

# Molecular Origin of the Temperature-Dependent Energy Migration in a Rigid-Rod Ladder-Phenylene Molecular Host\*\*

By Herbert Wiesenhofer, Egbert Zojer, Emil J. W. List, Ullrich Scherf, Jean-Luc Brédas, and David Beljonne\*

Resonance energy transfer (RET) is an ubiquitous process that can, for instance, be exploited in multicomponent device structures (containing polymer blends or molecularly doped polymer hosts) to tune the emission color of light-emitting diodes (LEDs)<sup>[1–4]</sup> or to drive photoinduced excitations towards dissociation zones in photovoltaic cells.<sup>[5]</sup> While diffusion of the electronic excitations to chemical defects or impurities is detrimental to luminescence quantum yields in LEDs,<sup>[6]</sup> it can result in efficient polymer-based (bio)chemical sensors, in which the light emission from an entire polymer chain can be quenched by a single analyte molecule.<sup>[7]</sup>

According to Bäessler and co-workers,<sup>[8]</sup> energy (or charge) transport in (disordered) conjugated polymers (CPs) occurs through a sequence of incoherent hopping steps among local-

ized chromophores with distinct excitation energies. The corresponding (usually Gaussian-shaped) density of states (DOS) provides the energy landscape for dispersive energy funneling. The energy transfer is an activated process and its temperature ( $T$ ) dependence has been interpreted on the basis of phenomenological approaches.<sup>[9]</sup> However, microscopic models for  $T$ -dependent RET taking into account the detailed chemical structure of the conjugated chains are lacking. Much effort has been recently devoted to addressing energy migration in well-defined molecular materials<sup>[10]</sup> or single polymer chains.<sup>[11]</sup> There, the inhomogeneous broadening (IB) or disorder (due to the presence of conjugated segments of various lengths) is reduced to values close to the ( $T$ -dependent) homogeneous broadening (HB). As shown for ladder-type polyparaphenylene (L-PPP) single chains,<sup>[11]</sup> raising  $T$  results in increased spectral widths, thereby enhancing energy transfer along the polymer chains (in contrast, at low  $T$ , energy transport is suppressed as a result of sharp spectral lines and, thus, small spectral overlap between emission and absorption; HB was found to become commensurate with IB at 120 K). The origin of such  $T$ -dependent linewidths and the resulting cross-over from slow to fast excitation migration are intriguing. Understanding the fundamentals of RET in CPs is of major importance for the design of a new generation of materials to be used in the optoelectronic and biochemical applications mentioned above.

Here, we provide a molecular description for the  $T$ -dependent emission lineshapes and linewidths in a model system for one of the most widely investigated class of CPs: phenylene-based ladder-type materials. On the basis of quantum-mechanical calculations combined with simulations of energy transport, we derive the  $T$  dependence of the spectral properties and determine how this impacts the dynamics of excitation diffusion in the host material. The theoretical predictions are compared to the results of experimental investigations that monitor the  $T$  dependence of energy trapping in the presence of a guest emitter. A quantitative estimate for the amount of disorder, which is central to excitation transport in CPs, is obtained.

The investigated system consists of a five-ring ladder-type paraphenylene oligomer host (hereafter referred to as 5LOPP) incorporated into an inert polystyrene matrix doped with a molecular guest that has a high luminescence quantum yield (a nine-ring polyaromatic hydrocarbon molecule, hereafter referred to as RS9),<sup>[12]</sup> at a doping level of 1 mol-% (see

[\*] Dr. D. Beljonne, Dr. H. Wiesenhofer  
Chemistry of Novel Materials, University of Mons-Hainaut  
Place du Parc 20, B-7000 Mons (Belgium)  
E-mail: David@averell.umh.ac.be

Dr. D. Beljonne, Prof. E. Zojer, Prof. J.-L. Brédas  
School of Chemistry and Biochemistry and  
Center for Organic Photonics and Electronics  
Georgia Institute of Technology  
Atlanta, GA 30332-0400 (USA)

