Strong coupling between excitons in J-aggregates and waveguide modes in thin polymer films

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We observe a large room temperature Rabi splitting for the transverse electric (190 meV) and transverse magnetic (125 meV) waveguide modes of a thin polymer film doped with J-aggregating dye, indicating strong coupling between propagating light modes and localized molecular excitons. We show that the difference in the measured splitting results from the different field distribution of the cross polarized modes. Numerical simulations indicate that the exciton-waveguide modes are as strongly coupled as exciton-surface plasmon polaritons supported by the same system. © 2011 American Institute of Physics. [doi:10.1063/1.3604014]

The creation of electron hole pairs (excitons) in molecules and semiconductors via the absorption of light is a means of energy transfer between light modes and electronic excitations in matter. This interaction is useful for numerous functional devices, e.g., light emitting diodes, lasers, photovoltaic solar cells, and photo-detectors. In the weak coupling regime, the time dynamics of excitons can be altered by controlling the electromagnetic environment. For example, the absorption and excitation rates, which are proportional to \( |\vec{E} \cdot \mu|^2 \), where \( \vec{E} \) is the light field and \( \mu \) is the transition dipole moment, can be enhanced by focusing the light and increasing the local intensity. On the other hand, the emission rate can be controlled by changing the photonic density of states in the vicinity of the dipole.1

In the strong coupling regime, the physical properties of the extended electromagnetic modes and the localized electronic excitations mix and create a hybrid light-matter state known as an exciton-polariton (EP).2 Strong coupling of light and excitons can be applied, for example, to transfer coherence from the electromagnetic mode to the EP which can result in low-threshold coherent radiation emission.3,4 Increased coupling between light and matter can be achieved by increasing the excitation rate, therefore, strong coupling is usually studied in cavities2–5 where both the excitation rate is increased by focusing of the light mode, and the emission rate is increased by Purcell enhancements.1 However, the cavity geometry limits the application of EPs to devices based on localized interactions.

Here, we report on the room temperature observation of propagating waveguide exciton-polariton (WGEP) modes in a thin polymer slab waveguide doped with a J-aggregating dye. We observed both transverse electric (TE) and transverse magnetic (TM) WGEP that have room temperature splitting values of 190 meV and 125 meV, respectively, that are on the same order as those measured in systems of J-aggregates embedded in micro cavities.5

Strong coupling of excitons and waveguide modes was reported previously, using semiconductor waveguides at cryogenic temperature6 or using semiconductor nanowires at room temperature.7,8 Here, we study the propagating strongly coupled WGEPs in organic slab waveguide at room temperature which makes this configuration simple and interesting for future device applications of WGEPs, e.g., WGEP based switchable interconnects and thin film optoelectronic devices.

The fabricated sample is illustrated in Fig. 1(a). To produce the polymer EP waveguide, we evaporated 30 nm of silver onto an indium tin oxide (ITO) coated glass which was pre-cleaned by sonication in solvents followed by O₂ plasma etching. ITO coated glass was used since it gives a cleaner surface with our process as compared to uncoated glass. We then spin-coated an aqueous solution of 5% polyvinyl alcohol (PVA) mixed in a 3:1 ratio with a 5.7 mM solution of J-aggregating cyanine dye. The cyanine dye used was the 5,6-dichloro-2-[3-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2(3H)-benzimidazolidene]-1-propenyl]-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide, inner salt, sodium salt, NK2203, Hayashibara (TDBC), which is known to form linear chains of J-aggregating molecules at low concentrations (>0.05 mM).5 The bonding interaction of the aligned transition dipoles of the J-aggregate molecule chain leads to red shifted absorption and emission with respect to that of the monomer dyes. In addition, the absorption and emission line widths become much sharper and the oscillator strength increases, which makes it possible to achieve strong coupling at room temperature, with large Rabi splitting values.10

The thickness of the polymer film was measured by a profilometer to be ~295 nm and the refractive index of the

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FIG. 1. (Color online) (a) Schematic diagram of fabricated sample and measurement geometry. (b) Fluorescence spectrum from the sample shows sharp emission at the J-band.

