

Room Temperature Polariton Emission from Strongly Coupled Organic Semiconductor Microcavities

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We report a room temperature study of the strong exciton-photon coupling regime in a planar microcavity, containing cyanine dye aggregates with delocalized exciton wave functions (J aggregates). Giant Rabi splittings of 80 meV between upper and lower polariton branches are observed and cavity polariton emission is detected from the lower polariton branch. The small linewidth and large oscillator strength characteristic of J aggregates make them a favorable physical structure to allow the observation of strong coupling for organic semiconductors. [S0031-9007(99)08927-9]

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There are two regimes into which interactions between an electromagnetic field and the optical transitions of a material can be classified, namely, weak and strong coupling. Optical microcavities have proved to be a very successful system for observing such interactions [1–3]. Strong coupling manifests itself in anticrossing of the coupled modes and, ideally, in the appearance on resonance of two equal intensity and equal linewidth transitions separated by the vacuum Rabi splitting energy. These new cavity polariton modes can be considered an admixture of the optical transition of the material and the cavity photon modes. Strong-coupling effects for inorganic semiconductor quantum well microcavities are the subject of intense scientific interest [1–7] and offer new possibilities for the modification and control of exciton-photon interactions. The coupled cavity-polariton states are, for instance, of interest for polariton lasing [4,5,7].

Organic semiconductor microcavities have been widely studied in the weak-coupling regime as structures which emit light with greater spectral purity and higher forward-directed intensity than noncavity structures [8]. Large oscillator strengths are a characteristic feature of conjugated molecules and thus Rabi splitting energies should be large. Strong-coupling effects were not, however, widely anticipated [9]. The problem lies with the equally characteristic large exciton linewidths (often of the order of 0.5 to 1 eV) which result from inhomogeneous broadening and the presence of a vibronic progression. In this case, strong coupling is expected to be difficult to observe [1–3]. This difficulty is not, however, insurmountable, and using a Zn porphyrin derivative with a narrow optical absorption linewidth, we recently made the first report of strong-coupling effects in an organic semiconductor microcavity [10]. A Rabi splitting of 160 meV was observed at room temperature, which is over an order of magnitude larger

than is observed in typical inorganic semiconductor quantum well microcavities [1–7]. This effect was attributed primarily to the exceptionally large oscillator strength of excitons in the Zn porphyrin [10]. The observation of giant Rabi splittings coupled with the large exciton binding energy typical of an organic semiconductor [11] offers good prospects for polariton lasing at room temperature.

In this Letter we present the results of a study of strong coupling in microcavities containing a different class of organic semiconductor, namely, cyanine dyes. Our results demonstrate the generality of giant Rabi splitting for appropriately chosen organic semiconductors and establish J aggregates as a desirable physical structure with which to achieve strong coupling. In addition, we make the first report of cavity-polariton emission from an organic semiconductor.

Cyanine dyes are a class of material that has found diverse uses in photography [12], as laser dyes [13], and in organic light-emitting diodes [14]. In common with other cyanine dyes, the material (2,2'-dimethyl-8-phenyl-5,6,5',6'-dibenzothiacarbocyanine chloride) that we have studied [see inset of Fig. 1(a)] carries a net positive charge which in suitable solvents drives a self-association of the molecules to form an extended J aggregate structure. In-line ordering of dipoles leads to a band of delocalized states of which only the lowest lying have dipole allowed transitions to the ground state [15,16]. The result is a red-shifted and strongly narrowed absorption peak relative to that of the isolated monomer, with reduced vibronic structure and a small Stokes shift [16] between absorption and emission peaks. It is the large oscillator strength and narrow linewidth, which are well suited to the observation of strong coupling, that we wished to utilize for our experiments. To form stable thin films containing J aggregates, the cyanine dye was dissolved with polyvinylalcohol

