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The Complex Excited-state Behavior of a Polyspirobifluorene Derivative: The Role of Spiroconjugation and Mixed Charge Transfer Character on Excited-state Stabilization and Radiative Lifetime

Susanne I. Hintschich,* Carsten Rothe, Simon M. King, Stewart J. Clark, and Andrew P. Monkman

Department of Physics, University of Durham, Durham, DH1 3LE, U.K.

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In this study, we report on the unusual fluorescence decay of an alkoxy-substituted polyspirobifluorene. Excited state behavior has been probed as a function of time, using femtosecond photobleaching, single photon counting, and streak camera techniques. Unusually complex decay kinetics are observed, which strongly depend on solvent viscosity and polarity, featuring decay components in both the tens of picoseconds and in the nanosecond time domain. These findings are explained by the consequences of spiroconjugation in combination with excited-state conformational relaxation. We propose that exciton wave function delocalization into the spiro units effectively traps the exciton, allowing it to relax further into a highly emissive state with a very long lifetime as compared to non-spiroconjugated polymer analogues. Frontier molecular orbitals and exciton orbitals have been calculated using a first principles density functional theory (DFT) approach. These results confirm the importance of spiroconjugation as both the highest occupied molecular orbital (HOMO) and the (lowest) exciton level are not localized on the polymer backbone but strongly extend into the side fluorene groups of the spirobifluorene units. The results of our calculations are very sensitive to the substitution pattern on the spirobifluorene units, in particular when oxygen is included. This finding may lead to new materials of this kind with optimized charge carrier transport properties and high luminescence quantum yields.

Introduction

Organic electroluminescent diodes have a great potential for display or general lighting applications. However, in order to make these OLEDs competitive with long-established technologies such as inorganic LEDs, the diode stability and light emission efficiency need to be improved. Both of these requirements are closely linked to the light emitting organic material itself, which should possess sufficient morphological and chemical stability to avoid aggregation and defect formation, respectively, but at the same time a high quantum efficiency. For polymers, the latter requirement is not difficult to achieve, for example, in dilute solutions many conjugated polymers exhibit quantum yields typically in excess of 90%. However, this value drops significantly in the solid state, which is most likely a consequence of low emissive aggregation and impurity sites, which trap migrating excitations. Much of the current research efforts are directed to blue-emitting polymers, especially polyfluorene derivatives. For these materials, a particularly well-known chemical degradation is the oxidation of the fluorene repeat unit into fluorenone.[1–3] One promising way to increase the chemical stability of the 9-position while keeping the high emission quantum yield employs a spiro linkage.[4–10] Furthermore, backbone and side groups are always forced into an orthogonal position around the binding carbon, which leads to a large steric hindrance of the individual polymer chains and in doing so prevents crystallization of small molecules or aggregation of polymer chains in the solid state. This has readily been observed by an increase of the glass transition temperature and makes small organic molecules and polymers morphologi-

cally more stable.[11,12] For most conjugated polymers the side groups facilitate solubility as well as yielding morphologically stable films, whereas it is mainly the polymer backbone that determines the electronic properties. However, the electronic properties of the backbone may be strongly influenced if another pi-conjugated unit is attached through a spiro linkage, such as in the case of spirobifluorene.[8,12] In this case, spiroconjugation leads to new molecular orbitals in the ground and/or in the excited state, which do not exist for the unsubstituted backbone.[13] Although the two fluorene units are strictly orthogonal because they are connected by a tetrahedral carbon, the π orbitals of the two units still overlap in space, giving rise to a degree of (spiro) conjugation of the two π systems.[14–16] This may be advantageous, as was recently demonstrated by Wu et al.[12] These authors report a dramatically increased electron mobility for a spirobifluorene oligomer versus a similar fluorene-type oligomer. On the basis of density functional theory (DFT) it was concluded that spiroconjugation of the HOMO level (highest occupied molecular orbital) facilitates intermolecular hole migration. Similarly, general knowledge usually considers polyfluorene as a hole transport material, but this situation seems to be reversed for the polyspirobifluorene investigated here, which in device configuration performs better when copolymerized with a hole transporting unit; that is, the homopolymer seems to be an electron transporting material.[17,18]

Thus, polyspirobifluorene emerges as a promising material for polymer LEDs as it possesses the combination of increased charge carrier mobility while at the same time being photochemically stable and nonaggregating. It would still be desirable to optimize or tailor the charge carrier transport of this polymer by chemical modification. To be able to achieve this, its basic photophysical properties must be better understood. This should

* Corresponding author. current address: Institut für Angewandte Photophysik, TU Dresden, George-Bähr-Str. 1, 01069 Dresden, Germany, email: susanne.hintschich@iapp.de.

