

Single-Molecule Spectroscopy of Uniaxially Oriented Terrylene in Polyethylene

Jacqueline Y. P. Butter,^[a] Brent R. Crenshaw,^[b] Christoph Weder,^[b] and Bert Hecht^{*[a]}

Single terrylene molecules doped into linear low-density polyethylene can be oriented by tensile deformation of the matrix. In measurements on ensembles at ambient and on single terrylene molecules at cryogenic temperature, strong orientation along the stretching direction was observed by polarization-resolved confo-

cal microscopy. At cryogenic temperatures narrow and spectrally stable zero-phonon lines were found. The low saturation intensity of 0.07 W cm^{-2} is consistent with an uniaxial orientation of terrylene in the sample plane.

Introduction

Single-molecule fluorescence excitation spectroscopy of various guest molecules in numerous matrices at cryogenic temperature has been used extensively to probe low-temperature dynamics of the matrix materials.^[1–3] Such studies exploit the sensitivity of the molecular zero-phonon line towards changes in the environment of the fluorescent guest molecules. In highly ordered materials the distribution of spectroscopic parameters due to environmental influences can be minimized and, as a consequence, single molecules at cryogenic temperatures behave as nearly ideal, rigidly fixed two-level quantum systems (TLSs). The latter feature makes them attractive model systems for a range of quantum optical experiments in which the position and absorption dipole orientation of the TLS must be well defined; for example, they may be precisely coupled to photonic structures such as cavities^[4] or antennas.^[5,6] In addition, a favorable orientation results in a maximum absorption cross-section, a high emission rate, and a high fluorescence collection efficiency.^[7]

Since the first detection of single molecules at cryogenic temperatures,^[8,9] a selection of possible matrices has been introduced,^[2,3] such as molecular crystals, Shpol'skii matrices, and amorphous or semicrystalline polymers. Unfortunately, none of the previously used systems combines all desirable features. In particular, the orientation of the transition dipole moments of guest molecules usually tends to be either random or particularly unfavorable, which leads to weak optical absorption in the latter case. Unfortunately, the host systems that show the least environmental influence on the single-molecule behavior, that is, the molecular crystals, either i) tend to incorporate the guest molecules in a way such that the molecular transition dipole moments are nearly parallel to the optical axis (terrylene in single crystals^[10,11] and more recently in ultrathin films of *p*-terphenyl^[12]), or ii) the molecules exhibit long triplet lifetimes (pentacene in *p*-terphenyl^[13]), or iii) the samples are delicate to

prepare and to handle (terrylene in naphthalene^[14]). For the first two cases this leads to unfavorably high saturation intensities due to a reduced absorption cross-section and to a low emission rate, respectively.

Mechanical treatment of polymeric materials, such as tensile deformation or rubbing, can be used to induce a high degree of uniaxial orientation of the polymer matrix, and likewise of form-anisotropic fluorescent guest molecules incorporated therein.^[15–17] Recent room-temperature experiments on uniaxially oriented films of ultrahigh molecular weight polyethylene (UHMWPE) doped with a poly(2,5-dialkoxy-*p*-phenylene ethynylene) derivative (EHO-OPPE)^[18] have shown that even at the single-molecule level, the (in this case polymeric) fluorescent guest molecules tend to adopt the preferential orientation of the surrounding matrix after uniaxial tensile deformation of the sample.

Terrylene in polyethylene is a well-known guest–host system that exhibits narrow zero-phonon excitation lines at cryogenic temperatures.^[19–22] Interestingly, all previous studies on this system were performed on disordered materials. We showed earlier that conventional melt-processing and subsequent tensile deformation of the resulting molecularly mixed blends of linear low-density polyethylene (LLDPE) and form-anisotropic fluorescent guest molecules allows thin films to be produced

[a] J. Y. P. Butter, Prof. Dr. B. Hecht
Nano-Optics Group, National Center of Competence
for Research in Nanoscale Science
Institute of Physics, University of Basel
Klingelbergstr. 82, 4056 Basel (Switzerland)
Fax: (+41) 61-267-3795
E-mail: bert.hecht@nano-optics.ch