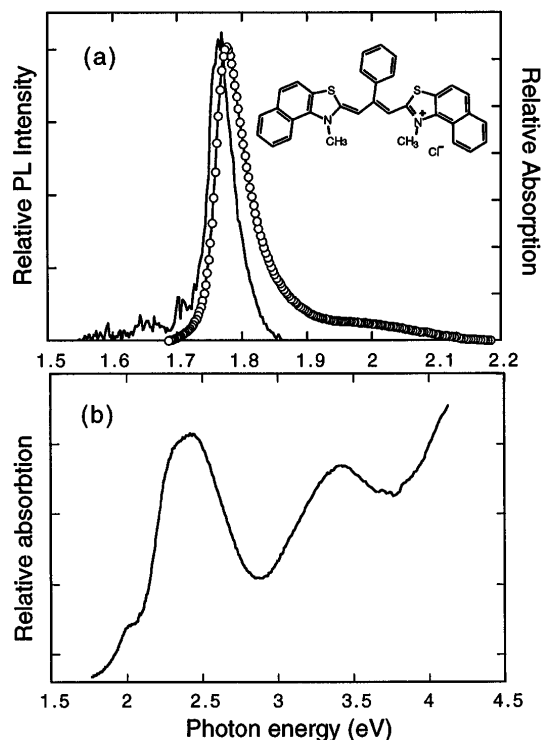


FIG. 1. (a) The absorption (open circles) and photoluminescence emission (solid line) spectra of a thin film of cyanine dye *J* aggregates dispersed in a PVA matrix. The inset shows the chemical structure of the specific cyanine dye studied here. (b) The absorption spectrum of a vacuum deposited thin film of cyanine dye on a quartz substrate.

(PVA) in a 1:1 mixture of water and methanol. The solution was then spin coated onto either quartz or dielectric mirror substrates to form excellent optical-quality films. Figure 1(a) shows the room temperature optical absorption and photoluminescence emission from a PVA matrix film prepared on a quartz substrate. The spectra are typical for *J* aggregates with an absorption full width at half maximum (FWHM) linewidth of 58 meV and an emission FWHM linewidth of 42 meV. As expected, the Stokes shift between absorption and emission maxima is small (13 meV) compared to the absorption linewidth. It is also clear that the vibronic replica in both absorption and emission is very weak.

Microcavities were fabricated using 1 cm^2 dielectric mirror substrates consisting of nine alternating $\lambda/4$ pairs of Si_xN_y ($n = 1.95$) and SiO_2 ($n = 1.45$) (with SiO_2 the uppermost mirror layer). The cyanine dye dispersed in PVA matrix was deposited by spin coating on top of the dielectric mirror and then a silver mirror was evaporated on top of the organic film. A cavity with a Q factor of 85 was formed for a $120 \pm 5 \text{ nm}$ thickness film ($n = 1.54$). Using a transfer matrix reflectivity (TMR) model we calculate that a $\lambda/2$ mode is confined by the last SiO_2 layer of the dielectric mirror and the PVA/*J* aggregate layer. An antinode of the confined photon

field was positioned at the interface between the SiO_2 and the organic layer, hence ensuring good coupling with the cyanine dye *J* aggregates. The cavity was designed such that at normal incidence the photon mode was approximately 150 meV lower in energy than the exciton mode (the peak of the cyanine dye absorption is at 1.78 eV). Angle tuning makes use of the variation of the photon mode energy as $1/\cos \theta_{\text{int}}$, where θ_{int} is the internal angle between the cavity axis and the measurement direction. By adjusting the measurement angle, one is thus able to map out the dispersion of the photon mode and observe its behavior as it approaches resonance with the exciton mode. Figure 2(a) shows the variation in room temperature reflectivity spectra

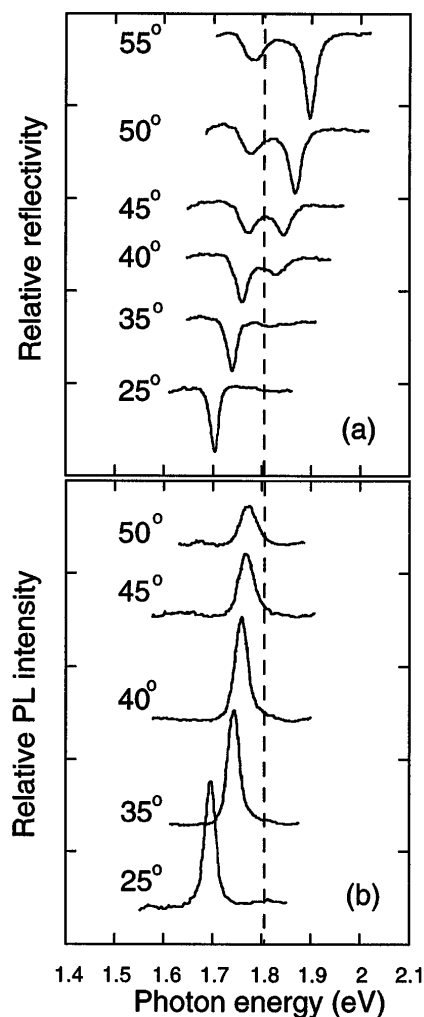


FIG. 2. (a) Reflectivity and (b) photoluminescence emission spectra recorded for a cyanine dye containing microcavity as the photon mode was angle-tuned through the exciton mode (see text). The spectra for different measurement angles (indicated in the figure) have been displaced vertically for clarity but are plotted on the same ordinate scale. The vertical dashed line marks the exciton energy used in the TMR simulations.

as the photon mode is angle-tuned through the exciton mode energy.