Dr. H. Wiesenhofer, Prof. E. Zojer, Prof. E. J. W. List  
Institute of Solid State Physics, Graz University of Technology  
Petersgasse 16, A-8010 Graz (Austria)

Prof. E. J. W. List  
Christian Doppler Laboratory of Advanced Functional Materials  
Institute of Solid State Physics, Graz University of Technology  
A-8010 Graz (Austria)

Prof. E. J. W. List  
Institute of Nanostructured Materials and Photonics  
Joanneum Research, A-8160 Weiz (Austria)

Prof. U. Scherf  
Department of Chemistry, Polymer Chemistry  
University of Wuppertal  
D-42097 Wuppertal (Germany)

[\*\*] We thank J. R. Reimers for providing the program to calculate the Huang-Rhys factors in the vibronic simulations and A.-D. Schlüter for providing the guest material (RS9). The work in Mons is partly supported by the Belgian Federal Services for Scientific, Technical, and Cultural Affairs (IUAP 5/3), the Belgian National Science Foundation (FNRS) and the European Commission project NANOCHANNEL (Grant No. HPRN\_CT\_2002\_00323). D.B. is an FNRS Research Associate. The work in Graz is supported by the Spezialforschungsbereich "Elektroaktive Stoffe" (Project F917) of the Austrian Science Foundation (FWF). The work at Georgia Tech has been partly supported by NSF (STC Program DMR-0120967 and Grant CHE-0342321), ONR, and the IBM-SUR Program.

chemical structures, Fig. 1). As an observable for the efficiency of energy diffusion within the host material, the  $T$ -dependent guest emission is monitored. Our model to describe the excitation dynamics relies on the use of Fermi's Golden Rule for the calculation of energy hopping rates,  $k_{mn}$ :

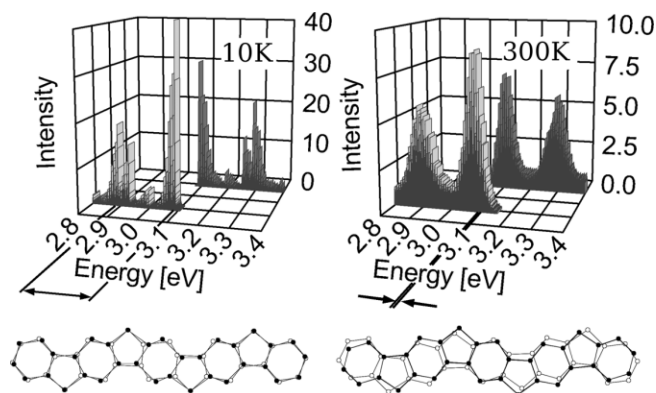
$$k_{mn} = \frac{2\pi}{\hbar} V_{mn}^2 \int_0^\infty f_m(\epsilon) a_n(\epsilon) d\epsilon \quad (1)$$

where  $\hbar$  is Planck's constant;  $V_{mn}$  denotes the electronic coupling between sites  $m$  and  $n$  and is calculated using the atomic-transition density method;<sup>[13,14]</sup>  $f_m(\epsilon)$  is the normalized emission spectrum of site  $m$ ; and  $a_n(\epsilon)$  is the normalized absorption spectrum of site  $n$  ( $m$  and  $n$  encompass both host and guest chromophores). The  $T$  dependence of the rates is contained in the spectral overlap between donor emission and acceptor absorption, evaluated here from a quantum-chemical description of the spectral lineshapes (that takes account of the chemical structure of the molecules<sup>[15]</sup>).

To model the exciton-migration dynamics under the experimental conditions described below, a  $5 \times 5 \times 4$  tetragonal unit cell containing 99 5LOPP donor molecules and one RS9 acceptor molecule (located at position (3,3,2), i.e., close to the center) was chosen as the building block for a three-dimensional (3D) periodic lattice. Positional disorder was introduced by considering random relative orientations of the molecules and fluctuations in the position of the molecular centers by up to  $\pm 1.5$  nm from the lattice points (with an average intermolecular center-to-center separation of 3.7 nm). The excited-state energies of the chromophores were picked randomly from a given Gaussian distribution to account for IB, *vide infra*. The excitation dynamics was then explored by solving Pauli master equations (PMEs) describing the time dependence of the populations on each molecular site (5LOPP as well as RS9).<sup>[16,17]</sup> The populations were generated over typically 1000 runs to average over (static) disorder.

