

Directional energy migration in an oriented nanometer-scale host/guest composite: semiconducting polymers threaded into mesoporous silica

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Abstract

In this paper, we show that the semiconducting polymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) can be incorporated into the channels of an aligned mesoporous silica host. Polarized fluorescence spectroscopy is used to show that more than 80% of the polymer in the composite is aligned by incorporation into the host. Time-resolved transient absorption spectroscopy further indicates that the incorporated chains are isolated from each other, while the unincorporated polymer is aggregated, probably at grain boundaries or surfaces. Control of the fraction of polymer inside versus outside the pores can be achieved by selective oxidation of the unincorporated polymer. Because of the unique nanoscale geometry of this material and the existence of multiple environments, excitations in this composite are funneled from outside the pores down into the aligned, isolated polymer chains inside the pores. Time-resolved stimulated emission spectroscopy is used to follow this process by monitoring the increase in luminescence polarization with time. The results show that control of polymer morphology through host/guest chemistry can be used to direct the motion of excitations and thus to deliver energy to specific regions of a material. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Energy transfer; Conjugated polymer; Mesoporous silica; Host/guest composites; Aligned chromophores

1. Introduction

Host/guest composite materials with nanometer-scale order offer an exciting new direction for control of materials properties on the molecular level. One particularly promising class of hosts are surfactant-templated mesoporous silicas [1,2]. Be-

cause of the range of pore sizes and shapes that can be produced, these materials offer a variety of options for controlling molecular interactions at a fundamental level, while still allowing for the incorporation of a wide range of different guests [3–10]. One area where this type of control is likely to be particularly valuable is in manipulating the optical properties of semiconducting polymers. Control over the interactions between polymer chains is critical to obtaining the desired optoelectronic properties of these technologically

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promising materials [11]. In solution, π -conjugated polymers such as poly(*para*-phenylene vinylene) show strong absorption and luminescence [12] with simple, single exponential excited-state relaxation dynamics [13]. When these same polymers are cast into thin films for device applications, however, luminescence quantum yields go down [14], and the excited state relaxation dynamics become multi-exponential and complex [13]. The differences between solutions and films can be ascribed to interactions between polymer chains, including energy transfer between chains and the formation of interchain shared excited state species [11,15].

One way to control interactions between polymers is to isolate the chains of a substituted poly(*para*-phenylene vinylene) in an insulating matrix. Many researchers have attempted to do this by blending semiconducting polymers with non-conducting polymers [13,16]. Because the entropy of mixing for polymers is exceedingly low, however, phase separation usually takes place, leaving the chains of the semiconducting polymer in contact [16]. Instead, the approach described here utilizes an ordered, nanoporous silica as a host which serves to both isolate and align the polymer chains [17,18].

The host that we have chosen is a P6mm hexagonal surfactant-templated silica [1,2]. A macroscopically oriented host is produced by aligning an inorganic/organic liquid crystal precursor in a magnetic field [19]. Subsequent condensation of the silica component of the material and removal of the surfactant via calcination affords an oriented, polycrystalline, nanoporous solid [20]. While the orientation of the host material is not perfect ($\sim 50^\circ$, full width at half maximum height), net alignment of the majority of the domains is achieved. The surface of the host is then silylated to make it compatible with the polymer, and the polymer is incorporated into the pores from solution [17]. Heat treatment is used to drive the polymer into the pores. We have chosen the soluble polymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) [21], and have shown that polymer can be incorporated into the silica pores from solution without disruption of the net alignment of the composite [17].

This mesoporous silica/conjugated polymer composite serves as a unique testing ground for understanding and controlling the electronic properties of isolated polymer molecules. Below, we describe the results of both continuous wave (CW) and time-resolved spectroscopies that were used to examine the properties of the polymer/silica composites. The results provide a model for exploiting nanoscale host/guests composites to control the flow of energy in complex materials.