Polyspirobifluorene Derivative

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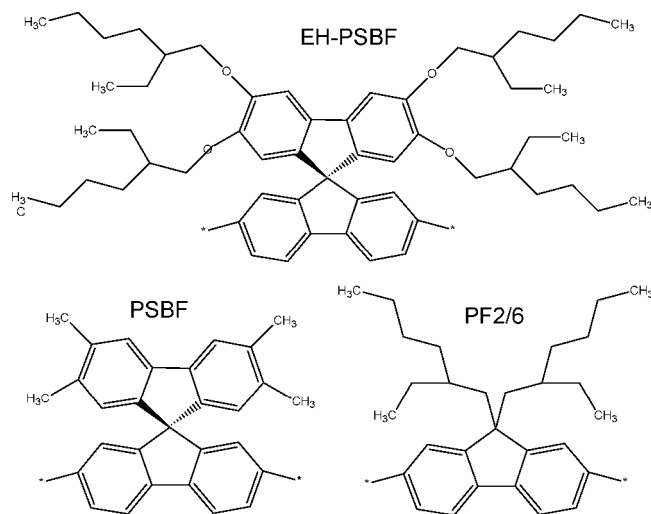
Figure 1. Repeat units of the polymers investigated in this work.

be done relative to common polyfluorene derivatives to unveil the unique features that are introduced by the spiro-linkage. So far, very little is known about the excited-state decay of spiro-type molecules. Milota et al. investigated the fluorescence decay of a symmetric molecule with two branches linked by a spirobifluorene.[19] These authors found nearly monoexponential decays and concluded that there is little interaction between these two parts of the molecule. We present the first time-resolved study of a spirobifluorene-type polymer, where we measure the excited-state decay for dissolved, that is, isolated, polymer chains as a function of solvent parameters such as viscosity and polarity. These decays are surprisingly complex compared to polyfluorene. To explain our findings, we propose that, through the spiroconjugation, excitons can become localized as their wave functions spread into a spiro sidearm. Fast, initial excited-state relaxation (of the backbone geometry) leads to increased spiroconjugation driving this exciton trapping, manifest by a fast excited-state decay into an extremely long-lived fluorescent state. Supporting DFT calculations have been performed, which demonstrate that the orthogonally attached fluorene side groups strongly participate in both the HOMO and the exciton orbital and as such verify our idea of the role being played by spiroconjugation in this particular polymer.

Relaxation of the backbone structure will affect greatly the spiroconjugation, which is very sensitive to the orbital overlap and thus the delocalization of an exciton into the side spirofluorene unit. Further, due to the ether linkages of the solubilizing alkyl groups on each spiro unit, the excited-state does gain some degree of charge transfer character, which can be thought of as a mixing of excitonic and charge transfer wave functions.[20]

Experimental Section

A polyspirobifluorene with a molecular weight of 770 000 g/mol was synthesized by the Merck OLED GmbH.[21] This material contains four branched alkoxy side chains in its repeat unit; compare chemical structures in Figure 1. Since this is of some importance later on, and to avoid confusion, we will call the actual polymer EH-PSBF and a theoretical version where the ethylhexyloxy side chains are replaced by simpler methoxy groups, M-PSBF. For the purpose of comparison, some experimental data of the polyfluorene derivative PF2/6 with $M_W = 160\,000$ g/mol are also shown; see Figure 1 for the chemical structure. To keep this work as clear as possible, only solution data at room temperature are considered. Results obtained for

solid state and temperature-dependent measurements have been reported elsewhere.[22] Also, for brevity, we only show data obtained with three different solvents, namely, chlorobenzene, toluene, and decalin, which we believe to be the best combination with respect to solvent polarity and viscosity. In view of the high molecular weight, special care was taken to prepare these solutions, although the spiro repeat unit structure and multibranched alkyloxy chains provide the polymer with a very high solubility. Here, the polymer solution (1 mg/g) was first stirred overnight at room temperature and then stirred for a further hour at a solvent-specific temperature (up to 90 °C). This master solution was then diluted to a maximum optical density of about 0.1 per cm, corresponding to a concentration of approximately 10^{-6} wt/wt. At these very low concentrations, no obvious signs of (particulate) scattering where observed in optical measurements, and the steady state excitation spectra were free of any features associated with aggregate formation. Emission and absorption of these solutions were characterized using a Jobin Yvon Fluorolog and a Lambda 19 Perkin-Elmer absorption spectrometer.

For the picosecond emission studies, the solutions were excited by frequency-doubled, ∼2 ps, pulses of a Coherent Mira 900 laser. The sample emission was passed through a spectrograph and detected by a C5680 Hamamatsu streak camera. The use of this setup allows probing of the emission kinetics simultaneously to the spectral evolution, with 12 ps overall time resolution and typically 4 nm spectral resolution. Alternatively, emission decays were measured via time-correlated single photon counting (TCSPC), which used a flip mirror inside the monochromator to direct the sample emission through a second subtractive dispersive monochromator and onto a microchannel plate (MCP) detector. After deconvolution with the excitation signal, we obtain an approximate time resolution of 4 ps with this experiment. Full details for both experiments can be found in ref 23.