At first, we analyzed the nature of the vibrational modes that couple to the electronic excitation in 5LOPP, as they determine the  $T$ -dependent shapes of the absorption and emission spectra. For that purpose, restricted Hartree–Fock

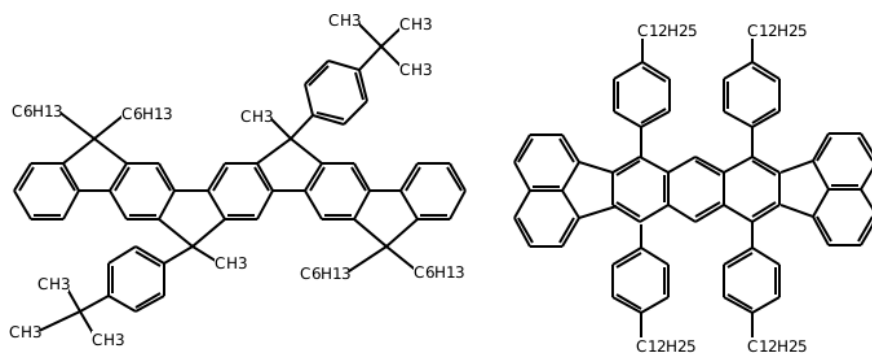
(RHF) and RHF/configuration interaction-singles (CIS) ab-initio geometry optimizations (using a 3-21G\* basis) were performed for the ground state and lowest singlet excited state of the 5LOPP molecule, respectively. The resulting structural deformations were then mapped onto the corresponding normal modes using curvilinear coordinates.<sup>[18,19]</sup> Besides the high-frequency modes associated mostly with breathing of the phenylene rings, soft modes also couple significantly to optical excitation in 5LOPP (Fig. 2); they are crucial to the  $T$ -dependent spectral shapes of the absorption and emission spectra, as they affect the “effective” homogeneous linewidths through Boltzmann-weighted population distributions in the



**Figure 2.** Top: Simulated optical spectra of 5LOPP at 10 and 300 K. (light shading: emission with vibronic sidebands; dark shading: absorption with vibronic sidebands). Bottom: Displacement patterns for the relevant vibrational modes in 5LOPP. The left pattern shows the high energy C–C bond stretching mode with a frequency of  $1604 \text{ cm}^{-1}$ . The right pattern shows the longitudinal acoustic mode with a frequency of  $57 \text{ cm}^{-1}$ , which is responsible for the  $T$ -dependent HB. The  $1604 \text{ cm}^{-1}$  mode gives rise to the vibronic progression of  $0.20 \text{ eV}$  indicated by the arrow in the top left graph; the  $57 \text{ cm}^{-1}$  mode is responsible for the more narrow progression with a line-spacing of  $0.007 \text{ eV}$  indicated by the double-arrows in the top right graph. The spectra have been renormalized on an energy scale.

corresponding vibrational manifolds (note that these soft modes cannot be resolved at room temperature (RT); therefore, HB will hereafter, in fact, refer to the full linewidth at half maximum of the envelope function encompassing the vibrational progression associated with these modes). In the rigid-rod 5LOPP molecule, the most strongly coupled low-frequency vibrations involve in-plane deformations of the bond angles, leading to an overall compression/widening of the whole molecule (see Fig. 2; these are longitudinal-acoustic modes with vanishing frequencies for infinite chain length).<sup>[20]</sup>

