Enhanced Dipole-Dipole Interaction in a Polymer Microcavity

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We present experimental evidence for the enhancement of dipole-dipole interaction in a microcavity. We have studied the excitation energy transfer in poly(phenyl-p-phenylene vinylene) (PPPV) doped with 4-dicyanmethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) molecules, placed within a Fabry-Pérot resonator. As the spectral position of the cavity resonant mode is tuned across the DCM absorption profile, the transfer efficiency from PPPV to DCM changes significantly as revealed by photoluminescence studies. This behavior is clear evidence for the increase of the dipole-dipole interaction at spectral positions where the cavity modes are in resonance with the electromagnetic field emitted by the excited dipoles. [S0031-9007(99)09175-9]

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There has been considerable interest in the optical and electronic properties of conjugated polymers and molecularly doped polymers during recent years due to their prospective applications in electronic and optoelectronic devices [1,2]. At the same time, there has been much progress in the rapidly developing field of cavity quantum electrodynamics (QED) [3–6]. Within a resonant—or off-resonant—cavity, fundamental optical processes are modified in a characteristic way. Among the phenomena that have been observed are, e.g., inhibition or enhancement of spontaneous emission [7–9], thresholdless laser action [10], strongly directed emission [11], and spectral narrowing [12] of otherwise broad molecular fluorescence [13,14]. Cavity effects on the photo- and electroluminescence of organic thin films have also been reported [11,12,15–19]. Yet, it is expected that not only the radiative emission process will be modified by cavity effects but also the coupling between different states mediated by the dynamic dipole-dipole interaction. Experimental and theoretical studies on the dipole-dipole interaction in strongly scattering media [20,21], in photonic band gap structures [22–24], as well as studies on energy transfer in dielectric microparticles [25,26] have been reported.

Recently, it has been proposed that dipole-dipole interaction can be modified in an optical cavity [27–29]. We report here clear experimental evidence for the enhancement of dipole-dipole interaction in a resonant polymer microcavity. The active part of this cavity consisted of poly(phenyl-p-phenylene vinylene) (PPPV) doped with the laser dye 4-dicyanmethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM). It has been demonstrated [30–32] that in this system energy transfer from PPPV to DCM occurs via dipole-dipole interaction. Our data demonstrate that this energy transfer can be significantly enhanced in a resonant microcavity.

The samples investigated consisted of a dielectric multistack reflector as the bottom mirror and an aluminum mirror as top reflector. The dielectric mirror consists of five pairs of tantalum oxide ($n = 2.1$) and silicon oxide ($n = 2.46$) quarter-wave layers (each layer is about 50 nm thick), respectively, having a reflectivity of about 95% in the spectral range between 2.25–2.7 eV. The transmission characteristic is shown in Fig. 1. A layer of polycarbonate (PC, $n = 1.59$) doped with 19.7% PPPV and 0.21% DCM (by weight) was deposited by spin coating from chloroform solution on top of the dielectric mirror. Film thicknesses were chosen to give $\lambda/2$ cavity resonances between 2.25 and 2.61 eV. The cavity structures were completed by vacuum evaporation of an aluminum mirror on top of the polymer layer. The above PC:PPPV:DCM ratio was chosen on the basis of energy transfer studies without the cavity showing that the transfer efficiency for this composition is such that the contributions of PPPV and DCM to the overall

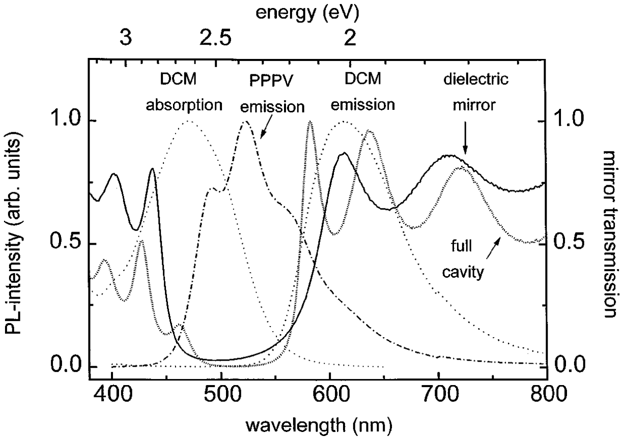

FIG. 1. Photoluminescence spectra of thin films of PPPV(19.7%)/PC (dash-dotted line) and DCM(5%)/PC (dotted line). For comparison, the DCM absorption is displayed, too (small dotted line). The transmission characteristics of the dielectric mirror alone as well as for a completed cavity (dielectric mirror + polymer + Al mirror) are also shown (full line and short dashed line, respectively).

