

Origin of spectral broadening in π -conjugated amorphous semiconductorsJ. M. Lupton,^{1,*} I. D. W. Samuel,² and P. L. Burn³¹*Max Planck Institute for Polymer Research, Ackermann-Weg 10, D-55128 Mainz, Germany*²*Organic Semiconductor Centre, School of Physics and Astronomy, University of St. Andrews, North Haugh, St. Andrews, Fife KY16 9SS, United Kingdom*³*The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QY, United Kingdom*

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We present a study of the picosecond fluorescence dynamics of π -conjugated semiconducting organic dendrimers in the solid state. By varying the degree of branching within the dendrons, referred to as the dendrimer generation, a control of intermolecular spacing of the emissive core and therefore of the lattice parameter for Förster-type energy transfer is achieved. This allows a distinction between spectral diffusion and excimer formation as the two main sources of spectral broadening in organic semiconductors. Whereas Förster-type dispersive spectral relaxation is independent of temperature but strongly dependent on the interchromophore distance, excimer formation is also strongly thermally activated due to temperature-dependent conformational changes and the influence of thermally activated dynamic disorder. The rapid spectral diffusion allows a determination of the excimer rise in the emission, which is shown to have a profound impact on the steady state luminescence properties of dendrimer films. We show that the dendrimer generation not only allows a microscopic control of intermolecular interactions but also a direct control of the rate of spectral diffusion. Implications for the design of novel materials for optoelectronic devices are discussed.

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I. INTRODUCTION

π -conjugated amorphous semiconductors constitute an increasingly important branch of science and technology. Many of the electronic properties of these highly versatile materials derive from the excitonic nature of primary photoexcitations. It was realized early on in the study of these materials, however, that a substantial influence on the bulk material properties may be exerted by excitations formed by interactions between the electronic levels of adjacent molecules or polymer chain segments.¹⁻⁷ Such interactions can significantly modify the bulk material properties and may lead to a dramatic reduction in luminescence yield, which is particularly undesirable in the case of organic light-emitting diodes (LEDs) or lasers. A further important property of amorphous π -conjugated semiconductors is the intrinsic disorder, which results from a broad range of possible molecular conformations and the close correlation between conformation and electronic structure. Although excitations in these materials are highly localized and are generally considered to be tightly bound carrier pairs, exciton migration, also referred to as spectral diffusion, may take place due to resonant dipole-dipole coupling between adjacent molecules.⁸⁻¹¹ This process has been shown to result in a significant redshift of the emission spectra with time during the lifetime of the primary photoexcitations, and also leads to a further modification of the bulk steady state emission properties with respect to dilute solutions. However, in general it is not trivial to distinguish directly between excimer emission and spectral diffusion. In the case of conjugated polymers, where intrachain as well as interchain relaxation may occur, it becomes even harder to pinpoint the origin of the bulk luminescence properties. In two recent studies of poly(1,4-phenylenevinylene) (PPV) (Ref. 12) and polyfluorene (PF) (Refs. 13, 14) it was suggested that whereas the spectral relaxation and broadening in PF results purely from Förster-

mediated relaxation to lower energy molecular conformations, in PPV most of the spectral broadening arises from emissive inter-chain species. However, due to the broad range of conceivable chain orientations, conformations and lengths, it is hard to distinguish clearly between the two possible origins of spectral broadening.