2. Experimental

The synthesis of the mesoporous silica/semi-conducting polymer host/guest composites has been published elsewhere and will only be briefly summarized here [17]. Silicate/surfactant liquid crystals were aligned in an 8.7 T magnetic field by heating the liquid crystal phase just below its order-to-disorder phase transition temperature. Once the composite was oriented, it was cooled to room temperature, removed from the field, and the silica was crosslinked by exposure to HCl vapor. Calcination in O_2 at $500^\circ C$ yielded an oriented porous host. Silylation was performed with phenyldimethylchlorosilane. MEH-PPV was synthesized by established methods [21] and incorporated into the pores from a chlorobenzene solution. The solution was heated at $80^\circ C$ to drive the polymer into the pores. The composites were washed for ~ 2 h in chlorobenzene to remove unincorporated polymer, and then index matched in glycerol to improve optical quality. A sample two-dimensional X-ray diffraction pattern from an oriented composite is shown in Fig. 1. Both the raw data (top) and the chi plot (bottom) indicate net alignment of the sample, with a distribution of orientations. The data shows that host orientation is preserved upon silylation and polymer incorporation.

CW polarized fluorescence was obtained with a home-built system utilizing the 488 nm line of an Ar^+ laser for excitation and a Princeton Instruments intensified diode array for detection. For polarized measurements, care was taken to scramble the luminescence polarization before detection because of the known polarization bias

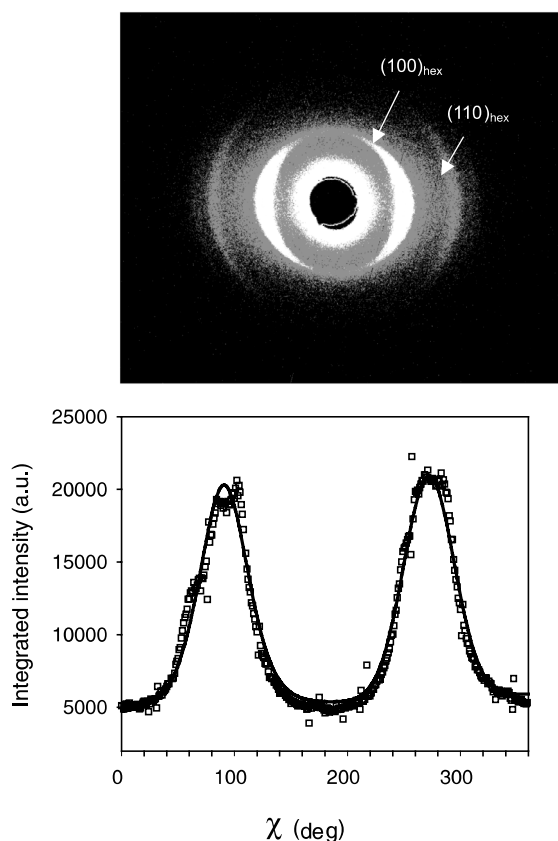


Fig. 1. Two-dimensional X-ray diffraction pattern of the MEH-PPV loaded, phenyldimethylchlorosilane treated aligned silica used for fluorescence measurements: (top) raw diffraction data, (bottom) angular distribution of pore orientation obtained from integrating over 2θ for the fundamental, $(100)_{\text{hexagonal}}$, diffraction peak.

of ruled-grating monochromators. Time-resolved stimulated emission and transient absorption measurements were made using a regeneratively amplified Ti:Sapphire laser which produces ~ 120 fs light pulses centered at 800 nm with 1 mJ of energy at a 1 kHz repetition rate (spectra physics). These pulses pump a dual-pass optical parametric amplifier (OPA). For the stimulated emission experiments, signal and idler beams from the OPA were then used to generate pump and probe light at 485 and 590 nm, respectively by sum frequency mixing (SFM) with the residual 800 nm light. The transient absorption measurement utilized the 485 nm pump light and the residual 800 nm pulse for

use as the probe. Further details of the femtosecond apparatus can be found in Ref. [11].

