How Strain Controls Electronic Linewidth in Single β-Phase Polyfluorene Nanowires

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ABSTRACT

Low-temperature single-molecule fluorescence spectroscopy reveals pure, virtually defect-free chains of the one-dimensional crystalline β-phase of polyfluorene. The likelihood of β-phase formation is shown to correlate directly with the initial shape of the polymer chain, with extended chains preferentially forming this planarized phase. Planarized chains, characterized by a distinct spectroscopic signature can, however, exhibit substantial bending within the plane. This bending results in a strong increase in the elementary transition linewidth of the conjugated segment. The transition linewidth provides a lower limit to the electronic dephasing time of the excited state of >3 ps at 5 K. Remarkably, bending does not appear to disrupt the π-electron conjugation so that the emission from a single bent β-phase chromophore is not necessarily linearly polarized as is generally assumed.

While conjugated polymers are often cited for their opto-electronic properties,[1] they constitute equally fascinating autofluorescent model systems for polymer physics. As chain conformation influences electronic structure, optical spectroscopy can reveal signatures of physical chain packing and alignment.[2,3] Structure−property correlations become most apparent on the single-molecule level, where disorder broadening is overcome.[4−17] The observed emission linewidth provides a *lower limit* for the coherence time of the excited state,[11−13,16] which is crucial in deriving a microscopic picture of energy and charge-transfer rates within conjugated polymers in optoelectronic devices.[3] We demonstrate here how this linewidth is directly controlled by the chain conformation in polyfluorene polymers. Polyfluorenes can adopt a conformational phase of high intrachain order, known as the β-phase, in which the monomer units lie in the same plane. Because of the long-range translational order of this phase, it can be likened to a one-dimensional crystallite.[15,18−21] We demonstrate that a bend within the plane of this planar β-phase, corresponding to intramolecular strain, increases the emission linewidth. Remarkably, in all cases, only one narrow transition line is observed, suggesting that the exciton remains mobile throughout the conjugated segment of one and the same chromophore. A consequence of this on-chain

mobility is that the single chromophore emission can become unpolarized. The work illustrates how nanoscale physical *shape* may offer a route to controlling the linewidth and thus the lower limit for the electronic coherence time, a material parameter that has previously received little consideration in molecular electronics. The excited-state coherence and the elementary electronic linewidth impact directly on charge carrier and exciton mobility,[11] which is important in devices such as solar cells and light-emitting diodes.

Poly(dioctyl-fluorene) is a remarkable conjugated polymer as it exists in two distinct structural phases.[18] X-ray scattering has unambiguously identified a disordered glassy phase with short diffraction coherence lengths and a more ordered planarized conformation referred to as the β-phase.[18] These two phases have notably different optical properties in terms of luminescence, absorption, vibronic coupling, and photophysical stability.[15] While the spontaneous planarization of the biphenyl fluorene units required to generate long-range order and extended conjugation was originally attributed to intermolecular interactions, the identification of both conformers in single molecules demonstrated that spontaneous ordering is a purely intramolecular effect.[15] Formation of the β-phase effectively corresponds to crystallization in one dimension, a remarkably uncommon phenomenon in nature.[22] While thermal cycling and solvent swelling of polyfluorene films increases the yield of β-phase molecules by straining the polymer chains,[18] the origin of the driving force responsible for one-dimensional crystallization of adjacent monomer units remains unclear. Intuitively, an extended