[b] B. R. Crenshaw, Prof. Dr. C. Weder
Department of Macromolecular Science and Engineering
Case Western Reserve University
2100 Adelbert Road, Cleveland, Ohio 44106-7202 (USA)

in which the guest molecules adopt a very high degree of uniaxial orientation.^[17] Here we present the first single-molecule spectroscopic study of highly oriented terylene-doped LLDPE samples. The orientational distribution, stability, line width, and saturation properties of terylene molecules at 1.8 K and, where applicable, under ambient conditions are reported. Our results indicate that tensile deformation leads to uniaxially oriented terylene molecules with microenvironments that show enhanced local ordering and/or a decreased significance of local vibrational degrees of freedom.

Experimental Section

Commercial-grade LLDPE containing 1.2% octene as a comonomer was received from Dow Chemical Company (Dowlex BG 2340, $\rho = 0.942 \text{ g cm}^{-3}$). A binary blend of LLDPE and terylene (40 $\mu\text{g dye/g polymer}$) was prepared by feeding 100 μg of terylene and 2.5 g of LLDPE into a recycling, corotating twin-screw mini-extruder (DACA Instruments, Santa Barbara, CA), mixing for 5 min at 180 °C, and subsequent extrusion. A second blend containing 1 $\mu\text{g dye/g polymer}$ was subsequently prepared by combining 62.5 mg of the 40 $\mu\text{g dye/g polymer}$ blend with 2.44 g of neat LLDPE and extruding the material in the same manner. Films were prepared by compression-molding the blends between two aluminum foils with four spacers in a Carver press at 180 °C for 4 min. Samples were subsequently cooled to about 15 °C between water-cooled plates. The resulting films had a homogeneous thickness of about 250 μm . Films were cut to 1 cm widths and uniaxially stretched at 90 °C to a draw ratio $\lambda = (l - l_0)/l_0 = 10$, as measured by the displacement of ink marks on the samples.

Thin films of terylene-doped LLDPE with $\lambda = 10$ and a thickness of about 80 μm were investigated by polarization-resolved fluorescence scanning confocal optical microscopy and spectroscopy. The samples were mounted between two microscopy coverslips, which were held together by two tiny drops of vacuum grease, placed far away from the sample. The home-built scanning confocal microscope was designed for operation at both room temperature and 1.8 K.^[23] A single-mode ring dye laser (Coherent 699-21, Rhodamine 6G) with a bandwidth of about 1 MHz operating at wavelengths between 569.5 and 571 nm, pumped by an argon ion laser, was used as excitation light source. This range of wavelengths is sufficiently close to the absorption maximum of the terylene-doped LLDPE films, which was measured in an ensemble experiment to be at 566 nm under ambient conditions. The output power of the laser was stabilized by a power stabilizer (CRI LS100)

and collimated to a beam of 10 mm in diameter. The diameter of the laser beam exceeded that of the entrance aperture of the microscope objective. A $\lambda/2$ plate was used to control the direction of the electromagnetic field vector of the linearly polarized light, and a 1-nm-wide bandpass filter for spectral filtration. A glass wedge was used at a small angle of incidence to reflect a small fraction (4%) of the excitation light into a bath cryostat. The excitation light was focused onto the sample by a microscope objective (Microthek, 0.85 NA, 60 \times) which, as the sample, resided directly in the liquid helium.

The fluorescence and resonantly scattered light were collected via the same objective and transmitted by the wedge (96% transmission). The light was filtered by a holographic notch filter, and the Stokes-shifted fluorescence was focused on an avalanche photodiode (SPCM-AQR13). At cryogenic temperatures, fluorescence excitation spectra over a range of up to 25 GHz were recorded by scanning the laser frequency. Alternatively, the sample was scanned over a range of up to $34 \times 34 \mu\text{m}^2$ with an improved home-built bimorph scanner, also placed within the helium bath.^[23] At room temperature, the same sample scanner had a ten-times-larger range and thus allowed sample scans of $340 \times 340 \mu\text{m}^2$.