3. Results and discussion

Fig. 2 shows an example of polarized photoluminescence data obtained on the mesoporous silica/conjugated polymer composites. VV indicates that the pores were excited with vertically polarized light and that the vertically polarized luminescence was detected. VH similarly refers to vertically polarized excitation and horizontally collected luminescence. In all cases, the pores (and thus the majority of the polymer chains) are oriented vertically in the laboratory frame. The results show strong anisotropy in the polarization of the emitted light for both V and H excitation. The

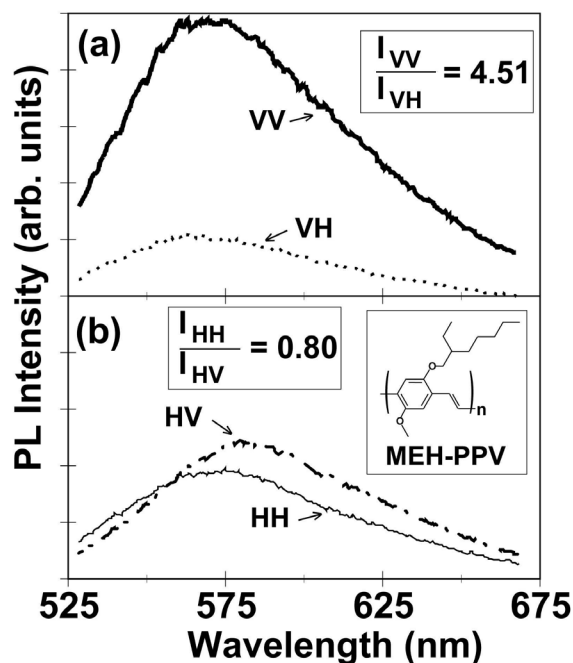


Fig. 2. Luminescence from MEH-PPV in the nanostructured composite with the excitation light (a) polarized along the pores, and (b) polarized perpendicular to the pore direction. Solid curves show data collected with parallel emission and excitation polarization. Dashed curves show data collected with perpendicular emission and excitation polarization. These data can be used to calculate the fraction of polymer chains contained within the silica nanopores.

majority of the light is emitted with vertical polarization, suggesting macroscopic alignment of the polymer chains.

The data in Fig. 2 can be used to determine the fraction of polymer guests incorporated within the silica nanopores. Using the known direction of the transition dipole with respect to the chain axis ($\sim 20^\circ$) and the distribution of pore orientations determined by two-dimensional X-ray diffraction (Fig. 1), a geometric model can be constructed to fit the observed luminescence polarization ratios [17]. Comparison of the model with the anisotropy shown in Fig. 2a allows us to calculate that over 80% of the polymer chromophores in the composite are aligned and isolated within the silica nanopores. The remaining $\sim 20\%$ of the polymer is randomly oriented, presumably located outside of the pore environment [17].

Transient absorption spectroscopy (Fig. 3) shows that the polymer chains contained within the pores are, in fact, isolated, while the 20% of polymer chains outside of the pores are in contact with other chains in a more film-like environment. When the pump and the probe polarizations are both oriented perpendicular to the pore direction, fast transient absorption decays are observed, similar to those observed for polymer films. By contrast, slow transient absorption decays are observed when the pump and the probe polarizations are oriented parallel to the pore direction, similar to that seen for the polymer in dilute solution. While there is some variation in the transient absorption decay time observed in different solutions, the data presented here corresponds to dilute solutions in a solvent that shows the longest decay and in which the polymer has the highest quantum yield [15].¹ It is thus reasonable that the solution decay presented here is indicative of loosely coiled, isolated polymer chains. Fig. 3 thus characterizes the different polymer environments