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photoluminescence (PL) emission are comparable [30]. This allows determination of their emission ratio with good accuracy. The frequency doubled output of a Ti:sapphire laser at 3.16 eV was used to excite the samples with 70 fs pulses at a repetition rate of 82 MHz. The PL emission was collected with a lens (numerical aperture of 0.1), dispersed by a monochromator with a 300 lines per mm grating, and detected with a diode array. Sample excitation and PL detection were done through the dielectric mirror. In order to minimize *direct* excitation of DCM the excitation wavelength has been set to a spectral position where the ratio between the extinction coefficient of the neat PPPV film ($\varepsilon_{\mathrm{PPPV}}$) and the extinction coefficient of the pure DCM solution ($\varepsilon_{\mathrm{DCM}}$) has a maximum.

The PL spectra of thin films of, respectively, 19.7% PPPV and 5% DCM in PC matrix on quartz substrates are shown in Fig. 1. Also shown in Fig. 1 are the transmission characteristic of the dielectric mirror, as well as the transmission of the active cavity (for a particular resonance). Finally, the main DCM absorption band is also depicted in Fig. 1. The PPPV emission shows the well-known structure due to the vibronic progression of the inhomogeneously broadened $S_0 \rightarrow S_1$ transition [17]. The DCM emission results from the same recombination process, yet, the vibronic side bands are not resolved.

In Fig. 2 we show three examples of microcavity PL spectra with resonances at 2.33, 2.41, and 2.53 eV, respectively, and the free space emission of the PPPV/DCM sample for comparison. The widths of the cavity modes are about 0.03 eV (FWHM), close to the theoretical limit as calculated from the refractive index, the mirror reflectivities, and the cavity thickness [19,33]. The PL at energies lower than 2.17 eV is essentially the free-space emission modulated by the transmission of the quarter-wave stack. The intensity of this low energy part of the spectrum decreases as the cavity mode shifts to lower energies (Fig. 2). A comparison of the cavity spectra in Fig. 2 with the free-space emission of DCM and PPPV (Fig. 1) reveals that the PL at the cavity resonances is almost exclusively due to PPPV, while the cavity emission at energies lower than 1.94 eV originates mainly from DCM. This provides the base for our analysis presented below.

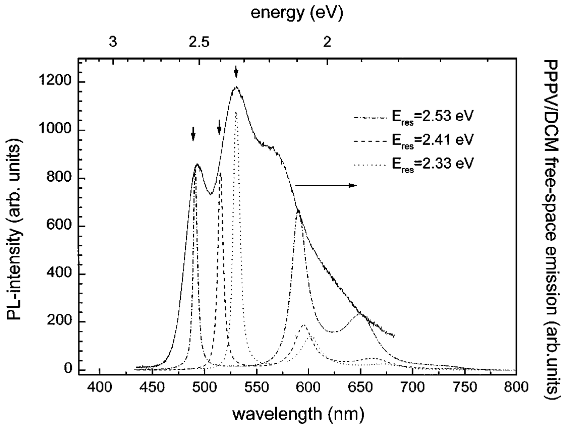

FIG. 2. Room temperature PL spectra of three PPPV/DCM/PC microcavities of different thickness (different resonance wavelength). Excitation energy was 3.18 eV (390 nm). The arrows mark the spectral positions of the respective cavity resonances. The PL at energies <2.17 eV is essentially the free-space emission of the DCM modulated by the transmission of the dielectric mirror (see Fig. 1 for comparison). The free space emission of the PPPV/DCM is shown for comparison (full line).

Before doing so we will recall briefly the physical picture describing the energy transfer between the excited PPPV molecules and the DCM emitter. This resonant energy transfer is mediated by the total electrical field related to the excited molecules. Here, dipole-dipole interaction is dominant with two distinct contributions. One, the so-called Förster-Dexter term [34,35], is usually included in the total Hamiltonian of the equation of motion for the density matrix of the given material system. This term, which has been shown to provide a satisfactory description of both time-integrated [30] and transient PL behavior [31,32] of the PPPV/DCM system in nonrestricted geometries, results in the well-known R^{-6} dependence of the energy transfer. This instantaneous part of the dipole-dipole interaction, which is mediated by longitudinal fields, is not sensitive to boundary conditions.