As an alternative to the fluorescence decay, we also probed the time-dependence of the overall excited-state population, using photobleaching recovery with femtosecond time resolution. This experiment is based on a Coherent Mira 900-F Ti: sapphire oscillator and a Coherent RegA 9000 Ti-sapphire amplifier. The 780 nm laser output is frequency doubled and then split into pump and probe beam with the probe pulse being optically delayed by means of a Newport IMS-600. The change in transmission of the probe beam is then monitored by a photodiode and standard lock-in techniques. Full details are given in ref 24.

To gain further insight, we carried out a sequence of first principles electronic structure calculations using the Castep electronic structure code.[25,26] In particular, we examined the HOMO and LUMO orbitals and also the excitonic state. The calculations were performed using the density functional formalism within the generalized gradient approximation[27] applied to the electronic exchange and correlation interactions. Nonlocal ultrasoft pseudopotentials generated by the method of Vanderbilt[28] were used to describe electron−ion interactions. The valence electron wave functions were expanded in a plane wave basis set with a kinetic energy cutoff of 450 eV. This converged total energy differences in the system to better than 0.005 eV/atom. The electronic structure calculation used a preconditioned conjugate gradients energy minimization scheme and density mixing algorithm using the plane wave coefficients as variational parameters. The geometry of the molecules was performed by relaxing the Hellmann−Feynman forces to lower than 0.01 eV/Å.
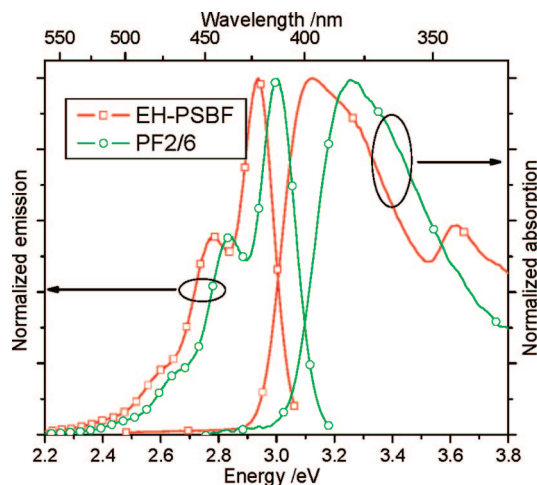
Figure 2. Comparison of the normalized steady state absorption and emission spectra of the common polyfluorene derivative PF2/6 and the polyspirobifluorene EH-PSBF, both dissolved in toluene.


Figure 3. Normalized steady state absorption and emission spectra of EH-PSBF in three different solvents, as indicated. The dashed line depicts a broad unstructured emission feature, which underlies the fluorescence of chlorobenzene.

Excited-state Decay Kinetics. The ground-state absorption and fluorescence of EH-PSBF and of the archetypical polyfluorene derivative, PF2/6, are shown in Figure 2. The spectra of the spirobifluorene derivative are red-shifted by about 10 nm with respect to those of PF2/6. Also, a new feature appears in the absorption spectrum of EH-PSBF around 3.7 eV. After several studies, we can still only speculate about its origin. In view of the fact that excitation into this additional absorption band changes neither the decay kinetics nor the spectrum of the fluorescence, we assumed that it is the higher energy split-off band from the spiroconjugated system[14] and that excitation into this higher energy band simply decays rapidly through internal conversion to the lower lying excited state (LUMO). Otherwise, the shape of the fluorescence and absorption spectra of EH-PSBF are similar compared to those of PF2/6. Therefore, given just these spectra, one would assume that the polyspirobifluorene simply exhibits a longer average conjugation length in both ground and excited-state as compared to polyfluorene.