At 25° , the photon mode is ~ 80 meV from resonance with the exciton mode and can be identified as a sharp reflectivity dip with 20 meV FWHM. At such large detunings, the interaction between the photon and exciton is weak and thus the exciton feature cannot be detected in reflectivity. As the measurement angle increases the photon mode approaches resonance with the exciton, and the signatures of strong coupling are observed. The reflectivity spectrum evolves into a pair of reflectivity dips as the exciton mode takes on a photon character. The lower energy feature broadens and loses intensity. At 45° , two nearly equal intensity and linewidth features separated by 84 meV are observed. For larger angles beyond resonance, the higher energy mode gains in intensity and narrows in linewidth. These data are replotted in the form of a dispersion curve in Fig. 3(a). A clear anticrossing of the photon and exciton modes is observed. A TMR fit to the data is shown using a solid line. Figure 4(a) plots the mode separation as a function of angle and shows that the closest approach occurs between 40° and 42.5° and is approximately 80 meV. This defines zero detuning between the photon and exciton and, hence, resonance. The angular variation in the linewidths of the two modes is plotted in Fig. 4(b). The uncoupled exciton and photon linewidths are marked

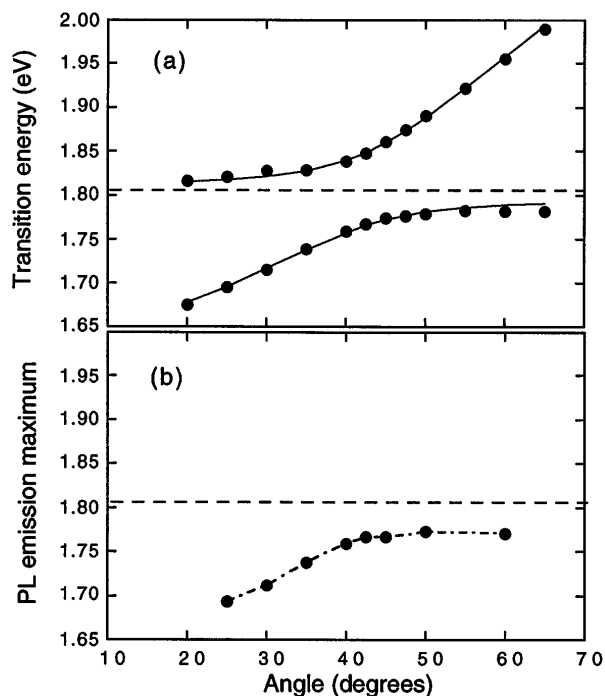


FIG. 3. Dispersion curves as a function of measurement angle for (a) the reflectivity and (b) the photoluminescence emission spectra of a cyanine dye containing microcavity. The solid line in (a) is a TMR fit with an exciton energy marked by the horizontal dashed line. The dash-dotted line through the data in (b) is a guide to the eye.

by horizontal dashed lines and were determined, respectively, from the absorption spectrum in Fig. 1(a) and from the reflectivity spectrum of the microcavity far from resonance. Equal linewidths are not observed exactly on resonance (between 40° and 42.5°) but instead occur at 45° , corresponding to a slight positive detuning between the photon and exciton. Such effects have been shown to be a consequence of an asymmetric inhomogeneously broadened exciton distribution that is significantly broader than the cavity photon mode [17,18]. It is clear that the J aggregate absorption is indeed asymmetric [see Fig. 1(a)], and has a linewidth substantially larger than the cavity photon mode. Our TMR simulations predict that equal linewidths occur at 44° .