In this paper we present a novel route to addressing the origin of the solid state emission properties of conjugated amorphous semiconductors. By using dendrimers, which consist of a luminescent conjugated core surrounded by conjugated dendrons, we have previously demonstrated a microscopic control of intermolecular interactions and charge transport.^{15,16} We show below that the dendrimer generation, which describes the number of branching levels shielding the dendrimer core¹⁷⁻¹⁹ from adjacent cores in the solid state, not only influences the formation of intermolecular excitations, namely excimers, but also directly controls the diffusion of primary photoexcitations to both lower energetic conformers and quenching sites. Using this approach we are able to extract the spectral relaxation components due to diffusion to lower energy sites and the rise and decay of a long-lived excimer component. The present study employs a family of tris(distyrylbenzyl)amine (ADSB) based amine cored dendrimers, shown in Fig. 1.^{15,16,20} This family of dendrimers is particularly interesting, since it has been shown to make efficient LEDs and also allows a microscopic control of the charge carrier mobility.¹⁵

II. EXPERIMENTAL

The synthesis and characterization of the dendrimers used is described in detail elsewhere.²⁰ Films of the dendrimer approximately 100-nm thick were spin coated onto glass substrates from toluene solutions of concentration 10 mg/ml. These were mounted in a continuous flow helium cryostat under helium atmosphere. The PL was excited with 180-fs laser pulses from a frequency-doubled mode-locked titanium

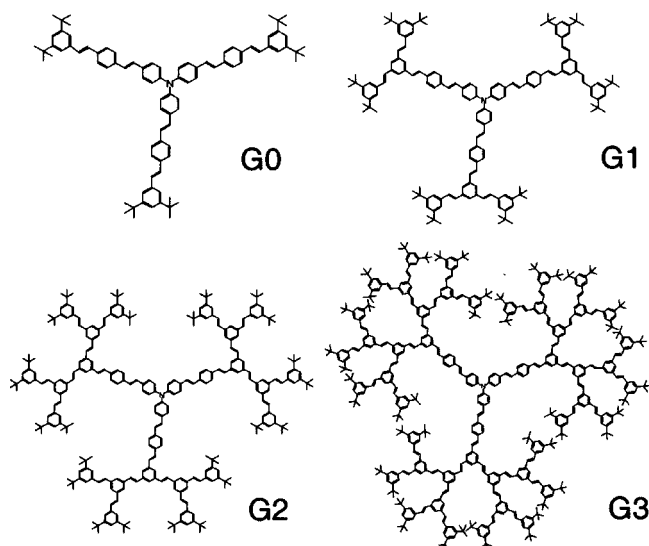


FIG. 1. Structures of the family of Tris(distyrylbenzyl)amine dendrimers with stilbene dendrons of generation (G) 0 to 3.

sapphire laser operating at 370 nm and a repetition rate of 80 MHz. The excitation spot was focused down to a diameter of approximately $100\ \mu\text{m}$. The average excitation power was less than 1 mW. Time resolved PL spectra were detected through a 400-nm long-pass filter and were recorded using a Hamamatsu C4742 streak camera coupled to a 0.5-m monochromator with a 50 lines/mm grating. The overall temporal resolution of the detection system was 3.5 ps.

III. RESULTS

We have previously shown that the steady state EL and PL spectra of the dendrimer films at the focus of the present study exhibit a striking narrowing with increasing dendrimer generation.^{15,16} As the solution PL spectra of all dendrimer generations have been found to be identical, we have assigned the broad low energy tail observed in the G0 film luminescence to emission from an intermolecular excited state species.²⁰ Figure 2 shows the PL spectra of the G0 dendrimer at 290 and 4 K obtained at different delay times after excitation. At room temperature the spectra broaden substantially and the emission maximum shifts to the red as the delay time is increased. The shape of the spectra depend significantly on the delay time. In contrast, at 4 K the vibronic features are well pronounced. The spectral shape is mostly conserved as the detection window is delayed and the spectra simply shift to longer wavelengths. The insets compare the decay dynamics of the main emission band (480–500 nm) of G0 and G3 at both temperatures. The decay is much faster for G0 at 290 K, but identical for both generations at 4 K. For comparison, solutions of the G0 dendrimer were also investigated. Apart from a broadening and redshift on the scale of a few ps,²¹ no change in the emission spectrum was detected up to 4 ns after excitation.