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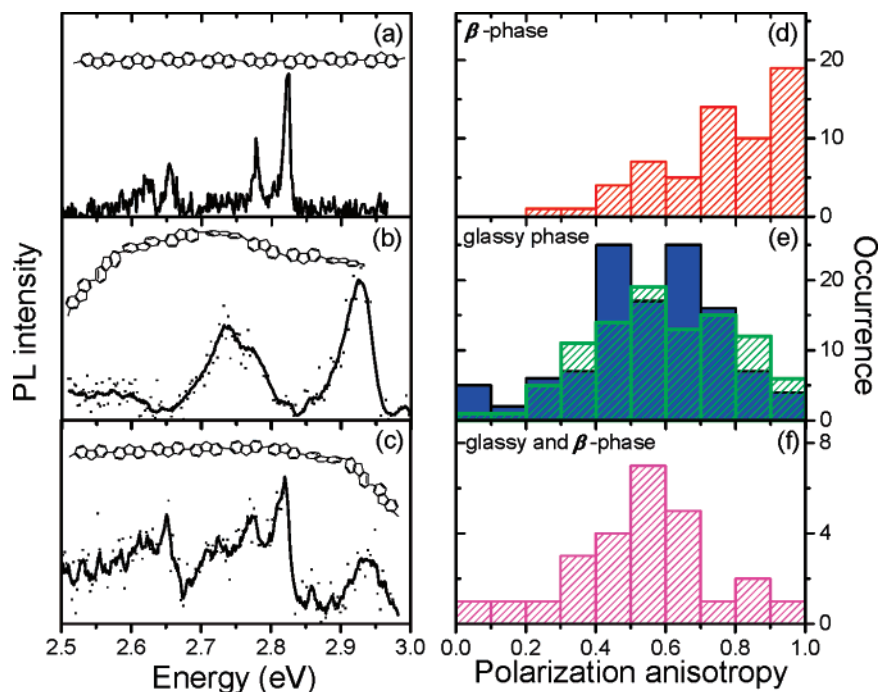† Ludwig-Maximilians-Universität.
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Figure 1. PL spectra and excitation polarization anisotropy of single polyfluorene chains at 5 K, excited at 400 nm: (a) β-phase, (b) glassy phase, (c) dual glassy and β-phase. Insets are schematics of chain segments in the different conformations. Note that the side groups are not shown. Panels (d−f) are the corresponding excitation polarization anisotropy histograms that indicate chain conformation. The blue histogram in panel (e) represents glassy phase molecules not subjected to the swelling procedure.

chain conformation should be favorable to spontaneous chain planarization.

Single-molecule samples were prepared from a solution of poly(9,9-di-*n*-octyl-fluorene) (American Dye Source Inc., 220 kDa, concentration 10^{-6} mg/mL) and Zeonex in toluene. Spin-coating this solution at 5000 rpm on a 0.17 mm thick glass substrate gave thin films (20−50 nm) with highly dispersed single polymer chains in the Zeonex matrix. The films were mounted on the cold finger of a liquid helium flow cryostat under a vacuum of $<10^{-6}$ mbar and cooled to 5 K. A home-built wide-field fluorescence microscope was used to perform imaging and spectroscopy as described in detail earlier.[14] The second harmonic of a tunable Ti:sapphire femtosecond oscillator (bandwidth 20 meV, power 300 W/cm^2 at 80 MHz) was focused onto the sample to excite the single-molecule fluorescence. The luminescence of the polyfluorene molecules was dispersed using a spectrograph with two different gratings of 2.5 and 0.35 meV resolution at 2.82 eV and imaged onto a front-illuminated CCD camera.

Figure 1 shows typical low-temperature photoluminescence (PL) spectra of single polyfluorene chains in the β-phase (Figure 1a) and the glassy phase (Figure 1b). The glassy phase emits around 2.95 eV, whereas the β-phase peaks at 2.8 eV and differs in terms of the vibronic progression. The single chain can also adopt a *mixed* phase configuration in which both spectral signatures are observed at once, as shown in panel c of Figure 1. The polarization anisotropy in excitation $P = (I_{max} - I_{min})/(I_{max} + I_{min})$, obtained by rotating the plane of polarization of the laser with a $\lambda/2$ plate, provides insight into the chain conformation[9] of the three spectrally distinct cases. As anticipated, it is the

more extended chains with high *P*-values that tend to form the β-phase so that their polarization anisotropy histogram shown in panel d of Figure 1 peaks at 1, corresponding to absorption in only one plane of polarization. Both glassy and mixed phases (panels e and f of Figure 1) peak at 0.5 anisotropy and have a negligible contribution of fully extended chains. The mixed phase anisotropy, determined by considering the 0−0 line of the β-phase contribution to the emission, is not unexpected because intramolecular energy transfer can occur from higher energy glassy segments to β-units[21] so that the mixed phase polarization anisotropy is dominated by the glassy phase chain conformation. The observation of a mixed phase is, however, itself quite remarkable as it implies that a single molecule can contain both "amorphous" and "crystalline" domains. Such dual-phase character of a single molecule is reminiscent of secondary and tertiary order in large protein molecules. The probability of observing the β-phase increases dramatically after vapor swelling of the polyfluorene/polystyrene film,[18] following the procedure described by Grell et al.[18] (exposure to toluene vapor in a saturated chamber for 12 h at 40 °C). The swelling procedure only affects the degree of planarization of the chains, not the overall extension, i.e., it does not induce stretching of the chains. The histogram in Figure 1e shows the polarization anisotropy (the measure of chain extension) for glassy phase molecules before (blue) and after (green) swelling, which is found to remain virtually unchanged by the treatment.