Results and Discussion

A typical $340 \times 340 \mu\text{m}^2$ fluorescence excitation image of an LLDPE film containing 1 $\mu\text{g g}^{-1}$ of terylene recorded at ambient temperature is displayed in Figure 1A. Highly fluorescent, stripelike structures with intermittent darker areas oriented

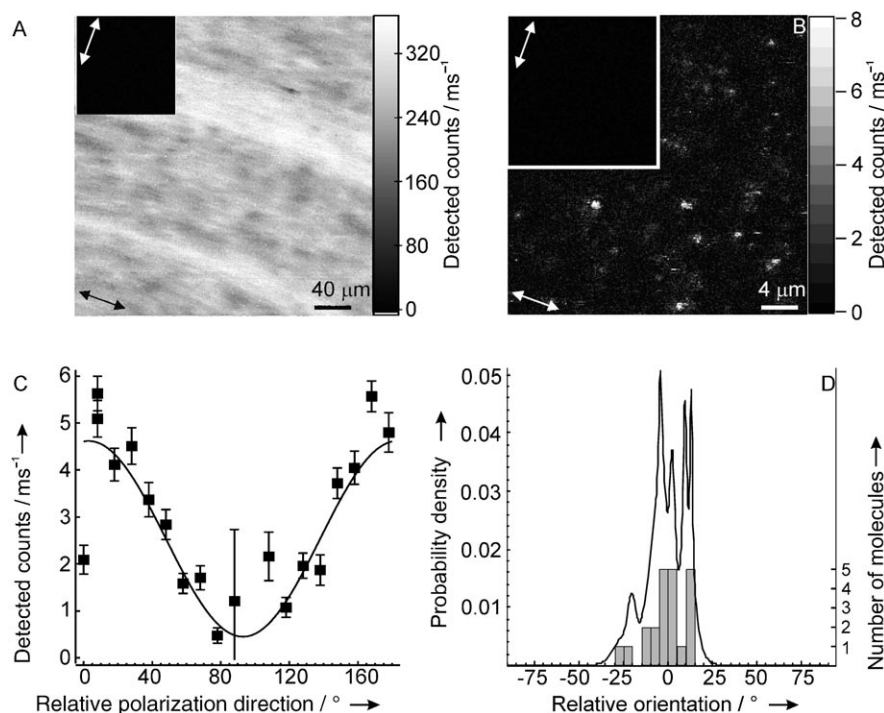


Figure 1. A) Scanning confocal optical image of a stretched ($\lambda = 10$) film of LLDPE containing 1 $\mu\text{g g}^{-1}$ of terylene at room temperature. The arrows denote the polarization direction. B) Scanning confocal optical image of the same film at 1.8 K. The integration time in A) and B) was 2.6 ms per pixel. Insets in A) and B): excitation with the polarization turned by 90°. C) Modulation of the fluorescence of a single terylene molecule as a function of the polarization. D) Left axis (solid line): Probability density function of finding a single terylene molecule with a certain orientation. Right axis (bars): histogram of the orientation of the molecules.

parallel to the direction of tensile deformation (hereafter referred to as orientation direction of the film) are observed.^[18] For this experiment, the orientation direction of the film was chosen to coincide with the direction of the electromagnetic field vector of the linearly polarized excitation light, which is used as a reference direction (relative polarization 0°) in the following. The inset shows the emission for excitation with light polarized perpendicularly to the film's stretching direction. The pronounced contrast of these images reflects the high degree of orientation of an ensemble of terrylene molecules in the stretched LLDPE film. Similar images with the same depth of modulation obtained on different parts of the film indicated macroscopic homogeneity of the sample. Although these measurements only allow a definite assignment of the orientation of the absorption dipole projected onto the sample plane, it is perspicuous that possible out-of-plane components are small.