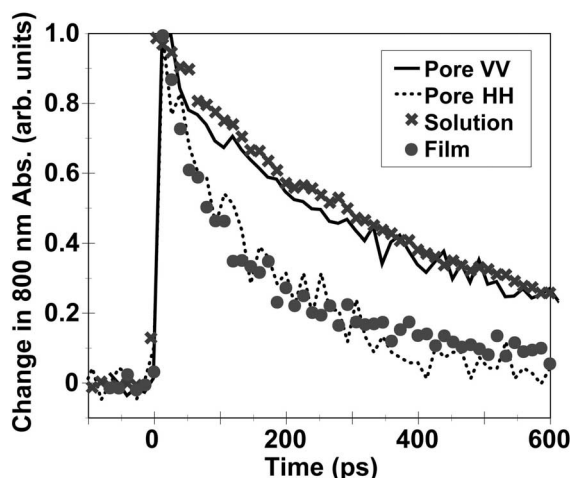


Fig. 3. Ultrafast transient absorption dynamics of MEH-PPV (pump 490 nm, probe 800 nm). Crosses and circles show excited state absorption decay of MEH-PPV in a chlorobenzene solution and a spin-coated film. For MEH-PPV in the mesoporous silica composite, the solid curve is the absorption decay with the pump and probe pulse polarizations parallel to the pore direction, and the dotted curve shows the absorption dynamics with the pump and probe polarized perpendicular to the pores. Film-like behavior is observed for horizontal excitation, while solution-like behavior is seen for vertical excitation.

present in the composite, and shows that both isolated and interacting polymer domains can be included within a single material.

Control of the fraction of polymer chains incorporated inside versus outside of the pores can be obtained by selective oxidation of the exterior polymer. Photooxidation of substituted poly(*para*-phenylene vinylene) polymers in air has been well documented [22,23]. Fig. 4 compares the polarized fluorescence of a freshly made sample (left) to a sample that has been allowed to oxidize at ambient conditions for about 6 weeks (right). The degree of emission polarization is clearly much greater for the oxidized sample, showing that the degree of aligned versus unaligned polymer can be controlled by oxidation. More importantly, this result indicates that the polymer chains contained within the pores are protected from oxidation. This protection may stem from reduced oxygen diffusion into the confined porous region, or may result from reduced UV irradiation due to absorption by the porous silica host. Regardless of the mecha-

¹ Changing solvent from the good solvent used here (chlorobenzene) to a poorer solvent (such as THF), which causes the chains to coil up, can result in a 50% decrease in transient absorption decay time. The effect of concentration is smaller, with a $15\times$ increase in concentration resulting in only about a 15% decrease in absorption decay time due to quenching via interchain interactions. See Refs. [11] and [15] for more details.

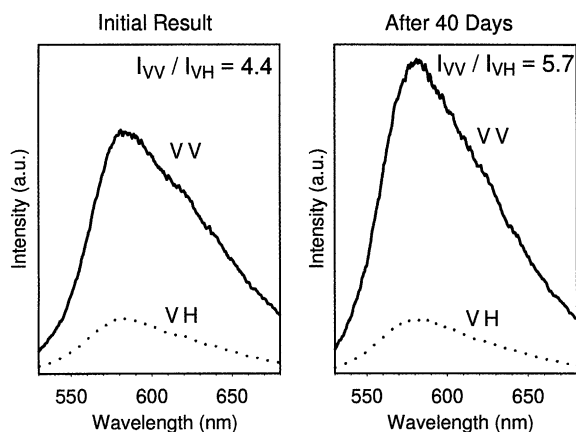


Fig. 4. Polarized luminescence from MEH-PPV in the nanostructured composite with the excitation light polarized along the pores. Solid curves show data collected with parallel emission and excitation polarization. Dashed curves show data collected with perpendicular emission and excitation polarization. The curve on the left was taken immediately after preparation of the composite; the curve on the right was taken ~ 6 weeks later. Oxidation of the unincorporated polymer in the aged sample results in a net increase in polarization of the fluorescence.

nism, the silica nanopores can be used not only to align polymer chains and control their morphology, but also to protect the chains from unintentional oxidation.