While the glassy and the β-phase constitute the two conformational extremes of the polymer, the histogram in Figure 1d could be interpreted as the β-phase also arising in
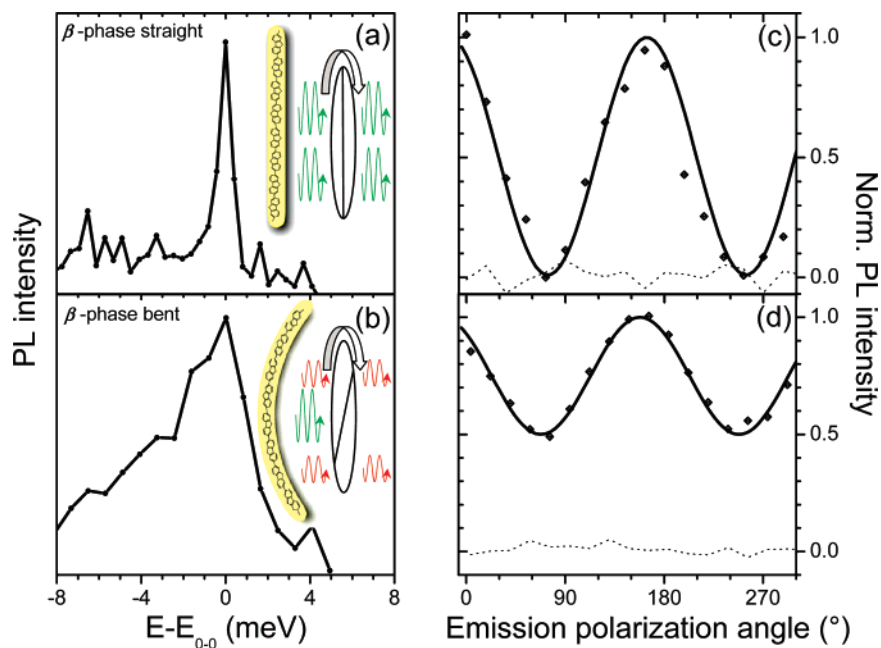
Figure 2. Correlation of the electronic transition linewidth of single β-phase molecules with chain extension under excitation at 412 nm. (a) Narrow emission spectrum (linewidth 0.7 meV) shifted by the $0-0$ transition energy, exhibiting linearly polarized emission ($P = 0.98$) as shown in panel (c). (b) The broad emission spectrum (linewidth 2.40 meV) of a different single chain is only weakly linearly polarized ($P = 0.33$, panel (d)). The dotted lines in (c) and (d) indicate the fluorescence background.

slightly bent (though still fully planarized and spectrally distinct) chains. However, the polarization anisotropy $P < 1$ in *excitation* can potentially also result from the absorption of multiple β-phase chromophores within the polymer chain. Such simultaneous emission from chromophores of different emission energies has previously been demonstrated for ladder-type poly(*para*-phenylenes).[16] Although the emission energies in polyfluorene scatter widely from molecule to molecule by up to 90 meV[15] (also see Figure 3b), we typically only observe *one single transition line* from a single (β-phase) molecule. Out of the 400 β-phase molecules studied at low temperatures, only three showed indications of multichromophoric (i.e., multiline) β-phase emission under broad band (20 meV spectral width) excitation. Moreover, no evidence of emission switching between different (nondegenerate) chromophores was observed during the rotation of the analyzer. In contrast, ladder-type poly(*para*-phenylene) of much shorter chain length generally shows distinct spectral signatures of multichromophoric emission with near-perpendicular transition dipole orientations.[16] The present observation suggests that most β-phase chains may contain only *a single* active β-phase chromophore, with conjugation extending along the (potentially bent) crystalline part of the chain.