The single-molecule detection level was not reached due to the broad absorption lines at ambient temperature, but the same sample was used for further studies at cryogenic temperatures, where single molecules with narrow zero-phonon lines were addressed by fluorescence excitation spectroscopy.

Figure 1B shows a typical $34 \times 34 \mu\text{m}^2$ fluorescence excitation image of the same sample with the same polarization directions at 1.8 K. It exhibits well-separated diffraction-limited fluorescence spots of variable intensity for parallel polarized excitation (0°) with respect to the orientation direction of the film, but no spots could be observed upon excitation with perpendicularly polarized light. To investigate this preferential orientation in more detail, a series of images was acquired by changing the polarization direction of the excitation light in 18 steps of 10° . Only molecules that could be observed in the entire series of images were selected for further analysis. The orientation of the transition dipole moment of these molecules was determined by fitting the spots observed in the images to two-dimensional Gaussian functions with Igor Pro (Wavemetrics). The amplitude of the resulting two-dimensional Gaussians was then plotted as a function of relative polarization. An example is shown in Figure 1C. The data were fitted with a \cos^2 function, which allows us to determine the extremes. A minimum around 90° and a maximum around 0° can be observed. The result of each fitting procedure can be used to construct a probability density function (PDF) that specifies the probability for measuring a certain orientation of the transition dipole moment of a molecule. The normalized sum of all the PDFs obtained for different molecules results in an overall PDF that characterizes the probability of finding a molecule with a certain orientation in the sample (see Figure 1D). The overall PDF exhibits a clear maximum around 0° , which indicates that the probability of finding molecules with a transition dipole moment outside the interval $[-40^\circ, 25^\circ]$ is virtually zero. The narrow peaks displayed by the overall PDF are due to the fact that even the transition dipole moments of well-oriented molecules show a slight deviation from the orientation direction of the sample. For example, the data shown in Figure 1C translate into an offset of $3 \pm 1^\circ$ with respect to the film axis.

Another important property of a single-molecule system, in particular in view of quantum optics experiments, is the stability of the absorption frequency of single molecules over time. In polymers and glasses the stability of the absorption frequency is deteriorated by local degrees of freedom, which at cryogenic temperature can be modeled by two-level tunneling systems that interact with the molecule via electric or strain fields.^[1] To investigate the spectral stability, repeated 10 GHz frequency scans were performed for about 75 min while recording the fluorescence. The result of this experiment is shown in Figure 2. The excitation intensity was adjusted to be

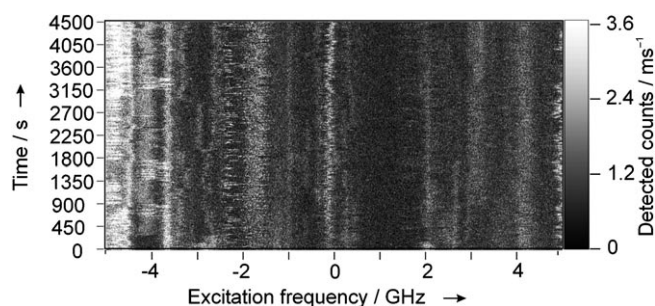


Figure 2. Repeated fluorescence excitation scan to monitor the stability of single molecules over more than 1 h. Most molecules show a high degree of photostability. Some small jitter in the absorption frequencies of individual molecules can be observed. Only a few molecules undergo spectral jumps (e.g., the molecule at -3.4 GHz jumps to -3.0 GHz and back). The integration time was 8.5 ms per pixel.