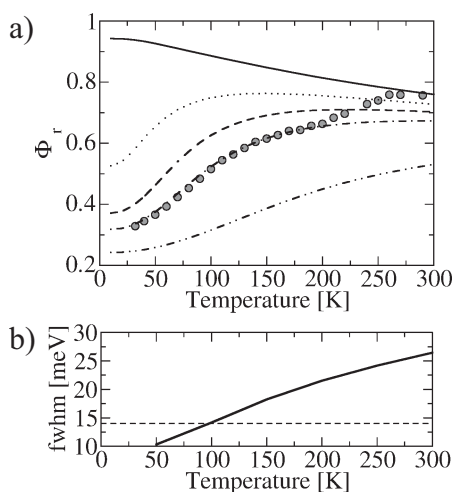
The absorption and emission spectra were then simulated within the Franck–Condon approximation using the nine most strongly coupled modes, and plug-



**Figure 1.** Molecular structures of the investigated chromophores (5LOPP left, RS9 right).

ging the frequencies (after compression with the usual factor of 0.9<sup>[21]</sup>) and Huang–Rhys factors into a displaced-harmonic-oscillator model; the resulting vibronic transitions, weighted by the transition moment squared and the appropriate frequency factors for absorption and spontaneous emission, were convoluted with Lorentzian functions. Their full width at half maximum (fwhm) linewidths were fixed at 1.2 meV, a representative value for the linewidth of single-chromophore emission in a L-PPP at 5 K<sup>[11]</sup> (consistent with dephasing times of a few hundred femtoseconds in CPs<sup>[22]</sup>).

As in polymers (although to a lesser degree), the overall widths of the absorption and emission features of molecules in the bulk are strongly influenced by the amount of inhomogeneity (static disorder), which arises primarily from chromophores lying in different local environments. This is taken here as a free parameter varied from 0 to 30 meV (standard deviation, IB) in the simulation of the spectral shapes for exciton migration, assuming a Gaussian distribution for the site energies. Using these spectral shapes to solve the PME, we can simulate the  $T$  dependence of  $\phi_r$ , the guest/host emission ratio, for different values of IB. This is shown in Figure 3a. Inspection of Figure 3a calls for the following comments: i) The relative emission arising from the guest and, hence, the efficiency for energy migration, is maximized in the absence of



**Figure 3.** a) Simulated guest/host emission ratio,  $\phi_r$ , as a function of temperature for different amounts of disorder IB (standard deviation): 0 meV (solid line), 5 meV (dotted line), 10 meV (dashed line), 14 meV (dashed-dotted line), 30 meV (dashed-dotted-dotted line). The circles represent the measured values. b) Calculated  $T$ -dependent “effective” (fwhm) homogeneous linewidth (a Gaussian function was fitted to the anti-Stokes component of the highest-energy peak of the simulated single-molecule spectra); the dashed line indicates the value of the IB, as obtained from the best fit to the experimental data in Figure 3a.

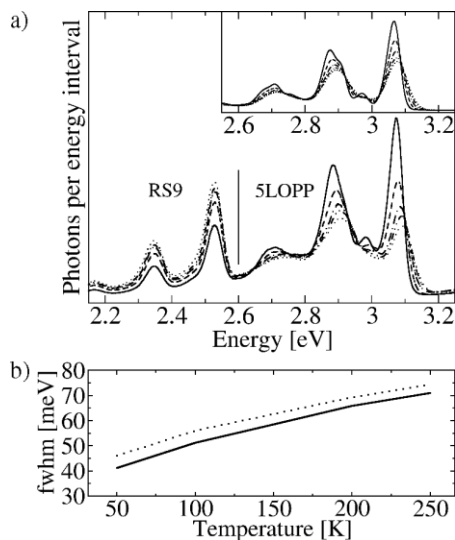
disorder and, in this case, shows a (weak) decrease with increasing temperature.<sup>[23]</sup> ii) A more conventional activated behavior (with faster excitation migration at higher temperature) is recovered when a small amount of inhomogeneity is

introduced in the simulations. iii) The evolution of  $\phi_r$  with temperature follows a sigmoid-type function, whose inflexion point,  $T_i$ , is shifted to higher  $T$  when the IB is increased.