The combination of anticrossing, intensity, and linewidth averaging of the photon and exciton modes provides conclusive evidence for strong coupling [19]. The correct description of the coupled modes is then given as cavity polaritons with their resonance separation being the Rabi-splitting energy. For these cyanine dye microcavities we find a room temperature Rabi splitting of 80 meV. For a specific material, the Rabi splitting is expected to vary as $(\alpha_0 L)^{1/2}$, where α_0 is the peak absorption coefficient and L is the film thickness [3]. The 160 meV Rabi splitting that we previously reported for a Zn porphyrin microcavity was for a film of substantially

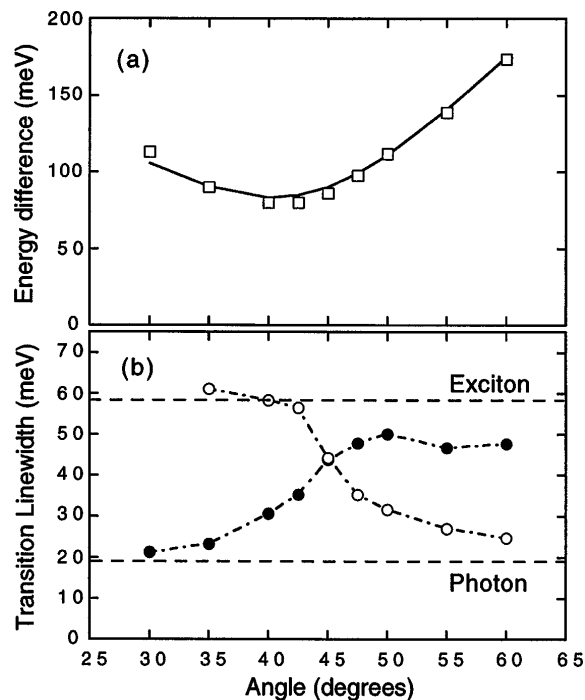


FIG. 4. Angular variation of (a) the separation of the upper and lower polariton modes and (b) their linewidths. The solid line in (a) is constructed using the TMR fit data from Fig. 3(a). In (b) the lower and upper energy modes are represented by filled and open circles, respectively. The dashed-dotted lines through the data in part (b) are guides to the eye.

larger optical density than for the cyanine dye in PVA film used here. By increasing the optical density of the cyanine dye we have achieved Rabi splittings of up to 180 meV.

Additional experiments were made to investigate the cw emission properties of the strongly coupled system. Nonresonant excitation was with 5 mW cm^{-2} radiation from a HeNe laser (1.96 eV, 632.8 nm). Experiments were performed at room temperature with the excitation light directed onto the microcavity at normal incidence. The photoluminescence (PL) emission spectra collected for a range of measurement angles are shown in Fig. 2(b). The emission peak disperses as a function of angle as shown in Fig. 3(b). It is clear that the emission follows the dispersion of the lower polariton branch with no emission from the upper branch. Similar behavior has been previously reported for PL from InGaAs quantum well microcavities in the strong-coupling regime. There the emission closely followed the polariton absorption multiplied by a Boltzmann occupancy factor [20]. The large reservoir of uncoupled excitons could scatter into both the upper and lower polariton branches, and the exciton linewidths (determined by a Boltzmann distribution) could then control the relative proportion of excitons scattered into each polariton branch and hence the spectral distribution of PL. In the present case, the emission comes from a relaxed population (as evidence by the finite Stokes shift) and so there is a significant dominance of the polariton emissions from the lower branch. At large negative detunings (low angles), the energy of the upper branch starts to overlap that of the emissive species. Scattering of excitons into these states does not, however, result in photon emission, since at such detunings the upper branch is principally excitonlike and thus cannot be easily detected outside of the cavity. In contrast, at low angles the lower polariton branch is photonlike and therefore the excitons that scatter into these polaritons can decay radiatively.

It is apparent that the J aggregate structure is very significant in allowing the observation of strong coupling. Figure 1(b) shows the absorption spectrum of the cyanine dye used in these experiments but deposited as a thin film directly onto a room temperature quartz substrate by vapor deposition. Vapor deposition produces an essentially amorphous film in which there is little opportunity for the molecules to self-organize and produce J aggregates [21]. The linewidths of these transitions are of order 700 meV; this contrasts with the optical spectra of the aggregate which has optical transitions which are over an order of magnitude narrower. Thus while the isolated molecules would be poorly suited for observing strong coupling, the J aggregate structure makes this regime readily accessible.

Recent theoretical work has discussed that optical properties of hybrid organic-inorganic structures [9]. It

was predicted that the Mott-Wannier excitons of an inorganic quantum well could be mixed with Frenkel excitons in an organic layer via their mutual coupling to a confined photon mode. The resulting hybrid exciton systems may be of importance in creating new types of semiconductor devices and in generating enhanced optical nonlinearities [22]. Such coupling requires the excitons of both the organic and inorganic components of the hybrid system to be of similar energy. Cyanine dye J aggregates appear to be well suited for this since there are a range of examples that have exciton resonances that span the red to near-infrared spectral range at wavelengths compatible with excitons in a variety of different inorganic semiconductors [3].

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