far below saturation in order to minimize photoinduced frequency jumps of the molecules. Figure 2 reveals a number of interesting features displayed by the terrylene molecules in an oriented LLDPE matrix. First, most of the molecules can be followed during the entire experiment, which means that no major frequency jumps take place. Second, the molecules are relatively stable in their absorption frequencies, staying all the time relatively close to the original value. Third, the molecules can be divided into two groups, according to the ranges in which the absorption frequencies vary. The absorption frequency of one group of molecules varies in a range of 130–160 MHz, while the other group of molecules shows variations of 300–450 MHz in their absorption frequency. Similar fluctuations over a spectral range of 50–400 MHz were reported by Tchénio et al.^[21] However, it is not clear whether different ranges of fluctuations for different molecules were observed in this prior work. Finally, only few molecules undergo larger discontinuous frequency jumps, irrespective of the line width. Examples are the molecule at -3.4 GHz that jumps to -3.0 GHz and back and the molecule at -4.8 GHz that jumps several times to -4 GHz and back. However, larger jumps over several GHz, as those reported in ref. [21], were not observed in our stretched samples. In conclusion, the stability of the absorption frequency of the molecules in the present system does not reach that of crystalline matrices of low-molecular-weight organic compounds (e.g., see ref. [24]), but single molecules can very well be excited and followed over extended periods of time.

We further investigated the saturation properties of terylene guest molecules in the oriented LLDPE matrix. Saturation properties are relevant to achieving optimized experimental conditions, and they can provide some insight into the out-of-plane component of the orientation of the molecular transition dipole moment.^[7] Saturation data of single terylene molecules were extracted from repeated frequency scans while varying the excitation power. Typically, 5–10 frequency scans were recorded for each excitation power. From these spectra the emission rates and the line widths of single molecules were determined by fitting to a Lorentzian line shape. Due to fluctuations in the absorption frequency of the molecules, the line width and emission rate vary for one and the same molecule in separate frequency scans. For this reason, the values determined from at least five spectra with the same excitation intensity were averaged, and the standard deviations were taken as a measure for the uncertainties in these values. An example of saturation data is shown in the inset of Figure 3A. The fit was

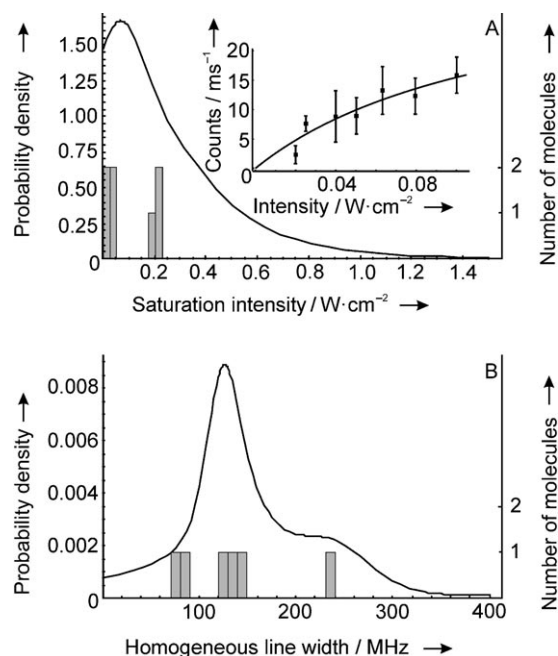


Figure 3. A) Probability density (solid line, left axis) of finding a molecule with a given saturation intensity. The inset shows a typical saturation curve of the detected emission rate vs. excitation intensity. Data points were obtained from the average of the detected emission rates of at least five frequency scans. The histogram (gray bars, right axis) shows the distribution of saturation intensities. B) The solid line, left axis, shows the probability density of finding a molecule with a given line width, and the histogram (gray bars, right axis) shows which line widths were found. The most probable homogeneous line width is clearly broader than the lifetime-limited line width. A shoulder at 200 MHz suggests the existence of a second population of molecules in less favorable environments.

weighted by the uncertainties of the individual data points and yielded the saturation intensity and the maximum emission rate with the respective uncertainties.