However, a second term contributes to the energy transfer within a cavity which is related to the transverse electric field, i.e., to the induced optical polarization. It follows from Maxwell's equation that this induced polarization leads to the emission of an electromagnetic field resulting in a so-called dynamical dipole-dipole interaction due to the retarded field. It is this dynamical dipole-dipole interaction which is sensitive to the boundary conditions due to a modified photon density of states via the geometry of the resonator in which the radiation occurs. A complete theory, of course, has to include both contributions and the influence of the cavity on the total field has to be considered. However, in a first approach we concentrate our interpretation on the dynamical dipole-dipole interaction mediated by the transverse field.

Figure 3 depicts the dependence of the enhancement factor ($\Gamma = I_{\mathrm{res}}/I_{\mathrm{free}}$) of the emission from a PPPV/DCM/PC sample on the wavelength of the cavity resonance. I_{res} and I_{free} were determined by integrating the PL spectra from 1.55 to 2.15 eV for a microcavity sample and for a sample without photon confinement, respectively. Γ is a direct measure for the enhancement of the resonant energy transfer from PPPV to DCM. Additionally, the absorption, $\varepsilon_{\mathrm{DCM}}(h\nu)$, of a DCM (5%)/PC film in the relevant spectral regime is displayed for comparison by the full line. The enhancement factor Γ increases by almost 1 order of magnitude by tuning the cavity resonance from the wing of the DCM absorption profile into its maximum. For a DCM free sample (neat PPPV/PC)

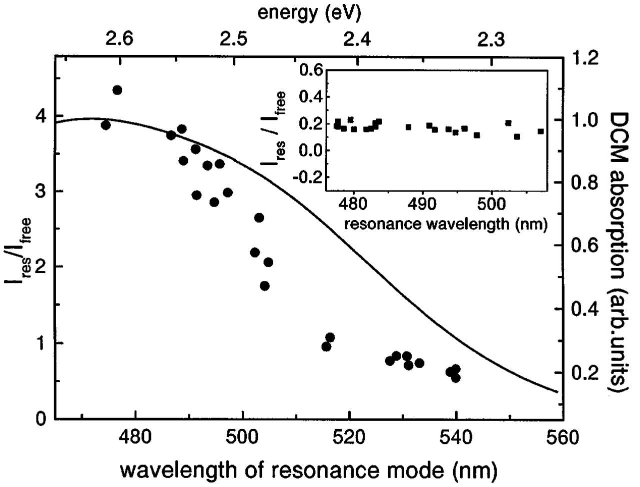

FIG. 3. Ratio of the integrated DCM emission in the spectral range of 1.55 to 2.15 eV for the microcavity (I_{res}) and the free thin film (I_{free}) versus wavelength of the resonance mode. The absorption profile of DCM is included as a line for comparison. The inset displays the emission ratio versus cavity resonance for an undoped PPPV/PC sample.

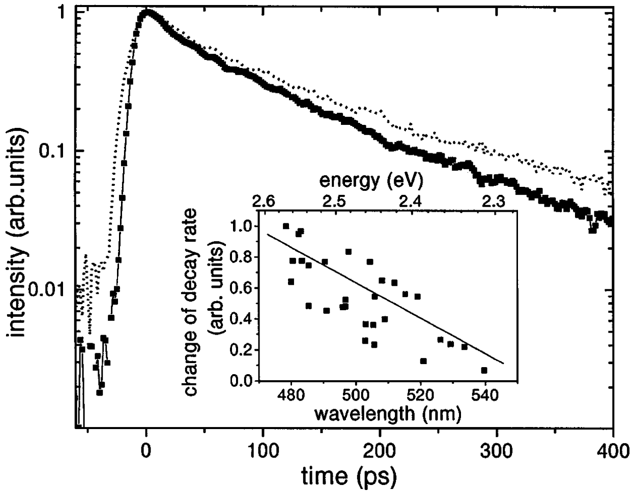

FIG. 4. Photoluminescence transients detected at the cavity resonance (2.55 eV in this case) for a PPPV/DCM/PC microcavity structure (black squares) as well as for a neat PPPV/PC sample (dashed line). The inset shows the change of the decay rate (R_{cav}-R_{free}) inferred from the $1/e$ decay times for the PPPV/DCM/PC sample versus the cavity resonance. An increase is revealed as the cavity resonance approaches the maximum of the DCM absorption. The line is a guide to the eye.