Figure 3 shows the time dependence of the blue edge of the emission spectra (defined as 10% of the peak intensity) for G0 and G3 at 290 and 4 K. For G0 the shift occurs within 40 ps at both temperatures, whereas for G3 the relaxation

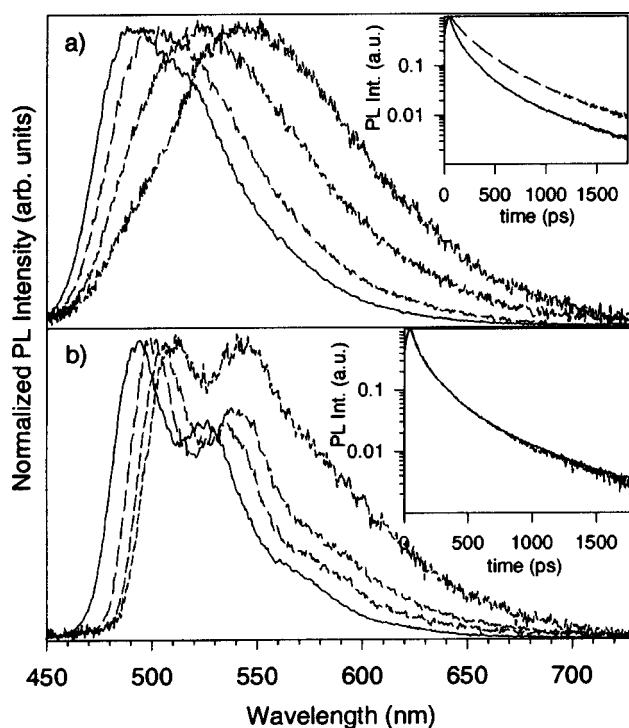


FIG. 2. Time dependent PL spectra of G0 dendrimer film measured at 290 (a) and 4 K (b). The spectra evolve to the red with increasing delay after excitation. The time windows chosen are (spectra from left to right): 0 ps (5 ps window), 100 ps (5 ps window), 500 ps (50 ps window), and 1500 ps (400 ps window). The insets show the decay of the emission maximum (integrated from 480 to 500 nm) for G0 (solid line) and G3 (dashed line).

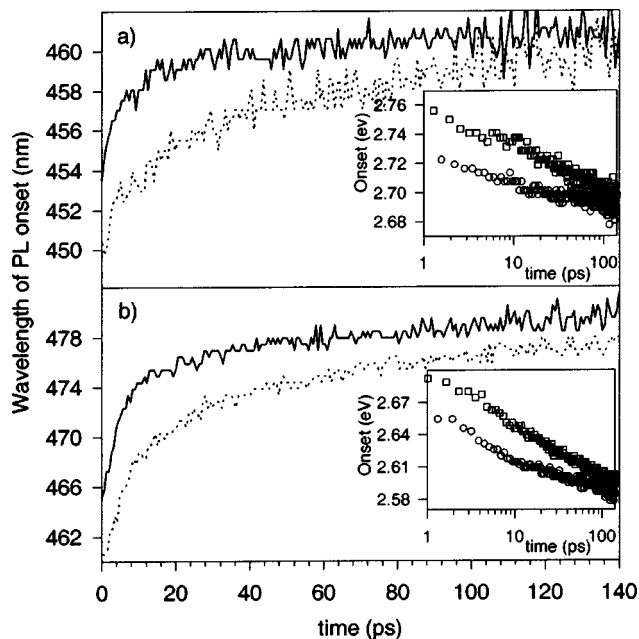


FIG. 3. Change of the PL onset (defined as 10% of the PL peak) with time for G0 (solid line) and G3 (dotted line) at 290 (a) and 4 K (b). The insets show the energy shift to the red on a semilogarithmic scale (G0: circles, G3: squares).