From the individual values of saturation intensity and homogeneous line widths with respective uncertainties, again overall

PDFs were constructed, as shown in Figure 3A and B. The most probable saturation intensity is at $I = 0.07 \text{ W cm}^{-2}$ and the most probable homogeneous line width is 126.3 MHz. The shoulder in the line-width distribution around 200 MHz is consistent with the above discussion of Figure 2. The probability density for line widths below the lifetime limit (about 50 MHz) is not zero, due to the uncertainties in the homogeneous line widths, which are caused by spectral jumping of the molecules during the time of a scan.

The high degree of optical anisotropy displayed by the oriented terylene-doped LLDPE samples and the fact that the absorption maxima of terylene ensembles and single terylene molecules coincide with the orientation direction of the sample clearly indicate that the terylene molecules are oriented with their geometric long axis parallel to the sample axis and that the optical transition dipole moment of terylene matches with the geometric long axis of the molecule, in agreement with ref. [25]. The data further suggest that the off-axis components of the transition dipole of terylene are very small. The films display so-called "fiber symmetry". While all the terylene molecules are oriented with their long axes parallel to the orientation direction, they can freely rotate around this axis. So the "planes" of the terylene molecules are not parallel to the film plane, but rotate around the long axis. However, the projected dipole moment of a single terylene molecule is identical if looked at from the "face" and from the "edge". This finding is further supported by the analysis of the saturation intensity (see above), which is not only important from an experimental point of view, but also provides some insight into the three-dimensional orientation of the fluorescent molecules with respect to the laboratory coordinates.^[7] Indeed, the intrinsic saturation intensity of terylene, that is, of a single molecule oriented parallel to a substrate, was estimated to be $80 \pm 30 \text{ mW cm}^{-2}$. Gratifyingly, the saturation intensity of 70 mW cm^{-2} that we experimentally determined in the present study is in good agreement with this value, consistent with the fact that the terylene molecules in uniaxially deformed samples indeed have negligible out-of-plane transition dipole components. This architecture results in an optimized absorption cross-section.

The range of observed homogeneous line widths in our stretched LLDPE samples is comparable to the values reported in the literature for disordered guest–host systems of terylene and different polyethylenes.^[20,21] The most probable homogeneous line width that we determined in the present study is close to the average homogeneous line width reported for terylene incorporated in a disordered high-density polyethylene matrix,^[20] and slightly broader than the most frequently observed homogeneous line width found for the latter system. On the other hand, the most probable homogeneous line width determined here is at the lower limit and partly below the range quoted for terylene dispersed in a low-density polyethylene.^[21] This suggests that the terylene molecules in our stretched films of LLDPE experience a local environment which is more ordered than in low-density polyethylene.^[21] In fact, the local order is comparable to that found in higher density, that is, more crystalline, polyethylene,^[20] but with the impor-

tant additional feature that the terrylene molecules are all lined up.

Conclusions

We have discussed single-molecule spectroscopy of terrylene molecules in uniaxially oriented films of LLDPE. Using single-molecule spectroscopy and microscopy techniques at ambient and cryogenic temperature, we demonstrated that these films are suited for single-molecule experiments down to cryogenic temperatures. Most importantly, the terrylene molecules were found to be uniaxially aligned along a macroscopic direction that coincides with the macroscopic direction of deformation imposed on the film. The observed orientation is of particular interest for experiments that require an optimized absorption cross-section. The observed range of line widths suggests that the local environment seen by individual terrylene guest molecules is increased by the deformation process.

Acknowledgments

The authors gratefully acknowledge H.-J. Güntherodt for his continuous support and S. Karotke and A. Lieb for stimulating discussions and experimental support. B.R.C. and C.W. gratefully acknowledge financial support from the Petroleum Research Funds (ACS-PRF 38525-AC7). This material is based upon work supported by the National Science Foundation under Grant No. 0428208. J.Y.P.B. and B.H. gratefully acknowledge financial support by the Swiss National Science Foundation via the National Center of Competence in Research (NCCR) in Nanoscale Science and a research professorship for B.H.