This can be explained on the basis of the interplay between the effective HB and IB and the resulting spectral overlap: i) In the limiting case of zero disorder, the spectral overlap between two host molecules at low  $T$  is mainly dominated by the 0–0 phonon lines in emission and absorption. Increasing  $T$  leads to a broadening of the spectra, as vibrational excited levels get thermally populated (compare Fig. 2, left and right). As a consequence, the absorption/emission intensity is shifted away from the 0–0 line, which, therefore, results in a decreased spectral overlap.<sup>[23]</sup> ii) The picture changes significantly in the presence of energetic disorder, which is accounted for here by introducing a shift between donor emission and acceptor absorption. Indeed, in such a case, the spectral overlaps also include contributions from thermally activated vibrational sidebands (provided the excess vibrational energy is commensurate with the magnitude of the energetic disorder, i.e., the rigid shift between the absorption and emission spectra). In a more phenomenological picture, energy transfer is now an activated process (its efficiency increases with  $T$ ), as thermal energy is required to overcome the barriers induced by the fluctuations in site energies. iii) The apparent “cross-over” between “slow” and “fast” migration takes place at a temperature for which HB (i.e., the fwhm of the HB) of the single-molecule spectra reaches the energetic spacing between chromophores expressed by IB, the standard deviation of the Gaussian distribution of site energies,<sup>[24]</sup> hence the increase in  $T_i$  with increasing IB (Fig. 3b).

To verify the theoretical predictions, blends of 5LOPP and RS9 (1%) were prepared from toluene solutions and embedded in an optically inert polystyrene matrix (in a 1:8 weight ratio). The steady-state  $T$ -dependent photoluminescence (PL) spectra measured for the guest–host–matrix system (Fig. 4a) clearly show that an increase in  $T$  results in an increased relative contribution of the RS9 emission (in the spectral range 2.3–2.6 eV) at the expense of the 5LOPP donor emission (from  $\sim 2.7$  to 3.2 eV). This is fully consistent with enhanced diffusion, with increasing  $T$ , of the electronic excitations within the host, followed by trapping at guest sites.

As shown in Figure 3a, the measured ratio  $\phi_r$  between the guest and host emissions (for spectra integrated over the range quoted above) is in excellent agreement with the simulations for an IB of 14 meV.  $\phi_r$  is found to decrease from  $\sim 0.75$  at 300 K to  $\sim 0.32$  at 32 K, indicating substantial slowing of the excitation migration in 5LOPP upon cooling. It is remarkable to note that the measured evolution from “slow” to “fast” migration in Figure 3a follows the predicted sigmoid-like dependence, with  $T_i \sim 100$  K, i.e., the temperature for which HB and IB are of comparable magnitude (Fig. 3b). These results are fully consistent with those obtained from single-molecule spectroscopic investigations of a ladder-type phenylene polymer.<sup>[11]</sup> The origin of the deviations between theory and experiments for  $T > 230$  K are not fully understood yet. Concentration-dependent measurements, however, allow us to rule out effects related to self-absorption.



**Figure 4.** a) Measured PL spectra (photons per energy interval normalized to unit area) as a function of  $T$  in a 1:100 RS9/5LOPP blend. The inset shows the simulated emission spectra of the host material as a function of  $T$  for a disorder IB (standard deviation) of 14 meV (50 K (solid line), 100 K (dashed line), 150 K (dashed-dotted line), 200 K (dashed-dotted-dotted line), 250 K (dotted line)). b) Simulated (solid line) and experimental (dotted line) total linewidths of the highest-energy peak in the 5LOPP PL spectra.

The detailed shape of the measured emission spectrum and the changes upon cooling are very well accounted for by the simulations when considering a value of 14 meV for the static disorder (Fig. 4a). In particular: i) the  $T$ -dependent measured and calculated PL linewidths (Fig. 4b) are found to be in excellent agreement; and ii) the inhomogeneity of the site energies (i.e., the IB) results in the same blue-shift with temperature (by about 15 meV from 50 to 300 K) according to experiment and theory. While the excitations only explore the bottom of the DOS at low  $T$ , they can use their excess thermal energy to access higher-lying points of the energy landscape of the chromophore-energy distribution at higher temperature.