no change of the emission ratio is observed in the same spectral range as can be seen from the inset of Fig. 3 which proves that, in fact, the DCM emission intensity increases, which we attribute to the enhancement of the resonant dipole-dipole interaction due to the cavity mode, with the absorption profile of the DCM. This modification (enhancement or suppression [23,24]) of the energy transfer in restricted geometries of appropriate dimensions has been predicted in the theoretical work by Agarwal *et al.* [27] and Kobayashi *et al.* [28,29] who treat the problem of resonant dipole-dipole interaction in a Fabry-Pérot cavity by applying a full quantum response function theory and a mode expansion calculation, respectively. However, the total dipole-dipole interaction has not been considered. Therefore, these models are not expected to provide a quantitative description of our experimental findings. The experimentally observed enhancement results from the retarded dipole-dipole interaction by the presence of a cavity resonance mode. The convolution of the emission spectrum and the absorption spectrum (Ω), which determines the energy transfer is increased according to the increase of photon density at the cavity resonance expressed: $\Gamma \propto \Omega \rho(\tilde{\nu})$ where $\rho(\tilde{\nu})$ denotes the photonic density of states.

In addition to the observed variation in the enhancement factor Γ, the retarded dipole-dipole interaction should manifest itself as an increase of the transfer rate from PPPV to DCM. Therefore, we have investigated the dynamics of the PL by means of streak-camera measurements with 6 ps time resolution. Figure 4 depicts, for instance, the PL transients of the PPPV/DCM sample detected at the spectral position of the cavity resonance and at the same spectral positions for the sample without geometrical confinement (free space), for comparison. In the sample without a cavity the decay of the PPPV emission is determined by radiative and nonradiative recombination, trapping, energy relaxation, and energy transfer to the DCM molecules. In the case of the microcavity the decay of the luminescence is faster. A decrease of the decay time is *not* observed in cavities with neat PPPV films because the PL quantum efficiency is about 10% only, and thus in undoped PPPV films trapping and energy relaxation within the inhomogeneously broadened density of states (DOS) dominate the luminescence decay at these photon energies [18]. The observed decrease of the luminescence decay in doped films therefore must be attributed to energy transfer from PPPV to the DCM molecules enhanced by the presence of the cavity resonances. The inset in Fig. 4 displays the change of the decay rate (R_{cav}-R_{free}) obtained from the time in which the intensity drops to the value of $1/e$ versus the spectral position of the cavity resonance. In accordance with the spectral variation of the enhancement factor of the PL intensities a clear variation of the decay rate is observed when the cavity resonance is tuned across the DCM absorption profile.

In conclusion, we have performed photoluminescence measurements on dye-doped conjugated polymer samples embedded in a Fabry-Pérot resonator of suitable dimensions to study the cavity effect on resonant excitation energy transfer. Our experiments demonstrate a pronounced dependence of the emission ratio, and thus the energy transfer efficiency, on the spectral position of the cavity resonance. The DCM emission is considerably enhanced for cavity resonances at the maximum of the DCM absorption. This behavior is attributed to the modification of the dipole-dipole interaction by the microcavity. In view of the rapidly growing potential of these light emitting polymers for optoelectronic applications our results reveal another way of tailoring and optimizing their emission properties.

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[1] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. MacKay, R.H. Friend, P.L. Burn, and A.B. Holmes, Nature (London) **347**, 539 (1990).

[2] D. Braun, A. Brown, E. Staring, and E.W. Meijer, Synth. Met. **65**, 85 (1994).

[3] S. Haroche and D. Kleppner, Phys. Today **42**, 24 (1989).

[4] H. Yokoyama, Science **256**, 66 (1992).

[5] Y. Yamamoto and R.E. Slusher, Phys. Today **46**, 66 (1993).