Keywords: dyes/pigments · fluorescence spectroscopy · host-guest systems · polymers · single-molecule studies

- [1] *Single-Molecule Optical Detection, Imaging and Spectroscopy* (Eds.: T. Basché, W. E. Moerner, M. Orrit, U. P. Wild), VCH, Weinheim, **1997**.
- [2] T. Plakhotnik, E. A. Donley, U. P. Wild, *Annu. Rev. Phys. Chem.* **1997**, *48*, 181–212.
- [3] Ph. Tamarat, A. Maali, B. Lounis, M. Orrit, *J. Phys. Chem. A* **2000**, *104*, 1–16.
- [4] A. Badolato, K. Hennessy, M. Atatüre, J. Dreiser, E. Hu, P. M. Petroff, A. Imamoğlu, *Science* **2005**, *308*, 1158–1161.
- [5] P. Mühlischlegel, H.-J. Eisler, O. J. F. Martin, B. Hecht, D. W. Pohl, *Science* **2005**, *308*, 1607–1609.
- [6] J. N. Farahani, D. W. Pohl, H.-J. Eisler, B. Hecht, *Phys. Rev. Lett.* **2005**, *95*, 017402.
- [7] T. Plakhotnik, W. E. Moerner, V. Palm, U. P. Wild, *Opt. Commun.* **1995**, *114*, 83–88.
- [8] W. E. Moerner, L. Kador, *Phys. Rev. Lett.* **1989**, *62*, 2535–2538.
- [9] M. Orrit, J. Bernard, *Phys. Rev. Lett.* **1990**, *65*, 2716–2719.
- [10] S. Kummer, F. Kulzer, R. Kettner, T. Basché, C. Tietz, C. Glowatz, C. Krysch, *J. Chem. Phys.* **1997**, *107*, 7673–7684.
- [11] P. Bordat, R. Brown, *J. Chem. Phys.* **2002**, *116*, 229–236.
- [12] R. J. Pfab, J. Zimmermann, C. Hettich, I. Gerhardt, A. Renn, V. Sandoghdar, *Chem. Phys. Lett.* **2004**, *387*, 490–495.
- [13] J. Bernard, L. Fleury, H. Talon, M. Orrit, *J. Chem. Phys.* **1993**, *98*, 850–859.
- [14] H. Bach, *PhD thesis*, ETH Zürich, **1998**.
- [15] J. Michl, E. W. Thulstrup, *Spectroscopy with Polarized Light*, 1st ed., VCH, Weinheim, **1986**.
- [16] M. Grell, D. D. C. Bradley, *Adv. Mater.* **1999**, *11*, 895–905.
- [17] M. Eglin, A. Montali, A. R. A. Palmans, T. Tervoort, P. Smith, C. Weder, *J. Mater. Chem.* **1999**, *9*, 2221–2226.
- [18] W. Trabesinger, A. Renn, B. Hecht, U. P. Wild, A. Montali, P. Smith, C. Weder, *J. Phys. Chem. B* **2000**, *104*, 5221–5224.
- [19] M. Orrit, J. Bernard, A. Zumbusch, R. I. Personov, *Chem. Phys. Lett.* **1992**, *196*, 595–600.
- [20] L. Fleury, A. Zumbusch, M. Orrit, R. Brown, J. Bernard, *J. Lumin.* **1993**, *56*, 15–28.
- [21] P. Tchénio, A. B. Myers, W. E. Moerner, *J. Lumin.* **1993**, *56*, 1–14.
- [22] E. A. Donley, T. Plakhotnik, *J. Chem. Phys.* **2000**, *113*, 9294–9299.
- [23] J.-M. Segura, A. Renn, B. Hecht, *Rev. Sci. Instrum.* **2000**, *71*, 1706–1711.
- [24] S. Kummer, T. Basché, C. Bräuchle, *Chem. Phys. Lett.* **1994**, *229*, 309–316.
- [25] J. Sepioł, J. Jasny, J. Keller, U. P. Wild, *Chem. Phys. Lett.* **1997**, *273*, 444–448.

Received: July 22, 2005

Revised: October 11, 2005

Published online on December 19, 2005