To further probe the basic photophysics, the absorption and emission spectra of EH-PSBF were measured in three different solvents, namely decalin, toluene, and chlorobenzene, and are shown in Figure 3. This combination of solvents allows us, in a qualitative manner, to study the effects of polarity (toluene and decalin versus chlorobenzene) and viscosity (toluene and chlorobenzene versus decalin). Considering absorption, we observe no significant alterations of the spectral shape and only minor spectral shifts. From this we conclude that EH-PSBF has nearly the same ground-state molecular configuration in all three solvents. We note, however, that chlorobenzene (and many other chlorinated solvents) can give rise to some degradation of conjugated polymers after long-time illumination or high-intensity illumination through the formation of charged states between the polymer and the solvent.[29] This photodegradation typically gives rise to an unstructured, broad emission feature peaking at around 2.55 eV. Such a feature is revealed by subtracting the EH-PSBF emission spectrum measured in toluene from that recorded in chlorobenzene, as indicated by the dashed line in Figure 3. This degradation may also be responsible for the relatively low emission quantum yield in this solvent. Apart from this broad spectral feature there are no striking differences between the toluene and chlorobenzene solution, albeit the polarity of these solvents differs by 1 order of magnitude. Therefore, no strong effect of the solvent polarity on the initial excited-state is observed. In contrast, significant
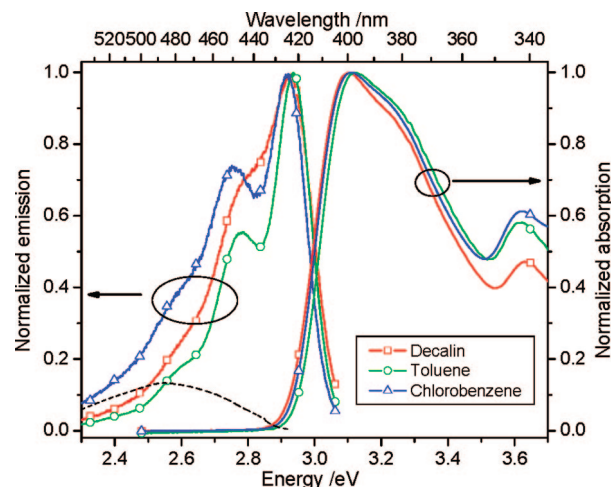
differences in the fluorescence spectra are observed between solutions made from low- and high- viscosity solvents, such as toluene versus decalin. For the latter, the vibronic spectrum is much less resolved, and the ratio of the 0−0 to 0−1 vibronic overtone is very different. Similarly, it was demonstrated that a reduced temperature and an increased viscosity have nearly identical effects on the fluorescence spectrum.[22] We take this to indicate that the excited-state configuration of EH-PSBF is influenced by the solvent viscosity and thus excited-state conformational relaxation.[30]

Proceeding to time-resolved spectroscopy, Figure 4, shows two original streak camera images of EH-PSBF dissolved in decalin and toluene, respectively. From these pictures one can clearly spot qualitative differences: for toluene, the fluorescence exhibits an initial fast decay within the first 50 ps, but there is also a pronounced long time component. In contrast, the fluorescence decay in decalin appears as a uniform nonexponential decay.

From these original data, we extracted the decay of the fluorescence intensity by integrating them over all wavelengths (excluding the excitation peak) and plotting the result versus time. These fluorescence decays are shown in Figure 5 for EH-PSBF dissolved in toluene, decalin, and chlorobenzene. Compared to these wavelength-integrated data, more accurate decay kinetics are obtained by a deconvolution of the measured signal with the excitation pulse shape. This can be done with both streak camera and single photon counting data. Deconvoluted TCSPC results of the same systems as in Figure 5 are given on a double logarithmical fashion in Figure 6. In both graphs, an analogous data set of PF2/6 dissolved in toluene is shown for comparison. As with other polyfluorene derivatives and almost independent of the solvent, the integrated fluorescence of PF2/6 decays nearly monoexponentially with a time constant of ∼380 ps.[23,30] Clearly, the decay kinetics of the polyspirobifluorene derivative investigated here are far more complex and strongly depend on the solvent used. For low viscosity solvents such as toluene and chlorobenzene, there is a pronounced short component of ca. 20 ps, which cannot be resolved completely despite deconvolution. However, this component only accounts for 0.02 and 0.14 of the overall emission respectively, see Table 1. The remaining fluorescence, 0.98 for toluene and 0.86 for chlorobenzene, is emitted much more slowly and decays exponentially with a lifetime of more than 2000 ps. In contrast, the
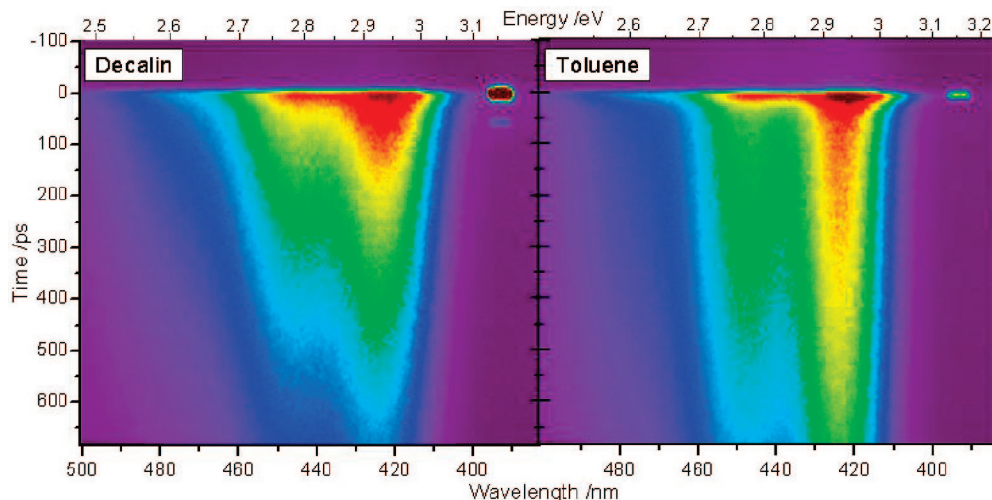
Figure 4. Original streak camera images of the emission of EH-PSBF dissolved in decalin and toluene. A scatter of the excitation pulse is recorded simultaneously at 3.15 eV.
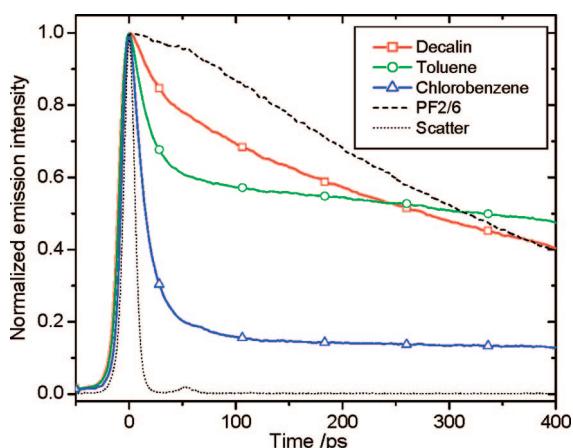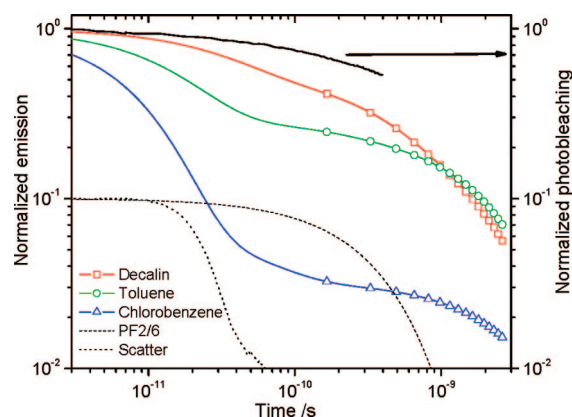