Once the material is well characterized, it becomes possible to follow the motion of excited state species in these composites using time-resolved stimulated emission anisotropy measurements. Because of the net alignment of the chromophores in the sample, this technique can directly monitor the fate of the emissive excitons created on the polymer chains. In these experiments, samples are excited with a short pulse of polarized light. The fluorescence intensity is monitored using a second pulse that is polarized either parallel (\parallel) or perpendicular (\perp) to the excitation pulse to cause stimulated emission. In the absence of energy migration, the emitted light will tend to have the same polarization as the excitation laser. When energy transfer takes place to a new segment with a different physical orientation, however, memory of the initial excitation polarization is lost until eventually there is no difference in intensity for emitted light polarized parallel or perpendicu-

lar to the excitation laser. The intensity of light emitted parallel or perpendicular to the polarization of the excitation light can be used to calculate the time-dependent anisotropy $r(t)$, which is a measure of the polarization memory [24]

$$r(t) = \frac{\parallel(t) - \perp(t)}{\parallel(t) + 2\perp(t)} \quad (1)$$

In an isotropic material, energy transfer results in a decay of the time-resolved anisotropy, $r(t)$, from an initial value of 0.4 down to 0 at long times [24].

Fig. 5 shows the dynamic stimulated emission anisotropy from the composite sample when the excitation laser is polarized along the pore direction. The initial value of the anisotropy, $r(0) = 0.53$, is larger than 0.4, confirming the net alignment of energy in the composite. There is a small initial rapid loss of anisotropy in the first few ps, which on the basis of previous studies [25–31], and the data presented in Fig. 3, we assign to Förster

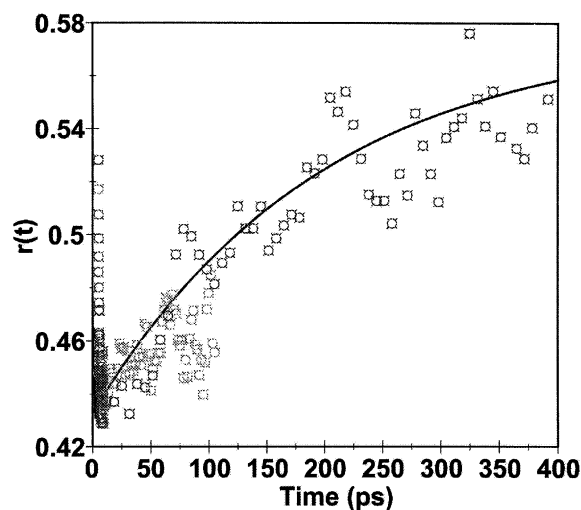


Fig. 5. Stimulated emission anisotropy of MEH-PPV in a mesoporous silica with the excitation pulse polarization parallel to the pore direction. The solid curve in the figure is a 250 ps exponential rise. The excitation and probe wavelengths are 490 and 590 nm, respectively. The different shaded symbols represent scans taken with different time spacings between points. The fast decay can be ascribed to Förster transfer between unincorporated polymer chains. The rise is ascribed to directional migration of excitations from the unincorporated polymer regions down into the aligned, isolated nanopores.

energy transfer between the $\sim 20\%$ of the conjugated polymer segments in the film-like environment outside the pores. Following the rapid decay however, we see an increase in the anisotropy that eventually tapers off at a value greater than $r(0)$. This increase is a direct result of the nanoscale architecture of the composite sample. The polymer segments located outside the pores are coiled, and thus have a short average conjugation length. From simple particle in a box type of considerations, these shorter segments are high-energy sites for excitations. By contrast, the polymer located within the pores should be relatively straight and thus excitations on these segments should be lower in energy. This energy gradient should cause excitations to move from the coiled polymer segments located outside the pores to the straight-chain segments located inside the pores, leading to emission which becomes spontaneously more aligned with time.