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film was deduced from dispersion relation measurements to be 1.55. The doped polymer film acts as the optical waveguide core and the thin metal film acts as a mirror to efficiently confine the mode, since the index step between the polymer and substrate is small (λ = 590 nm: \( n_{\text{glass}} = 1.52, n_{\text{PVA}} = 1.49 - 1.55 \) (Ref. 11)).

In order to verify that the dye molecules formed aggregates, we excited the sample using a green laser (continuous wave, \( \lambda_0 = 532 \) nm) and measured the fluorescence from the sample (LabRAM HR, Horiba Scientific). Figure 1(b) presents fluorescence measurements which show a sharp emission at the J-band. The peak of the emission was at 2074 meV and its width was 51 meV, which agrees with the values reported previously\(^{12} \) and indicates that the molecules formed aggregates.

We measured the dispersion relation of the waveguide modes using the prism coupling setup depicted in Fig. 1(a). Light from a Xe arc lamp was focused into an optical fiber. The light from the fiber was collimated with a lens, polarized, and directed onto a prism, which was optically coupled to the sample with index matching oil. The reflected light was focused by a lens into a second optical fiber and input to a spectrometer. The sample and prism were mounted on a rotation stage, enabling the angle of incidence \( \theta \) to be changed. Waveguide modes are excited when the parallel component of the wave-vector of the incident light \( n_g \lambda_0 \sin \theta \) matches the propagation constant \( \beta \) of the waveguide mode, where \( k_0 \) is the wavevector of light in free space, and these show up experimentally as a resonant loss in the reflection spectrum.

We rotated the stage in steps of 2° and at each angle measured the reflection spectra for both polarizations. Since the TE and TM modes are well-separated in phase space, the spectral dips we measure in reflection for each polarization are well separated in wavelength for a given incident angle. For each incident angle, we may thus normalize the TM reflection spectrum by the TE reflection spectrum without any loss of information. TE modes thus appear as peaks in our normalized spectra and TM modes appear as dips. This normalization method allows us to filter out the wavelength dependence of our measurement system (lamp power and optical components) and to depict the dispersion for both polarizations in a single plot.

Figure 2(a) shows the normalized measurement at \( \theta = 49.6° \). We can see Rabi splitting of the TM resonance into two dips around the exciton peak at \( \sim 595 \) nm. Figure 2(b) presents the measured normalized reflection spectra vs. the angle of incidence (\( \theta \) of Fig. 1(a)). We clearly observe anticrossing of the dispersion curves for both polarizations, which indicates strong coupling.

We simulated the experimental results using the rigorous coupled wave analysis (RCWA) method, where we used a single Lorentzian oscillator model for the permittivity of the J-aggregate doped PVA film,

\[
\varepsilon(\omega) = \varepsilon_\infty + \frac{f}{\omega_0^2 - \omega^2 - i\omega\Gamma},
\]

where \( \varepsilon_\infty = 1.55^2 \) is the off-resonance permittivity of the film, \( f \) is the oscillator strength which is a fitting parameter and was used to fit the splitting of the TM mode, \( \omega \) is the angular frequency, \( \omega_0 \) is the frequency of peak absorption of the exciton, and \( \Gamma \) is its width. The peak position and width values of absorption and fluorescence spectra of TDBC J-aggregates strongly overlap\(^{12} \), so, we obtained the values for the Lorentz oscillator \( (\omega_0 \) and \( \Gamma \) from the fluorescence measurements shown in Fig. 1(b). The simulation of reflection as a function of wavelength and angle of incidence is shown in Fig. 2(c). It can be seen that the experiments and simulations are in good agreement. Note that for angles below the critical angle \( \theta_c = \sin^{-1}(1/n_{\text{prism}}) \), the prism cannot be used to couple light into the waveguide.

By finding the position of the peaks and dips of Fig. 2(b), we can extract the dispersion relation \( E(k) \), where \( E \) is the energy and \( k \) is the momentum of the EP mode. This is plotted in Fig. 3. The splitting between branches of the dispersion curves indicates the strength of the coupling. We observe stronger coupling between the excitons and the photons for the TE mode (splitting 190 meV) than the TM mode (splitting 125 meV).