Figure 5. Normalized fluorescence intensities of EH-PSBF as a function of time for three different solvents as indicated. For comparison, a data set of PF2/6 in toluene is shown as well (dashed line). These graphs were obtained from streak camera images that were integrated over all wavelengths, excluding the excitation pulse. Selective integration over the excitation pulse gives the scatter, reference signal (dotted line) with a time resolution of 12 ps in this case.

Figure 6. Compendium of time-resolved fluorescence decays of EH-PSBF in three different solvents and PF2/6 in toluene. These are not directly measured data, but obtained from TCSPC data after deconvolution with the corresponding scatter signal (dotted line). The data sets are normalized at time zero. The uppermost solid line shows the time-resolved femtosecond photobleaching of EH-PSBF in toluene, probed and excited at 390 nm.

emission decay of EH-PSBF dissolved in highly viscous decalin is always nonexponential with no distinct fast and slow components. An effective "half-life" is estimated at ∼100 ps.

Typically, fast decay components are caused by excited-state quenching.[1,2] Emission quantum yields of the different solutions were therefore measured relative to that of Rhodamine 6G, using a comparative method, compare Table 1. In the cases of toluene and decalin, the PLQY exceeds 0.8. In chlorobenzene the value is lower at 0.44, but we attribute this to solvent-induced photodegradation, as previously discussed. In conclusion, excited-state quenching cannot be responsible for the short time decay, and this component must correspond to a rapid relaxation to a highly radiative state, which is extremely long-lived compared to other luminescent polymers.

Furthermore, we used the streak camera images presented in Figure 4 to extract the spectral position of the fluorescence emission as a function of time. The energy shift of the maximum of the first vibronic mode is plotted in Figure 7 for EH-PSBF dissolved in toluene and decalin. We find that these time-dependent spectral shifts are clearly correlated to the different decay regimes apparent in Figure 5 and 6: For toluene solution,

the fast decay component is accompanied by a rapid red shift of the fluorescence spectrum, but no further red shift is observed during the exponential, long-lived decay. On the other hand, for EH-PSBF dissolved in the viscous solvent decalin the fluorescence spectrum red-shifts continuously, which correlates to the lack of any exponential decay mode.