Since the composite samples are designed to have room for only one chain per pore, exciton migration to chromophores inside the pores must take place along the polymer backbone. The solid line in Fig. 5 is a fit to a 250 ps exponential rise, which indicates that although excitations can be forced to move along a single polymer chain into the aligned portion of our sample, they do so relatively slowly. The determination of this intra-chain energy transfer time can be used to explain a range of solution phase data on semiconducting polymers that had previously been quite controversial [32-34]. These composites can thus be used not only to control the flow of energy in a complex material, but also to rigidly define the polymer environment and thus simplify the electronic behavior [18].

4. Conclusions

The idea of controlling the motions of excited-state species is not new. Nature has developed an exquisitely efficient system to accomplish this in the light-harvesting antennae pigments of the photosynthetic reaction center [35]. Chemists have worked to imitate this effect with reasonable success using complex layered materials [36,37] or

specially designed polymeric species [38,39]. In all of these synthetic systems, chromophores are organized in such a way that energy is funneled from species with blue emission to those with redder emission. While this results in good directionality for energy transfer, energy is typically lost during the process. The unique thing about our work using host/guest chemistry is that only the conformation of the polymer chain is used to direct energy transfer. This provides the potential to control the fate of excitations with significantly less loss of energy. As our ability to organize materials on the nanometer length scale increases, the opportunities for this type of molecular control should also be enhanced. Host/guest chemistry involving mesoporous materials provides one of the most promising method to rigidly control the orientation, the aggregation, and the molecular conformation of large guest molecules.

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References

- [1] C.T. Kresge, M.E. Leonowitz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [2] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.T. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [3] J. Wu, A.F. Gross, S.H. Tolbert, *J. Phys. Chem. B* 103 (1999) 2374.
- [4] C.-G. Wu, T. Bein, *Science* 266 (1994) 1013.
- [5] C.-G. Wu, T. Bein, *Science* 264 (1994) 1757.
- [6] K. Möller, T. Bein, R.X. Fischer, *Chem. Mater.* 10 (1998) 1841.