Figure 2 presents examples of the spectroscopy of two β-phase molecules. Rather than considering the anisotropy of excitation as in Figure 1, we studied the polarization of the emission spectrum by rotating a $\lambda/2$ plate in front of a Wollaston prism placed before the entrance slit of the spectrograph and passing the laser through a $\lambda/4$ plate to ensure unpolarized excitation. This provides insight into the actual spatial configuration of the *emitting* chromophore, the conjugated segment of the polymer relevant to fluorescence

emission. Whereas the narrower spectrum shown in panel a of Figure 2 arises from fully polarized light (panel c of Figure 2), the luminescence in Figure 2b is only weakly linearly polarized ($P = 0.33$, panel d of Figure 2). This remarkable observation suggests that, while the dihedral angles between monomers are close to zero in both cases as required to form the spectrally distinct β-phase, in the latter case (panels b and d of Figure 2), the emitting unit appears to be bent *within* the plane. It was recently suggested that a chromophore can undergo a certain degree of structural deformation without causing scission of the π-electron system.[23,24] While there is a small chance that the broader spectrum in panel b of Figure 2 arises due to multiple chromophores, both the large energetic scatter of β-chromophore peak energies from molecule to molecule and the observed temporal stability of the PL line shape[15] make it highly improbable for two chromophores on a chain to merge to one spectral line. With a maximum linewidth of ~4 meV and an average energetic scatter from chromophore to chromophore of ~40 meV,[15] two chromophores on a chain should be spectrally distinct. Such a case was, however, only observed in 3 out of 400 β-phase chains studied. In addition, the line shape does not change during rotation of the analyzer. This would be expected if the broader, less polarized lines originated from nondegenerate chromophores of different orientations.

We propose that the *chain conformation controls the linewidth of the excitonic transition* by impacting on either the electronic coherence of the excited state or the underlying spectral diffusion of the transition, which adds to the homogeneous linewidth. Figure 3 shows a plot of PL linewidth versus polarization anisotropy for a total of 80 molecules (red circles). The linewidth, which varies from 400 μeV to 4 meV, correlates directly with the amount of
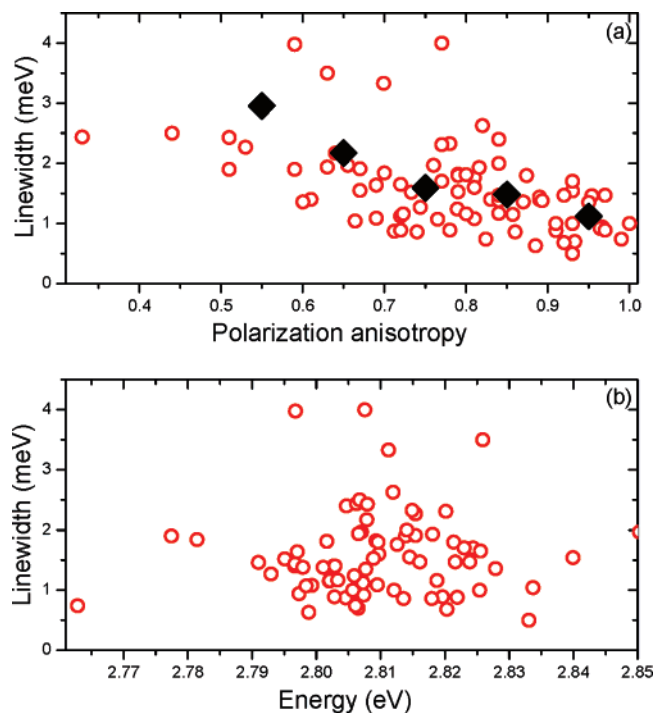
Figure 3. (a) Correlation between transition linewidth and polarization anisotropy in β-phase polyfluorene for a total of 80 β-phase single molecules (red circles), excited at 412 nm. The black diamonds indicate an average over steps of 0.1 in polarization anisotropy. The errors in the determination of linewidth and anisotropy are 0.25 meV and 0.03, respectively. The correlation coefficient of the data r of -0.5 translates to a $>99.9\%$ probability for the 80 data points of linewidth and anisotropy being correlated. (b) Scatter plot of linewidth and $0-0$ transition energy, showing that the transition energy of the β-phase does not correlate with the linewidth.