The splitting strength is expected to be proportional to the square root of the absorbance\(^{2,5,13} \) in the waveguide. The absorption of each mode is proportional to the relative energy density of the mode in the waveguide multiplied by the absorption dipole moment of the excitons aligned with...
the polarization of the exciting field. Different splitting strengths may, therefore, result either from different field confinement in the waveguide for the different polarizations or from anisotropic arrangement of the J-aggregate chains. We used finite element simulations to calculate the square root of the field confinement of the uncoupled modes (for undoped PVA) in the waveguide layer given by

$$\eta = \sqrt{\frac{\int_{\text{WG}} n(x) E(x) \cdot \hat{E}^* (x) dx}{\int_{\text{Mode volume}} n(x) E(x) \cdot \hat{E}^* (x) dx}},$$  \hspace{1cm} (2)$$

where $x$ is the transverse coordinate, $n(x)$ is the refractive index, and $E(x)$ is the electric field, and compared them to the splitting values obtained by the reflectance simulations. The integral in the numerator was performed over the waveguide, while that in the denominator was performed over the entire mode volume. The calculated ratio of the square root of the field confinement $\eta_{TE}/\eta_{TM} = 1.29$ was very close to the calculated ratio of splitting $\Delta_{TE}/\Delta_{TM} = 1.22$, but the experimental splitting ratio (1.55) was 27% higher than the simulated one. The difference between the simulation and the experiment could result from different experimental confinement of the modes due to the fact that TM modes are more sensitive to the thickness of the metal layer and are more susceptible to scattering effects or due to anisotropic arrangement of the J-aggregates and the consequential anisotropic absorption in the system which can result from the spinning process.\textsuperscript{14}

In 2004, Bellessa \textit{et al.}\textsuperscript{15} demonstrated strong coupling of excitons and surface plasmon polaritons (ESPP) in a similar system. Their sample did not support waveguide modes as the doped polymer layer that was used was too thin (50 nm). Of course, the ESPP is still present in our thick polymer sample, but it lies below the glass light line and cannot be accessed by our prism coupling setup. It can be accessed either by using grating coupling\textsuperscript{16} or by using a higher index prism. In order to investigate the relative Rabi splitting of WGEP vs. ESPP modes, we used RCWA to simulate reflection using a prism with a refractive index of 1.8. We use a 300 nm doped PVA film on a 50 nm silver film, which is more optimal for coupling into ESPP modes. The simulation results showing the emergence of the ESPP mode are presented in Fig. 4(a), and finite element method simulations of the associated mode profiles of the TE, TM, and surface plasmon polariton (SPP) modes are shown in Figs. 4(b)–4(d), respectively. The relative field confinement ratios of the TE and TM modes match the calculated splitting ratios ($\eta_{TE}/\eta_{TM} = 1.28$, $\Delta_{TE}/\Delta_{TM} = 1.25$) and are very close to earlier values. The TE and SPP modes have nearly identical confinement in the waveguide and, therefore, nearly identical splitting ($\eta_{TE}/\eta_{SPP} = 1.01$, $\Delta_{TE}/\Delta_{SPP} = 1.02$), though the TE mode fills the PVA layer and the SPP mode decays across the layer.

In conclusion, we report on the observation of strong coupling between excitons in a J-aggregate dye and waveguide modes of a thin polymer film which generates large splitting of the dispersion curves for both TE and TM modes. We numerically show that the difference in coupling strengths in the numerical simulation results from the difference in the confinement of the modes to the doped region. In the experiment, more factors have to be taken into account, e.g., scattering effects or anisotropy. In addition, we show numerically that this system allows the excitation of ESPP which has similar confinement in the doped waveguide compared to the TE mode. We anticipate that the ability to excite WGEP modes in thin polymer films could be employed in new applications of coherent light–matter excitations, such as waveguide polariton lasers and switchable or active interconnects. Moreover, different Rabi-splitting values for different polarizations and different modes which are associated with different time scales of energy transfer between the excitons and the electromagnetic modes can be adjusted and controlled by aligning the excitons in plane or out of plane of the waveguide.

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