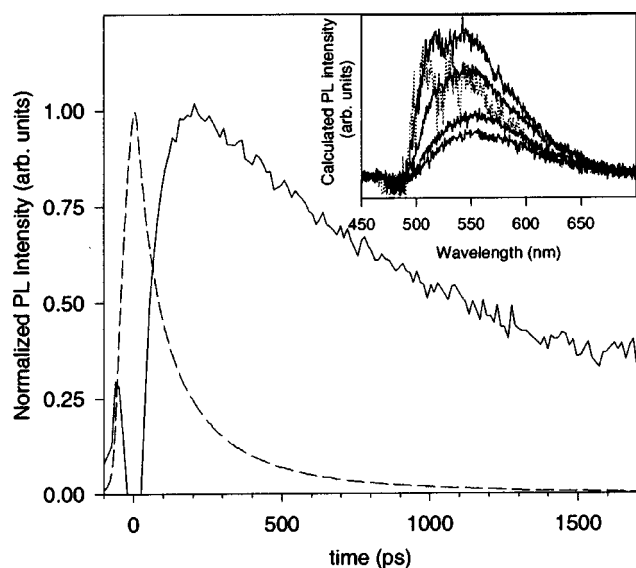


FIG. 4. Calculated excimer component in delayed G0 spectra at 290 K. The excimer spectra deduced by subtracting the molecular PL are shown in the inset for 80 ps delay (dotted) and 200, 500, 1000, and 1500 ps delay (from top to bottom). The rise and decay of the excimer component (solid line) is compared to the main emission band (dashed line).

appears to take in excess of 120 ps. This is clear evidence that the dendrimer generation not only influences the formation of intermolecular excited state species, but also the diffusion of excitations to lower lying energy sites. The time scales involved in relaxation are similar for 290 and 4 K. At 4 K there is an overall redshift of the emission spectra, which is likely to arise from a freezing out of ring torsions at low temperature resulting in more planar conformations. The insets show the relaxation of the onset energy on a semilogarithmic plot, demonstrating clearly a $E(t) \propto \ln(t)$ dependence characteristic of dispersive spectral relaxation, in accordance with previous measurements.¹³

The broad, redshifted, long-lived feature visible in the G0 emission spectrum at long delay times is indicative of an excimer emission. As the bulk of the spectral relaxation in G0 occurs within 40 ps, further changes of the spectrum with increasing delay time must result from an increasing contribution of excimer emission to the overall emission spectrum. In order to characterize the dynamics of the excimer it is therefore possible to subtract the G0 singlet emission component from the overall emission. The result is shown in Fig. 4. The extracted excimer emission exhibits a clear rise on the scale of 200 ps, comparable to the rapid initial decay of the main dendrimer emission band. This is followed by a slow decay. The inset in Fig. 4 shows the extracted excimer emission spectra, which are centered at 550 nm, determined at different delay times.

The appearance of an excimer emission band results in significant spectral broadening of the emission, which can be characterized in terms of the full width at half maximum (FWHM) of the spectrum. This is shown in Fig. 5. At low temperatures the increase in FWHM with time is virtually identical for G0 and G3. As the time increases, both spectra