[6] S. Haroche and J.M. Raimond, Sci. Am. No. 1, **268**, 54 (1993).

[7] R.G. Hulet, E.S. Hilfer, and D. Kleppner, Phys. Rev. Lett. **55**, 2137 (1985).

[8] P. Goy, J.M. Raimond, M. Gross, and S. Haroche, Phys. Rev. Lett. **50**, 1903 (1983).

[9] F. De Martini, G. Innocenti, G.R. Jacobovitz, and P. Mataloni, Phys. Rev. Lett. **59**, 2955 (1987).

[10] F. De Martini and G.R. Jacobovitz, Phys. Rev. Lett. **60**, 1711 (1988).

[11] T. Tsutsui, N. Takada, S. Saito, and E. Ogino, Appl. Phys. Lett. **65**, 1868 (1994).

[12] N. Takada, T. Tsutsui, and S. Saito, Appl. Phys. Lett. **63**, 2032 (1993).

[13] H. Bässler, M. Deussen, S. Heun, U. Lemmer, and R.F. Mahrt, Z. Phys. Chem. **184**, 233 (1994).

[14] H. Bässler, in *Optical Techniques To Characterize Polymer Systems,* edited by H. Bässler (Elsevier, Amsterdam, 1989).

[15] A. Dodabalapur, L.J. Rothberg, and T.M. Miller, Appl. Phys. Lett. **65**, 2308 (1994).

[16] V. Cimrova and D. Neher, J. Appl. Phys. **79**, 3299 (1996).

[17] A. Ochse, U. Lemmer, M. Deussen, J. Feldmann, A. Greiner, R.F. Mahrt, H. Bässler, and E.O. Göbel, Mol. Cryst. Liq. Cryst. **256**, 335 (1994).

[18] U. Lemmer, R. Hennig, W. Guss, A. Ochse, J. Pommerehne, R. Sander, A. Greiner, R.F. Mahrt, H. Bässler, J. Feldmann, and E.O. Göbel, Appl. Phys. Lett. **66**, 1301 (1995).

[19] W. Guss, H. Vestweber, M. Hopmeier, Y.H. Tak, and R.F. Mahrt, Synth. Met. **83**, 257 (1996).

[20] M. Tomita, K. Ohosumi, and H. Ikari, Phys. Rev. B **50**, 10 369 (1994).

[21] H.R. Stuart and D.G. Hall, Phys. Rev. Lett. **80**, 5663 (1998).

[22] S. John and T. Quang, Phys. Rev. Lett. **76**, 2484 (1996).

[23] G. Kurizki, Phys. Rev. A **42**, 2915 (1990).

[24] G. Kurizki and A.Z. Genack, Phys. Rev. Lett. **61**, 2269 (1988).

[25] L.M. Folan, S. Arnold, and S.D. Druger, Chem. Phys. Lett. **118**, 322 (1985).

[26] P.T. Leung and K. Young, J. Chem. Phys. **89**, 2894 (1988).

[27] G.S. Agarwal and S.D. Gupta, Phys. Rev. A **57**, 667 (1998).

[28] T. Kobayashi, Q. Zheng, and T. Sekiguchi, Phys. Rev. A **52**, 2835 (1995).

[29] T. Kobayashi, Q. Zheng, and T. Sekiguchi, Phys. Lett. A **199**, 21 (1995).

[30] M. Deussen, Ph.D. thesis, Philipps-Universität Marburg, 1995.

[31] P. Haring Bolivar, G. Wegmann, R. Kersting, M. Deussen, U. Lemmer, R.F. Mahrt, H. Bässler, E.O. Göbel, and H. Kurz, Chem. Phys. Lett. **245**, 534 (1995).

[32] U. Lemmer, A. Ochse, M. Deussen, R.F. Mahrt, E.O. Göbel, H. Bässler, P. Haring Bolivar, G. Wegmann, and H. Kurz, Synth. Met. **78**, 289 (1996).

[33] E.F. Schubert, N.E.J. Hunt, M. Micovic, R.J. Malik, D.L. Sivco, A.Y. Cho, and G.J. Zydzik, Science **265**, 943 (1994).

[34] Th. Förster, Ann. Phys. (Leipzig) **6**, 55 (1948).

[35] D.L. Dexter, J. Chem. Phys. **21**, 836 (1953).