Finally, we return to Figure 6 to compare the time-dependent emission and the photobleaching recovery of the polymer in toluene solution. Although the fluorescence signal is a measure of the population of emissive singlets that is present at a certain time, in contrast to this, the photobleaching signal is proportional to the overall excited-state population that has not decayed back to the ground state. Therefore, apart from singlet exciton states, the photobleaching measures all excited states irrespective of their radiative or nonradiative decay channel, such as triplet excitons or charge states. Thus, if the singlet exciton were the only excited state, one would measure identical decay kinetics for fluorescence and photobleaching signals. This, apart from a small modification due to triplet exciton formation via inter-system crossing,[24] is observed in polyfluorenes, such as PF2/6 at low excitation intensities.[31] In contrast to this, if the overall photobleaching signal decays more slowly than the fluorescence, then the singlet exciton state must relax into another (metastable)

TABLE 1: Fluorescence Lifetimes and Emission Quantum Yields for EH-PSBF as a Function of Solvent[a]

solvent	Viscosity [cP]	polarity	decay kinetics		Fractional intensity α_1	Fractional intensity α_2	quantum yield
decalin	3.55	0.011	$t_{1/2} \approx 100$				0.85 ± 0.04
toluene	0.60	0.018	$A_1 = 0.7, \tau_1 \approx 20$ ps	$A_2 = 0.3, \tau_2 \approx 2300$ ps	0.02	0.98	0.80 ± 0.04
chlorobenzene	0.8	0.15	$A_1 = 0.96, \tau_1 \approx 20$ ps	$A_2 = 0.04, \tau_2 \approx 3000$ ps	0.14	0.86	0.44 ± 0.04

[a] Values in brackets indicate the weighting. The solvent viscosities and the polarity (in terms of the Lippert function) are given as well. Fractional intensities of each decay component calculated using $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where each fraction is given by $\alpha_i = A_i\tau_i/\sum A_i\tau_i$. ($t$ is the time, τ is the fitted lifetime, and A is the fitted amplitude.)
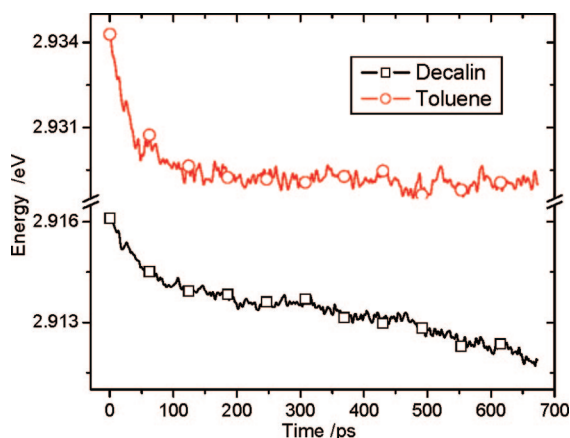

Figure 7. Spectral shift as a function of time of the center of the 0−0 vibronic mode of EH-PSBF dissolved in toluene and decalin, respectively.

state, which is not the ground state. This is indeed what we observe for EH-PSBF in Figure 6, although the photobleaching signal, due to limitations in the femtosecond experiment, does not extend as far in time as the fluorescence. The most important observation is that the fast fluorescence decay component has no equivalent in the photobleaching signal, that is, it does not represent a decay to the ground state, which is again indicative of a fast relaxation process to a lower energy radiative state.

Electronic Structure Calculations. To gain insight into the structural and electronic properties on a molecular level, DFT calculations have been performed. First, the frontier orbitals (the HOMO and the lowest unoccupied molecular orbital, LUMO) of a spirobifluorene oligomer with five repeat units, PSBF, as shown in the left panel of Figure 1, have been computed starting from the optimized molecular geometry. As with common polyfluorenes including PF2/6, the HOMO and LUMO orbitals of PSBF are mainly localized on the polymer backbone. Additionally, as can be seen in Figure 8, only the LUMO orbital slightly extends into the orthogonally attached fluorene side groups. These molecular orbitals agree very well with foregoing DFT calculations by Wu et al. on similar three-membered spirobifluorene oligomers.[12]

Next, the four oxygen atoms in the side groups were included, and similar calculations were performed for a five-membered EH-PSBF-type oligomer. However, for simplicity the branched ethylhexyloxy side chains of the real molecule have been truncated into methoxy, -O−CH$_3$, in the calculation. This truncated molecule is shown in the bottom and right part of Figure 8 and labeled M-PSBF. We believe that such a truncation does not alter the results in any significant way. It is found that the insertion of the oxygen atoms had little impact on the LUMO orbital, which again only slightly extends into the side chains, see middle panel of Figure 8. In striking contrast, the four additional methoxy groups have a huge impact on the HOMO level, which now significantly extends into the fluorene side

groups. Clearly, this extended orbital is a manifestation of spiro conjugation.[13] Given that the strength of spiroconjugation is very sensitive to the precise molecular configuration of the molecule, the huge impact of the oxygen atoms in the side groups becomes understandable. Similar effects on the HOMO level of alkoxy-substituted spirobifluorenes have been observed by Lee et al.[5] Finally, this increased conjugation of the ground-state orbital may also be the reason for the experimentally measured spectral red shift between the alkoxy-substituted polyspirobifluorene (EH-PSBF) and common polyfluorene (PF2/6).