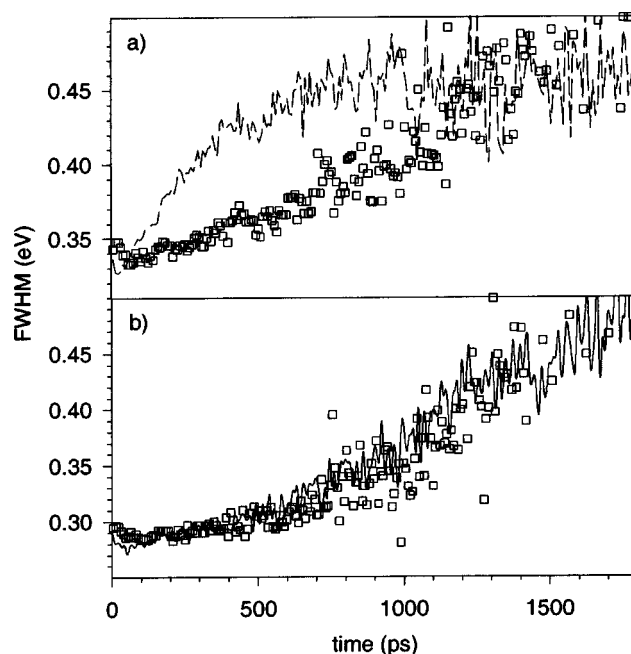


FIG. 5. Plot of FWHM for G0 (line) and G3 (squares) at 290 (a) and 4 K (b) as a function of time.

broaden due to an increased contribution from excimer emission. At longer times the G3 spectral width appears to become larger and less well-defined than the G0 width, resulting in an increase of noise on the FWHM curve. This is because the G3 delayed emission actually exhibits less long-lived excimer emission than the G0 emission, as would be expected. The result of this is that the overall spectral width of delayed G3 spectra is determined by both the singlet and the excimer component, whereas the G0 width is determined only by the excimer component at long times, and hence appears narrower. At room temperature the picture is very different. The spectra start out broader and the G3 spectrum broadens at a comparable rate to that observed at 4 K. The G0 spectrum broadens very rapidly on the time scale of 500 ps, explaining the major difference in the steady-state spectra. There are evidently many more sites where excimers can form present at 290 K, and diffusion to these is governed by the overall Förster radius, which in turn is controlled by the dendrimer generation.

A further interesting process occurring on the scale of a few ps is the molecular relaxation of the core, comparable to that previously observed in solution.²¹ Figure 6 compares the short- and long-wavelength rise at 290 and 4 K for G3. At 290 K the short wavelength fluorescence signal peaks at approximately 5 ps, whereas the long wavelength signal peaks at 15 ps. Whereas the rise of the longer wavelength component can clearly be identified at 290 K, the rise of both components is identical at 4 K. This long-wavelength rise at 290 K is associated with a molecular rearrangement upon excitation and is significantly faster than the redshift to lower energy conformers. A very similar rise was also observed for the G0 samples, demonstrating that this effect is a pure core effect, rather than a dendron-modified core-core interaction. This is confirmed by previous measurements on the ultrafast

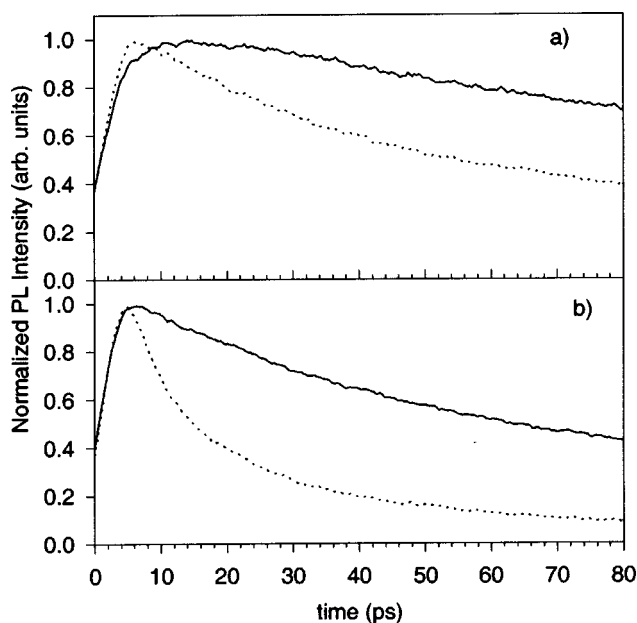


FIG. 6. Plot of G3 luminescence rise at 290 (a) and 4 K (b) for a detection window of 450 to 465 nm (dotted line) and 495 to 510 nm (solid line).

fluorescence dynamics of the dendrimers in solution, which show a clear fluorescence rise on the time-scale of 10 ps for the G0 dendrimer, i.e. for the dendrimer core.²¹ Also, the rapid conformational relaxation and strong intermolecular delocalisation have been linked with an ultrafast depolarisation of the emission on a similar time-scale.^{21,22}

Excitation was also performed at 420 nm, which corresponds to the absorption of the dendrimer core, whereas both core and dendrons absorb at 370 nm.^{16,22} No difference in the decay dynamics were observed, however.