tension exerted on the one-dimensional crystalline chain as it bends out of a linear rigid-rod configuration. The linewidth (Γ) provides a *lower* limit of the quantum coherence time T_2 of the exciton through $T_2 \geq 2\hbar/\Gamma$, corresponding to a minimum dephasing time of 3 ps. We stress that, as discussed above, it is very unlikely that such a correlation would arise from spectral broadening due to multichromophoric emission: the relative orientations and energies of chromophores on a chain should be random. In contrast to what one may expect for a quantum confined system, a bend in the one-dimensional crystal does not alter the transition energy, as shown in the scatter plot of transition energy versus linewidth in Figure 3b. Very recently, even narrower emission lines were reported by Feist et al.[25] in MEH-PPV at 1.2 K, but no correlation with the chromophore conformation was proposed. In this case, the excitation spectrum was found to be orders of magnitude narrower than the emission spectrum, suggesting substantial inhomogeneous broadening of the emission due to spectral diffusion. We expect that inhomogeneous broadening due to spectral diffusion also plays a role in these narrow polyfluorene lines but cannot quantify this effect at present.

Single polyfluorene molecules can exist in an effectively extended conformation with all phenylene rings lying in one plane. This observation is distinct from our recent demonstration of the correlation of polarization anisotropy in the

absorption of single phenylene—vinylene oligomers (OPVs) with linewidth and peak position:[17] OPV does not form an effectively crystalline structure and the exciton is therefore self-trapped[12] so that the *emission* is always linearly polarized; the transition widths are over an order of magnitude larger and the OPV chain almost 2 orders of magnitude shorter. The present situation, in which an extended single chain shows single-peak (i.e., most likely single chromophore[14]) emission, which does not originate from a linear transition dipole, however, does bear some resemblance to the case of polydiacetylene polymerized spontaneously in its monomeric crystal[11] in that both materials can be thought of as effectively one-dimensional crystals with long-range structural order. The important difference is that polyfluorene is suspended in an *amorphous* (Zeonex) matrix, whereas the highest quality polydiacetylene chains are formed in a single-crystal matrix of the monomer.[11−13] Both materials show the same transition linewidth, which has previously been taken as a measure of the coherence time in polydiacetylene.[11−13] Polydiacetylene chains are, however, much longer (many micrometers). Ballistic Frenkel exciton transport over such macroscopic distances has been demonstrated in polydiacetylene, which displays properties of a perfect quantum wire far superior to any artificial inorganic semiconductor nanostructure.[11−13] We propose that, in contrast to general understanding that invokes strong exciton self-trapping,[12] even seemingly *disordered* conjugated polymer systems may contain highly ordered regions such as the β-phase, which could then support coherence phenomena with ballistic exciton transport. A signature of such exciton transport along the chain may be drawn from the fact that the single chromophore *emission* is not linearly polarized; all regions of the conjugated segment are equally likely to emit. Conventionally, emission from an extended chromophore on a π-conjugated polymer chain is attributed to a *linear* transition dipole. This appears not to be the case for β-phase polyfluorene, permitting the tentative conclusion that the chromophore can be bent.[23] As the spatial extension of the exciton is much smaller than the chromophore,[20] weakly polarized emission is a signature of fluorescence emission occurring with equal probability on different spatial segments of the bent chromophore. Note that very little is known about structural relaxation energies in β-phase polyfluorenes. Whereas this energy can be tens of meV in phenylene—vinylenes, it appears to be negligible in polydiacetylenes, which do not display signatures of exciton self-trapping.[12] It is therefore conceivable that significant exciton self-trapping does not occur in the β-phase due to the high degree of structural order and rigidity of the backbone, enabling weakly polarized emission from a bent chromophore.

We conclude by discussing possible reasons for the correlation of the linewidth, a primarily intrinsic property of the chromophore on the polymer chain, with the extrinsic observable of the chain geometry. The β-phase corresponds to a one-dimensional crystalline structure, as witnessed by the large diffraction coherence observed in X-ray scattering.[18] The translational symmetry requirement of crystallinity can be maintained even under a slight distortion of the chain

within the plane of crystallization. Such a distortion corresponds to strain acting on the crystal, which in turn will reduce the intersite coupling strength and enhance scattering of the exciton wavefunction. An immediate consequence of increased scattering is accelerated excited-state dephasing, which may lead to an increase in transition linewidth depending on the homogeneous linewidth of the transition. In addition, the optical transition experiences spectral broadening due to spectral diffusion as a consequence of microscopic rearrangement of the chain environment following dissipation of excess energy in nonresonant excitation.[4,15] Spectral diffusion of single molecules is enhanced substantially in amorphous matrices with respect to crystalline environments due to the increased number of degrees of freedom.[26] We note that the immediate environment of the polyfluorene chain can be thought of as becoming less ordered upon bending within the plane of the β-phase. The nonpolar octyl side groups effectively form a covalently linked "Shpol'skii matrix"[4,26] for the fully extended chain, whereas any bend in the chain will be amplified by the steric interactions of the side groups, leading to a less ordered immediate environment of the chromophore.