Going one step further, we have attempted to model the excitonic state in the molecule. The relative changes in electron density have been computed for the situation that one electron of the HOMO is promoted into the LUMO orbital. The resulting electron density picture is shown in Figure 8 and can be considered as a visualization of the exciton. For the M-PSBF oligomer we find that the exciton clearly extends into the side fluorene groups. For obvious reasons, this must be qualitatively different from common polyfluorenes, such as PF2/6, which lack conjugated side groups. Furthermore, the exciton orbital is highly unsymmetrical, which can be interpreted in terms of self-localization.

As already inferred from the above experimental decays in different solvents, conformational relaxation seems to be operative in the excited state. However, shown in Figure 8 is the exciton orbital for a fixed molecular geometry, which initially was calculated as the energetically optimized molecular geometry of the molecule in the ground state. Excited state relaxation can, in principle, be modeled by optimizing the positions of all atoms with respect to the overall energy of the system in the excited state. Unfortunately, M-PSBF was too complex to put this calculation into practice, which might have unveiled some bending or rotations of the orthogonally attached fluorene groups in the relaxed excited states relative to the backbone. Note, in this context, the data shown in Figure 8 (especially the exciton orbital) already consumed several hours of time on the Durham University 64 Processor Beowulf Cluster.

Discussion

Unlike other polyfluorene derivatives, the emission decay of EH-PSBF in dilute solutions is strongly nonexponential, which, in view of the high emission quantum yields of >0.8, cannot be explained by a simple nonradiative quenching process. Furthermore, a comparison of the emission decay and the photobleaching data reveals that a large fraction of the initially excited states do not directly decay to the ground-state but relax via another metastable state of presumably lower energy. Whether this decay involves an energy transfer between the two states or proceeds gradually via excited-state relaxation cannot be fully answered from the data presented here, but given the measurements were made in dilute solution, with no apparent sign of interchain interactions visible in the excitation spectra, we favor the scenario of excited-state relaxation. This is also in line with

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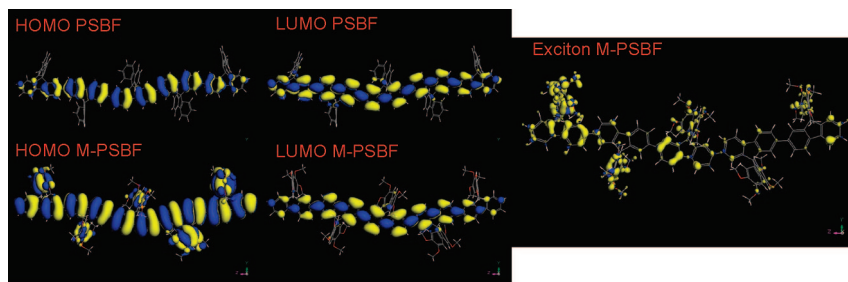
Figure 8. Mapped wave functions calculated by DFT. Top-left: HOMO and LUMO of the virtual PSBF. Bottom-left: HOMO and LUMO of an M-PSBF type oligomer. (Note: for simplicity, the ethylhexoxy side chains are truncated into methoxy.) Right: geometrically relaxed exciton of the M-PSBF type oligomer.

the self-localization found from DFT calculations, where the final, lower energy state would be considered as the natural relaxed excited-state of the molecule (see right-hand side of Figure 8). The relaxed state has a long fluorescence lifetime but, apparently, only few nonradiative decay pathways, which gives rise to high emission quantum yields.

The driving force of any excited-state relaxation is a reduction in the overall energy of the system, which may be quantified by measuring the red shift of the fluorescence. In this case, the initial emission would predominantly come from the nonrelaxed excited-state, whereas the long-time component would be associated with the relaxed state. From the measured spectral shifts, one concludes an absolute energetic relaxation greater than 5 meV.

The polarity of the solvent has important effects on the radiative decay rate of the relaxed state but does not greatly affect the emission spectrum. However, the excited-state lifetime in chlorobenzene is increased by ca. 30% as compared to that measured in toluene. From this, we conclude that the relaxed excited-state exhibits enhanced charge transfer character in the polar solvent, which acts to stabilize the relaxed state,[34] but the polarity of the solvent is not the driving force of the relaxation itself.[20] We note that in this particular polyspirobifluorene the two spiro units (of the monomer) are asymmetric and that the inclusion of the ether linkages for the alkyl side chains may be responsible for inducing some CT character into the excited state. This is supported by analogous measurements (unpublished) on a comparable polymer without ether linkages, where the fluorescence dynamics does not show a qualitative dependence on solvent viscosity but resembles the behavior observed for common polyfluorenes such as PF2/6.[30]