- [7] K. Moller, T. Bein, R.X. Fischer, *Chem. Mater.* 11 (1999) 665.
- [8] V.I. Srdanov, I. Alxneit, G.D. Stucky, C.M. Reaves, S.P.J. Denbaars, *J. Phys. Chem. B* 102 (1998) 3341.
- [9] J.R. Agger, M.W. Anderson, M.E. Pemble, O. Terasaki, Y.J. Nozue, *J. Phys. Chem. B* 102 (1998) 3345.
- [10] Q.S. Huo, D.Y. Zhao, J.L. Feng, K. Weston, S.K. Buratto, G.D. Stucky, S. Schacht, F. Schüth, *Adv. Mater.* 9 (1997) 974.
- [11] T.-Q. Nguyen, I.B. Martini, J. Liu, B.J. Schwartz, *J. Phys. Chem. B* 104 (2000) 237.
- [12] J. Stampfl, W. Graupner, G. Leising, U. Scherf, *J. Lumin.* 63 (1995) 117.
- [13] M. Yan, L.J. Rothberg, E.W. Kwock, T.M. Miller, *Phys. Rev. Lett.* 75 (1995) 1992.
- [14] N.C. Greenham, I.D.W. Samuel, G.R. Hayes, R.T. Phillips, Y.A.R.R. Kessener, S.C. Moratti, A.B. Holmes, R.H. Friend, *Chem. Phys. Lett.* 241 (1995) 89.
- [15] T.-Q. Nguyen, V. Doan, B.J. Schwartz, *J. Chem. Phys.* 110 (1999) 4068.
- [16] C. Weder, C. Sarwa, C. Bastiaansen, P. Smith, *Adv. Mat.* 9 (1997) 1035.
- [17] J.J. Wu, A.F. Gross, S.H. Tolbert, *J. Phys. Chem. B* 103 (1999) 2374.
- [18] T.-Q. Nguyen, J. Wu, V. Doan, B.J. Schwartz, S.H. Tolbert, *Science* 288 (2000) 652.
- [19] A. Firouzi, D.J. Schaefer, S.H. Tolbert, G.D. Stucky, B.F. Chmelka, *J. Am. Chem. Soc.* 119 (1997) 9466.
- [20] S.H. Tolbert, A. Firouzi, G.D. Stucky, B.F. Chmelka, *Science* 278 (1997) 264.
- [21] F. Motamedi, K.J. Ihn, Z. Ni, G. Srdanov, F. Wudl, *Polymer* 33 (1992) 1102.
- [22] F. Papadimitrakopoulos, M. Yan, L.J. Rothberg, H.E. Katz, E.A. Chandros, M.E. Galvin, *Mol. Cryst. Liquid Cryst.* 256 (1994) 663.
- [23] H. Antoniadis, L.J. Rothberg, F. Papadimitrakopoulos, M. Yan, M.E. Galvin, M.A. Abkowitz, *Phys. Rev. B* 50 (1994) 14911.
- [24] C.R. Cantor, P.R. Schimel, *Biophysical Chemistry* part II, W.H. Freeman, San Francisco, 1980, p. 474.
- [25] R. Kersting, U. Lemmer, R.F. Mahrt, K. Leo, H. Kurz, H. Bässler, E.O. Göbel, *Phys. Rev. Lett.* 70 (1993) 3820.
- [26] U. Lemmer, R.F. Mahrt, Y. Wada, A. Greiner, H. Bässler, E.O. Göbel, *Chem. Phys. Lett.* 209 (1993) 243.
- [27] G.R. Hayes, I.D.W. Samuel, R.T. Phillips, *Phys. Rev. B* 52 (1995) R11569.
- [28] R. Kersting, B. Mollay, M. Rusch, J. Wenisch, C. Warmuth, H.F. Kauffmann, *J. Lumin.* 72–74 (1997) 936.
- [29] Ch. Warmuth, A. Tortschanoff, K. Brunner, B. Mollay, H.F. Kauffmann, *J. Lumin.* 76–77 (1998) 498.
- [30] R. Kersting, B. Mollay, M. Rusch, J. Wenisch, G. Leising, H.F. Kauffmann, *J. Chem. Phys.* 106 (1997) 2850 and references therein.
- [31] T. Förster, *Ann. Physik.* 2 (1948) 55.
- [32] A. Watanabe, T. Kodaira, O. Ito, *Chem. Phys. Lett.* 273 (1997) 227.
- [33] A. Ruseckas, M. Theander, L. Valkunas, M.R. Andersson, O. Inganäs, V. Sundström, *J. Lumin.* 76–77 (1998) 474.
- [34] J.Z. Zhang, M.A. Kreger, Q.-S. Hu, D. Vitharana, L. Pu, P.J. Brock, J.C. Scott, *J. Chem. Phys.* 106 (1997) 3710.
- [35] M. Orritt, *Science* 285 (1999) 349, and references therein.
- [36] D.M. Kaschak, J.T. Lean, C.C. Waraksa, G.B. Saupe, H. Usami, T.E. Mallouk, *J. Am. Chem. Soc.* 121 (1999) 3435.
- [37] D.M. Kaschak, T.E. Mallouk, *J. Am. Chem. Soc.* 118 (1996) 4222.
- [38] M.A. Fox, *Acc. Chem. Res.* 32 (1999) 201.
- [39] J.K. Whitesell, H.K. Chang, M.A. Fox, E. Galoppini, D.M. Watkins, H. Fox, B. Hong, *Pure Appl. Chem.*, 68 (1996) 1469, and references therein.