Regardless of the physical origin, which will be the subject of future studies such as (single chain) site-selective fluorescence, photon statistics and PL lifetime, the data unequivocally illustrate how the shape of a translationally symmetric periodic macromolecule controls the transition linewidth. Conjugated polymers therefore provide surprisingly versatile model systems to study crystallization phenomena in one dimension and offer a unique toolbox to correlate the shape of an optically active nanostructure with its intrinsic electronic properties. As for the case of single quantum dots, for which electronic transition linewidths (and dephasing rates) have decreased by several orders of magnitude over the past decade,[27−31] chromophores on ordered polymer molecules may turn out to be of interest for quantum computing implementations at low temperatures.[32] As a polymer chain can potentially accommodate multiple two-level system-like chromophore units[4−17] (intentionally introduced chemical defects could enhance this in β-phase polyfluorene), coherent coupling and control[33,34] of these units may be achievable. Although intermolecular order has been shown to correlate strongly with device performance,[35] *intramolecular* crystallinity and long-range order is rarely considered when discussing the physical properties of conjugated polymers, which are typically highly disordered in the bulk.[2,3] It is likely, however, that these most ordered *single* molecules actually govern the physics of the bulk material; they display the best photostability,[15] the fastest exciton and charge transport,[36] and are most apt for electric field induced charge separation in photovoltaics.[12,37] A future goal must be to control the degree of chain order in the bulk by solvent swelling[18] or annealing techniques.[35] A selective addressing and exploitation of the most ordered chains for light harvesting or charge transport would help to improve the properties of conjugated polymers and enhance the potential of organic electronic devices.