Thus, to the best of our knowledge, our model provides, for the first time, an unambiguous correlation between the detailed chemical structure of the conjugated chains, the resulting  $T$ -dependent spectral lineshapes, and the diffusion dynamics.

To summarize, the temperature-dependent homogeneous broadening in the phenylene-based 5LOPP molecular host has been rationalized in terms of coupling of the electronic excitations to specific low-frequency vibrational modes. Taking a value of 14 meV for the amount of energetic disorder in 5LOPP, excellent agreement between experiment and theory is found for the evolution of the energy-transfer efficiency with  $T$ . The detailed  $T$ -dependent spectral lineshape and linewidth in the simulated emission spectra also agree remarkably well with experiment. The rate of RET is determined by the interplay between the temperature-dependent HB and the constant IB: at low  $T$ ,  $HB \ll IB$ , the donor emission and ac-

ceptor absorption spectra are sharp and well-separated, and excitation motion is slow because of small spectral overlap; at high  $T$ ,  $HB \sim IB$ , and in the presence of disorder, the spectral overlap is larger, resulting in faster hopping rates. Importantly, our work provides a simple molecular framework for the origin of the temperature dependence of the spectral lineshapes and the resulting energy-transfer efficiency in a model system for ladder-type conjugated polymers. The same methodology can be applied to other molecular architectures of interest, aiming at the design of conjugated materials with more efficient energy diffusion. Work is in progress along this line.

## Experimental

The blend of 5LOPP and RS9 (1 %) was prepared from toluene solution and embedded in an optically inert polystyrene matrix (in a 1:8 weight ratio). The material was spin-cast on a quartz-glass substrate and mounted on a closed-cycle cold-finger helium cryostat to allow variation of the temperature between room temperature and 32 K. The experimental spectra were recorded in high vacuum by illuminating the sample with a Coherent/Innova 300 Ar<sup>+</sup> Laser operated in multiline UV mode (3.53 eV, 3.41 eV) using an Oriol/Andor charge-coupled device (CCD)-spectrometer calibrated with an Oriol/Pen Ray lamp [25].

Received: July 18, 2005

Final version: October 12, 2005

Published online: January 3, 2006

- [1] S. Tasch, E. J. W. List, O. Ekström, W. Graupner, G. Leising, P. Schlichting, U. Rohr, Y. Geerts, U. Scherf, K. Müllen, *Appl. Phys. Lett.* **1997**, *71*, 2883.
- [2] T. Virgili, D. G. Lidzey, D. D. C. Bradley, *Adv. Mater.* **2000**, *12*, 58.
- [3] P. A. Lane, L. C. Palilis, D. F. O'Brien, C. Giebeler, A. J. Cadby, D. G. Lidzey, A. J. Campbell, W. Blau, D. D. C. Bradley, *Phys. Rev. B* **2001**, *63*, 235 206.
- [4] A. Pogantsch, G. Trattnig, G. Langer, W. Kern, U. Scherf, H. Tillmann, H.-H. Hörhold, E. Zojer, *Adv. Mater.* **2002**, *14*, 1722.
- [5] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, *Nature* **1995**, *376*, 498.
- [6] E. J. W. List, R. Guentner, P. Scanducci de Freitas, U. Scherf, *Adv. Mater.* **2002**, *14*, 374.
- [7] L. Chen, D. W. McBranch, H.-L. Wang, R. Helgeson, F. Wudl, D. G. Whitten, *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 12287.
- [8] H. Bässler, B. Schweitzer, *Acc. Chem. Res.* **1999**, *32*, 173.
- [9] A. Miller, E. Abrahams, *Phys. Rev.* **1960**, *120*, 745.
- [10] F. J. M. Hoeben, L. M. Herz, C. Daniel, P. Jonkheijm, A. P. H. J. Schenning, C. Silva, S. C. J. Meskers, D. Beljonne, R. T. Phillips, R. H. Friend, E. W. Meijer, *Angew. Chem. Int. Ed.* **2004**, *116*, 2010.
- [11] J. G. Müller, U. Lemmer, G. Raschke, M. Anni, U. Scherf, J. M. Lutpon, J. Feldmann, *Phys. Rev. Lett.* **2003**, *91*, 267 403.
- [12] E. Zojer, U. Rant, P. Buchacher, R. Müllner, F. Stelzer, F. Wudl, N. Schulte, A.-D. Schlüter, G. Leising, J.-L. Brédas, *Mater. Res. Soc. Symp. Proc.* **1999**, *598*, BB3.72.1.
- [13] The corresponding electronic transitions are calculated with the semiempirical INDO/SCI method, see, e.g., J. Ridley, M. C. Zerner, *Theor. Chim. Acta* **1973**, *32*, 111, on the basis of the RHF ab initio ground-state geometries. An active space including all  $\pi$ -orbitals was used in these calculations. In addition it should be noted that the electronic couplings can be assumed to be essentially temperature independent (as thermally activated intermolecular vibrations have a negligible effect due to the large interchromophore distances);

