T. Virgili *et al.*, Phys. Rev. Lett. **90**, 247402 (2003).

[11] W. Graupner *et al.*, Phys. Rev. Lett. **81**, 3259 (1998).

[12] M. C. J. M. Vissenberg and M. J. M. de Jong, Phys. Rev. Lett. **77**, 4820 (1996); D. M. Basko and E. M. Conwell, Phys. Rev. B **66**, 155210 (2002); V. I. Archipov, E. V. Emilianova, and H. Bässler, Phys. Rev. Lett. **82**, 1321 (1999).

[13] J. G. Müller *et al.*, Phys. Rev. Lett. **88**, 147401 (2002); A. Hayer *et al.*, J. Phys. Chem. A **106**, 11045 (2002).

[14] G. Cerullo *et al.*, Science **298**, 2395 (2002).

[15] G. Cerullo *et al.*, Phys. Rev. B **57**, 12 806 (1998).

[16] J. Chappell and D. G. Lidzey, J. Microsc. **209**, 188 (2003).

[17] B. Kraabel *et al.*, Phys. Rev. B **61**, 8501 (2000).

[18] Defined as $r = [(\Delta T/T)_{\text{par}} - (\Delta T/T)_{\text{perp}}]/[(\Delta T/T)_{\text{par}} + 2(\Delta T/T)_{\text{perp}}]$, where par and perp are parallel and perpendicular polarizations, respectively.

[19] M. Grell *et al.*, Acta Polymerica **49**, 439 (1998).

[20] I. V. Zuzulenko, Solid State Commun. **76**, 1035 (1990).

[21] C. Gadermaier *et al.*, Chem. Phys. Lett. **384**, 251 (2004).

[22] J. L. Bredas *et al.*, Acc. Chem. Res. **32**, 267 (1999).

[23] F. Guo, M. Chandross, and S. Mazumdar, Phys. Rev. Lett. **74**, 2086 (1995); A. Shukla, H. Ghosh, and S. Mazumdar, Phys. Rev. B **67**, 245203 (2003).