References

(1) Malliaras, G.; Friend, R. H. *Phys. Today* **2005**, *58*, 53−58.
(2) Schwartz, B. J. *Ann. Rev. Phys. Chem.* **2003**, *54*, 141−172.
(3) Brédas, J.-L.; Beljonne, D.; Coropceanu, V.; Cornil, J. *Chem. Rev.* **2004**, *104*, 4971−5004.
(4) Moerner, W. E.; Orrit, M. *Science* **1999**, *283*, 1670−1676.
(5) VandenBout, D. A.; Yip, W. T.; Hu, D. H.; Fu, D. K.; Swager, T. M.; Barbara, P. F. *Science* **1997**, *277*, 1074−1077.
(6) Huser, T.; Yan, M.; Rothberg, L. J. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 11187−11191.
(7) Sartori, S. S.; De Feyter, S.; Hofkens, J.; Van der Auweraer, M.; De Schryver, F.; Brunner, K.; Hofstraat, J. W. *Macromolecules* **2003**, *36*, 500−507.
(8) Sun, W. Y.; Yang, S. C.; White, J. D.; Hsu, J. H.; Peng, K. Y.; Chen, S. A.; Fann, W. S. *Macromolecules* **2005**, *38*, 2966−2973.
(9) Hu, D.; Yu, J.; Wong, K.; Bagchi, B.; Rossky, P. J.; Barbara, P. F. *Nature* **2000**, *405*, 1030−1033.
(10) van Oijen, A. M.; Ketelaars, M.; Köhler, J.; Aartsma, T. J.; Schmidt, J. *Science* **1999**, *285*, 400−402.
(11) Dubin, F.; Melet, R.; Barisien, T.; Grousson, R.; Legrand, L.; Schott, M.; Voliotis, V. *Nat. Phys.* **2006**, *2*, 32−35.
(12) Bässler, H. *Nat. Phys.* **2006**, *2*, 15.
(13) Guillet, T.; Berrehar, J.; Grousson, R.; Kovensky, J.; Lapersonne-Meyer, C.; Schott, M.; Voliotis, V. *Phys. Rev. Lett.* **2001**, *87*, 087401.
(14) Schindler, F.; Jacob, J.; Grimsdale, A. C.; Scherf, U.; Müllen, K.; Lupton, J. M.; Feldmann, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 1520−1525.
(15) Becker, K.; Lupton, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 7306−7307.
(16) Müller, J. G.; Lemmer, U.; Raschke, G.; Anni, M.; Scherf, U.; Lupton, J. M.; Feldmann, J. *Phys. Rev. Lett.* **2003**, *91*, 267403.
(17) Becker, K.; Da Como, E.; Feldmann, J.; Scheliga, F.; Thorn Csányi, E.; Lupton, J. M. submitted for publication, 2007.
(18) Grell, M.; Bradley, D. D. C.; Ungar, G.; Hill, J.; Whitehead, K. S. *Macromolecules* **1999**, *32*, 5810−5817.
(19) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477−487.
(20) Franco, I.; Tretiak, S. *J. Am. Chem. Soc.* **2004**, *126*, 12130−12140.
(21) Khan, A. L. T.; Sreearunothai, P.; Herz, L. M.; Banach, M. J.; Köhler, A. *Phys. Rev. B* **2004**, *69*, 085201.
(22) Meyer, R. R.; Sloan, J.; Dunin-Borkowski, R. E.; Kirkland, A. I.; Novotny, M. C.; Bailey, S. R.; Hutchison, J. L.; Green, M. L. H. *Science* **2000**, *289*, 1324−1326.
(23) Beenken, W. J. D.; Pullerits, T. *J. Phys. Chem. B* **2004**, *108*, 6164−6169.
(24) Grage, M. M.-L.; Zaushitsyn, Y.; Yartsev, A.; Chachisvilis, M.; Sundström, V.; Pullerits, T. *Phys. Rev. B* **2003**, *67*, 205207.
(25) Feist, F. A.; Tommaseo, G.; Basché, T. *Phys. Rev. Lett.* **2007**, *98*, 208301.
(26) Kiraz, A.; Ehrl, M.; Bräuchle, C.; Zumbusch, A. *J. Chem. Phys.* **2003**, *118*, 10821−10824.
(27) Landin, L.; Miller, M. S.; Pistol, M. E.; Pryor, C. E.; Samuelson, L.; *Science* **1998**, *280*, 262−264.
(28) Herz, L. M.; Phillips, R. T. *Nat. Mater.* **2002**, *1*, 212.
(29) Seidl, S.; Kroner, M.; Dalgarno, P. A.; Högele, A.; Smith, J. M.; Ediger, M.; Gerardot, B. D.; Garcia, J. M.; Petroff, P. M.; Karrai, K.; Warburton, R. J. *Phys. Rev. B* **2005**, *72*, 195339.
(30) Borri, P.; Langbein, W.; Schneider, S.; Woggon, U.; Sellin, R. L.; Ouyang, D.; Bimberg, D. *Phys. Rev. Lett.* **2001**, *87*, 157401.
(31) Berthelot, A.; Favero, I.; Cassabois, G.; Voisin, C.; Delalande, C.; Roussignol, P.; Ferreira, R.; Gérard, G. M. *Nat. Phys.* **2006**, *2*, 759−764.
(32) Li, X.; Wu, Y.; Steel, D.; Gammon, D.; Stievater, T. H.; Katzer, D. S.; Park, D.; Piermarocchi, C.; Sham, L. J. *Science* **2003**, *301*, 809−811.
(33) Kennedy, S. P.; Garro, N.; Phillips, R. T. *Phys. Rev. Lett.* **2001**, *86*, 4148−4151.

(34) Varnavski, O. P.; Ostrowski, J. C.; Sukhomlinova, L.; Twieg, R. J.; Bazan, G. C.; Goodson, T., III. *J. Am. Chem. Soc.* **2002**, *124*, 1736−1743.

(35) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C.-S.; Ree, M. *Nat. Mater.* **2006**, *5*, 197−203.

(36) Barford, W.; Duffy, C. D. P. *Phys. Rev. B* **2006**, *74*, 075207.

(37) Virgili, T.; Marinotto, D.; Manzoni, C.; Cerullo, G.; Lanzani, G. *Phys. Rev. Lett.* **2005**, *94*, 117402.