IV. DISCUSSION

The time resolved PL data show that the temporally integrated luminescence is built up of three main time dependent relaxation processes. First, at high temperatures there is a rapid rise in luminescence with increasing wavelength, which is associated with a molecular rearrangement of the dendrimer. This occurs typically on the time scale of a few ps. Secondly, excitations may transfer from one dendrimer core chromophore to the other via temperature independent resonant dipole-dipole coupling, which is controlled by the dendrimer generation. This relaxation process occurs on the scale of 10 to 100 ps. And thirdly, there is a long-term evolution of the luminescence due to the diffusion of excitations to sites where excimers can form. This diffusion process and the associated formation of excimers occurs on the time scale of hundreds of ps. The difference in the steady state spectra of films^{15,16} and the increase in PL quantum yield with generation²⁰ clearly show that these diffusive effects make up approximately 50% of the fluorescence observed and can be controlled by dendronization. Furthermore, the efficient exciton migration observed in the solid state also causes a strong reduction in PL quantum yield on going from solution

(70%) to film (approximately 10%).²⁰

At low temperatures, the clear redshift of emission spectra with time in combination with the conservation of vibronic structure (Fig. 2) indicates that the emission occurs predominantly from a single emissive species. The ADSB emissive core is known to be highly delocalized.²² A small change in conformation such as a modification of the planarity of the triphenylamine unit can result in a change in band gap.²² In the solid state a range of conformers are present with slightly different electronic levels but not necessarily different electronic and vibronic structure. The dispersive relaxation of excitations has previously been investigated in polymers,^{9,10} most recently in polyfluorenes,^{13,14} where the observed spectral redshift could be modeled by Monte Carlo simulations of Förster-type energy transfer to lower lying chain segments. It is not clear whether this model is fully justified for polymers, as interchain relaxation can occur in competition to intrachain relaxation with vastly different Förster radii. Also, on-chain migration to emissive defect sites can further complicate the interpretation in polyfluorenes.²³ In the case of dendrimers, the Förster point-dipole approximation clearly holds very well, as there is no possibility of intrachain relaxation and the Förster radius can simply be tuned by the dendrimer generation.

The relaxation times, that is, the redshift of the spectra with time, are very different for the two dendrimer generations, yet similar for both temperatures. This is consistent with Förster-type energy transfer, which should depend mainly on the Förster radius and spectral overlap, which in turn only depends slightly on temperature due to the change in molecular conformation.

We have previously shown in studies of the luminescence quantum yield and the fluorescence lifetime measured by time correlated single photon counting²⁰ that excimers are formed in the G0 dendrimer and result in a spectral broadening in the solid state with respect to the solution emission, as well as a long-lived long-wavelength emission component and a reduction in the luminescence efficiency. Excimers are known to contribute to the solid state emission properties of a wide range of organic materials, however, it is often hard to measure a luminescence rise associated with excimer formation due to the strong disorder and the resulting spectral diffusion in polymers. In the present case of dendrimers, where we have a well defined single core chromophore, we observe that the spectral shift due to spectral diffusion (Fig. 3) is much more rapid than the spectral broadening due to excimer formation (Fig. 5). This allows an extraction of the rise in excimer emission, which is clearly shown in Fig. 4. From the plot of spectral broadening against time in Fig. 5 it is seen that excimer emission does not contribute significantly to the steady state emission from G3 films, as most of the luminescence occurs prior to spectral broadening. Likewise, excimer emission does not contribute to the steady state spectra of either dendrimer generation at low temperature. We also note that excimers possess a finite mobility, which is expected to be smaller than that of the singlet exciton.²⁴ The initial excimer decay observed in Fig. 4 is rather fast and in the range of the singlet exciton lifetime in solution of 1.8 ns.²⁰ Fluorescence lifetime measurements using time-correlated single