We also note that it is possible to subtract the toluene spectrum from that measured in chlorobenzene to reveal an underlying low energy structureless emission band at 2.55 eV, which is very reminiscent of keto defect emission in polyfluorenes.[2] This may be indicative of photodegradation in this solvent or a signature of charge transfer emission from the polymer.[20] The energetic relaxation is accompanied by conformational changes of the molecule, which qualitatively explains the dependence of the emission spectrum and decay kinetics on solvent viscosity (and temperature).[22] Therefore, the main difference between this polyspirobifluorene and polyfluorene derivatives, which also show excited-state relaxation,[22,23] is the occurrence of decay components with extremely long lifetimes. One should naturally assume that this behavior is correlated to the existence of spiro-linked side fluorene groups, which do contribute to the photophysics of EH-PSBF, as is suggested by the DFT calculations. One can see subtle differences due to viscosity as well. In both toluene and chlorobenzene (after subtraction of the underlying CT emission band) the 0−0

vibronic dominates, showing that the ground and excited states have similar configurations, whereas in the highly viscous decalin the 0−1 vibronic replica is strong, indicative of an excited-state that is rather different in structure as compared to the ground state, that is, an unrelaxed excited state.

From our observations, we conclude that for the particular polyspirobifluorene studied here, spiroconjugation into the fluorene side arms is very important in the overall photophysics of the polymer. Excitons created along the polymer backbone relax rapidly via changes of the excited-state chain geometry and become localized or "conjugated" into the side arms. Such self-trapping gives rise to greatly increased emission lifetimes without quenching, which maintains the high emission yield. By extending some of their wave function into the spiroconjugated units, excitons lower their energy by ca. 5 meV and gain some CT character. Recently, we proposed the presence of such a charge transfer state in thin solid films and light-emitting diodes of EH-PSBF[22] based on pump−probe experiments. In agreement with the present results on dilute solutions, we found that room-temperature thermal activation suffices to populate sites with CT character from initially photoexcited backbone states via exciton migration. The solution results now shed light on the nature of CT state formation, which we now attribute to the intrachain process of conformational relaxation. In the solid state, one merely observes the population of already randomly existing CT sites.

From the point of conformational flexibility, a high-viscosity solvent such as decalin represents the intermediate between solid state and solution. Here, geometric relaxation of the backbone is hindered greatly by the solvent cage, which reduces the self-localization into the spiro side units. This gives rise to a much faster radiative decay rate but one that is complex and reminiscent of a dispersive mechanism.[32] In this case, the emission red shifts continuously as a function of time.

Considering that a spiro-bond is rigid with respect to twists, such relaxation could involve scissor-type motions of the spiro-bridge. By optimizing the distance between backbone and sidegroup for spiroconjugation, the molecule quickly adopts the lowest energetic excited-state configuration, allowing the exciton wave function to spread into the spiro arms. This simple picture can consistently be extended to thin solid films and temperature-dependent measurements.[22]

We note that the degree of CT character of these self-trapped excitons must be limited as the resultant emission retains its well structured vibronic structure; however, as we have previously shown, the excited-state can possess a mixed exciton (LE) and CT character where the equilibrium can be shifted by the local environment. This mixed character plays an important role in the photophysics of the excited state, helping to stabilize the

metastable excited-state to yield a long lifetime, as is clearly the case here.[20,33]

Conclusions

In this work, a polyspirobifluorene derivative is investigated that exhibits distinct nonexponential excited-state decay kinetics that are qualitatively different compared to polyfluorenes. This observation is explained by assuming an extended conjugation in this polymer by means of spiro conjugation. The strength of the latter is very sensitive to the exact molecular geometry. Therefore, small fluctuations, for example, of the distance between side group and backbone, can result in higher spiro-conjugation. Thus, as the chain undergoes rapid relaxation in the excited state, the exciton wave function can spread into the spiro side arms, effectively self-localizing the exciton. This highly relaxed state then radiatively decays very slowly back to the ground state but with very high quantum efficiency.

The polymer investigated here is not a simple polyspirobifluorene but possesses alkoxy side groups whose original function was mainly to facilitate the solubility of the polymer. However, these subtle chemical alterations induce striking differences between the molecular orbitals of substituted and unsubstituted polyspirobifluorene, which were made visible by ab initio electronic structure calculations. Similar effects have been reported for alkoxy groups attached to the polymer backbone and hetero atoms in the spiro side groups.[5,8] As the excited-state now interacts with these spiro side arms, it will gain some enhanced CT character, which adds to its stabilization and enhanced radiative lifetime. For the future, it may be worthwhile to investigate spirobifluorene-type polymers with different substitution patterns on the orthogonally attached fluorene unit, namely, electron-donating versus electron-withdrawing groups. This should easily lead to a morphologically and chemically stable polymer with the high charge carrier mobilities desired for polymer light-emitting diodes.

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