thus, details of the  $V_{mn}$  calculations do not affect the overall conclusions.

- [14] D. Beljonne, J. Cornil, R. Silbey, P. Millie, J.-L. Brédas, *J. Chem. Phys.* **2000**, *112*, 4749.
- [15] We note that, for the sake of simplicity, the optical absorption spectrum of the RS9 molecule is approximated by the spectrum calculated for 5LOPP red-shifted by 0.56 eV (the value derived from the experimental spectra).
- [16] V. May, O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems*, Wiley-VCH, Weinheim, Germany **1999**.
- [17] In the PME simulations, the following radiative lifetimes have been used: 1.1 ns (5LOPP) and 5.1 ns (RS9); typical values for the electronic couplings (for two donor molecules at a separation of 3.7 nm) are:  $V \approx 14 \text{ cm}^{-1}$  (cofacial configuration) and  $V \approx 38 \text{ cm}^{-1}$  (head-to-tail configuration); and typical values for the transfer rates at room temperature (300 K) for a distance of 3.7 nm and without disorder are:  $k \approx 20 \text{ ns}^{-1}$  (cofacial configuration) and  $k \approx 153 \text{ ns}^{-1}$  (head-to-tail configuration). Note, however, that these values can vary significantly with static disorder.
- [18] J. R. Reimers, *J. Chem. Phys.* **2001**, *115*, 9103.
- [19] To account for the side chains in the calculations, the mass of all hydrogen atoms on the bridging groups has been artificially increased from 1 to 75 amu, i.e., the approximate size of the long alkyl and aryl groups. We stress that a similar picture is obtained when actually neglecting the side chains. Increasing the effective masses of the H atoms on the bridging groups leads to reduced vibrational frequencies for the soft modes and PL spectral linewidths in better agreement with experiment.
- [20] J. Gierschner, H. G. Mack, L. Luer, D. Oelkrug, *J. Chem. Phys.* **2002**, *116*, 8596.
- [21] J. B. Foresman, A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd ed., Gaussian, Inc., Pittsburgh, PA **1996**.
- [22] S. P. Kennedy, N. Garro, R. T. Phillips, *Phys. Rev. Lett.* **2001**, *86*, 4148.
- [23] For the hypothetical case of zero disorder, the overall temperature-dependent migration dynamics is also affected by the last hopping step to the RS9 molecule and is sensitive to the value of HB.
- [24] According to numerical simulations, the expectation value of the energetic spacing between Gaussian distributions of donor and acceptor site energies amounts to  $\sim 1.13$  times the standard deviation of the Gaussian function.
- [25] Note that direct excitation of the RS9 molecule cannot be avoided as its absorption into higher-lying electronically excited states overlaps with the 5LOPP absorption. However, the influence of direct RS9 absorption is small as a result of the low concentration of the acceptor.