photon counting techniques showed a long-lived multiexponential decay.²⁰ This suggests that excimers may migrate to suitable molecular conformers in the solid state which allow the formation of lower energy excimers, giving rise to an apparent reduction in excimer lifetime in the present time frame.

We note that both spectral diffusion and excimer emission contribute to spectral broadening. There is presently a debate in the literature over the relative contributions of these two processes to spectral broadening as well as the possible influence of intrachain relaxation processes.^{12,14} Conjugated dendrimers provide an excellent means of probing the relative influences of these processes and also give a single parameter—the dendrimer generation—that may be varied by simply changing the dendrons¹² without modifying the electronic structure of the molecule. As noted above, the excimer component depends sensitively on temperature, as was also recently suggested in the literature.¹² This appears to be because more planar phenylene-vinylene segments arrange in a herring-bone pattern which is less favorable for intermolecular interactions to occur.¹² The result of this is clearly seen in an analysis of the overall spectral broadening shown in Fig. 5.

We have previously reported conformational relaxation upon excitation at room temperature, leading to a redshift in emission.^{21–22} At 4 K, the molecules are more planar, and excitation does not cause further planarization. This does not exclude the presence of an energetic distribution of conformers even at low temperatures, which then give rise to the spectral redshift. The observations from Fig. 6 show that dynamic, as well as static, disorder plays an important role in spectral diffusion. As molecular relaxation occurs quasi-instantaneously with respect to spectral diffusion, migrating excitations cause a perturbation in the electronic environment, which in turn modifies the subsequent migration steps. The occurrence of dynamic disorder associated with molecular relaxation at room temperature provides a further reason for the dramatic increase in excimer emission at room temperature and the associated reduction in singlet emission lifetime seen in the inset of Fig. 2. This arises because excitations may migrate between different dendrimer sites until trapping at a lower energy excimer site, which may be created by the presence of the excitation, occurs.

The measurements presented on our conjugated dendrim-

ers allow the development of a qualitative description of relaxation dynamics as a microscopic test of previous relaxation models put forward.^{9,10,12–14} Future work should include the application of these numerical simulations to our model system to allow a quantification of the relative contributions of the different processes observed.

V. CONCLUSIONS

Intermolecular interactions are of considerable importance for the understanding of molecular organic semiconductors. By using conjugated dendrimers of different generations we have been able to distinguish between intermolecular charge and energy transfer occurring by electronic delocalisation and wave function overlap in the case of excimer formation and by excitonic energy transfer in the case of spectral diffusion, which both give rise to spectral broadening. We find that excitonic energy transfer and the associated spectral broadening occurs on shorter time scales than excimer formation. We are also able to show that Förster-type energy transfer exhibits little dependence on conformation and therefore on temperature, whereas the formation of excimers is extremely sensitive to small changes in the molecular conformation, which occur as a function of temperature. Both spectral diffusion and excimer formation play a role in the emission from organic semiconductors, as do static and dynamic disorder. Dispersive energy relaxation accurately describes the fluorescence dynamics of dendrimers in the solid state in the framework of the point-dipole approximation, however, the observation of thermally activated excimer formation shows that caution should be exercised when extrapolating from isolated chains to the spectral properties of conjugated polymers in the solid state. We conclude that dendrimers are not only very interesting materials in terms of addressing fundamental issues in the physics of organic semiconductors, but are also useful optoelectronic materials, which allow a control of intermolecular interactions as well as the intermolecular mobility of excitations.

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*Email: john.lupton@physik.uni-muenchen.de

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