Ultrafast polariton population build-up mediated by molecular phonons in organic microcavities

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A key prerequisite for low-threshold polariton lasing in organic or inorganic microcavity systems is the efficient population of the lower polariton ground state. Here, we report the observation of a resonant phonon-mediated relaxation process which gives rise to nonthermal polariton population with sub 100 fs build-up times. This mechanism is manifested by discrete maxima of the angular-resolved photoluminescence intensity, with corresponding shortening of the photoluminescence rise time at respective phonon resonances. The realization of enhanced relaxation rates in disordered J-aggregate systems is important for developing room temperature organic laser sources with less fabrication complexity than their crystalline counterparts. © 2011 American Institute of Physics. [doi:10.1063/1.3645633]

Organic semiconductors combine simplicity of processing methods with flexibility in tailoring optical properties.[1] Such favourable characteristics, combined with large oscillator strengths, allow the realization of strongly coupled organic microcavities with large Rabi splitting at room temperature.[2] For example, commonly used J-aggregates offer complete control of the Rabi splitting and oscillator strength by varying the dye concentration.[3] However, the large intrinsic disorder in J-aggregates and the coexistence of polaritons with large populations of uncoupled excitons reduce the quantum yield and represent a significant loss channel.[4,5] Thus, compared to inorganic systems, it is harder to achieve the required conditions for polariton lasing and other cooperative phenomena crucial for next generation ultralow power optoelectronic devices such as laser and optical switches.

Up to now, nonlinear emission in an organic microcavity has only been achieved in crystalline anthracene microcavities,[6] where the scattering from the exciton reservoir (ER) to the polariton ground state is enhanced by pronounced vibronic resonances.[7] The importance of analogous polariton relaxation assisted by longitudinal optical-phonons in inorganic microcavities was discussed, e.g., in Ref. 8 and a reduced stimulation threshold was recently accomplished in this way.[9] In J-aggregate microcavities, the important role of discrete molecular phonons in the polariton relaxation was recently suggested[10] and studied as a function of temperature.[11]

In this letter, we present clear evidence that the scattering of excitons with the discrete molecular vibrational modes of a J-aggregate microcavity creates an efficient relaxation channel for fast and controllable nonthermal population of lower polariton (LP) branch states. For non-resonant excitation, the overwhelming majority of the injected carriers pop-

ulate the ER incoherent states.[3,7] Strong enhancement of light emission is observed from LP states whose energy separation from the ER matches the discrete J-aggregate molecular vibration energies extracted from the Raman spectra (Fig. 1(b)). Fast radiative decay allows for the observation of photoluminescence (PL) from such nonequilibrium states prior to thermalization to the bottom of LP branch. Furthermore, our ultrafast pump-probe measurements clearly demonstrate the shortening of polariton population build-up time at specific phonon resonances. All microcavity samples studied here have the structure shown in Fig. 1(a): two dielectric mirrors consisted of 11 $\lambda/4$ pairs of SiO_2 and Nb_2O_5, separated by a 220 nm thick active layer of 5,6-dichloro-2-[[5,6-dichloro-1-ethyl-3-(4-sulphobutyl)-benzimidazol-2-ylidene]-propenyl]-1-ethyl-3-(4-sulphobutyl)-benzimidazolium hydroxide, sodium salt inner salt (TDBC)[12] dispersed in a gelatine matrix and spin coated to form the cavity region of the device. Despite the differences in dye concentration between different samples, the optical characteristics of the
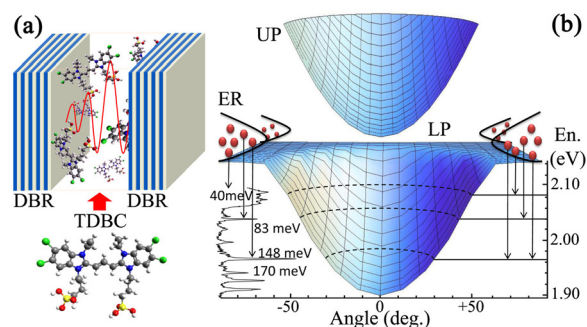

FIG. 1. (Color online) (a) A schematic of the organic microcavity structure containing J-aggregates dispersed in matrix. (b) Upper and lower polariton branches and uncoupled exciton reservoir states. Population of lower polariton states occurs through resonant coupling of exciton reservoir via molecular phonons in accordance with the J-aggregate Raman spectrum.

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active film are similar and defined by an absorption linewidth of 51 meV peaked at the exciton resonant energy at 2.09 eV. The Q-factor of the cavities has a value of 300, corresponding to a polariton radiative lifetime of 100 fs.

To study the relaxation of the LP populations, we performed angle-resolved PL experiments at room temperature, by exciting non-resonantly at a 7.58 kHz rep rate with a quasi-CW 0.51 ns pump pulse tuned at 532 nm. By tilting the sample with respect to the excitation/collection lens, we were able to image on a CCD detector the angular PL in the range from 0° to 60°, which allowed us to characterize the entire LP dispersion. Due to strong birefringence of the spin coated film caused by the alignment of the J-aggregates inside the matrix,[13] we used linearly polarized detection in the direction perpendicular to the transition dipole moment. This geometry meets the resonant condition for Raman scattering, which is strongly dependent on the polarization.[13,14]

In Fig. 2, we present a series of PL contour plots with varying exciton-photon detuning. By tuning the exciton-photon resonance, we control the LP branch-ER energy separation and allow for different discrete molecular vibrations to create resonant relaxation channels from the exciton reservoir into rapidly radiating polariton states. The comparison between experiment (upper panel) and theory (lower panel) in Fig. 2 demonstrates a non-thermal population of different regions of the LP branch, which is controlled via the detuning. Indeed, our measurements indicate that a resonantly enhanced relaxation mechanism prevails over other scattering processes and could potentially be used to achieve macroscopic polariton occupancies necessary for lasing.[6,15,16]

To interpret and guide the experiment, we calculated the time-dependent LP populations by deriving density matrix equations of motion following Refs. 10 and 17. Our Hamiltonian includes a J-aggregate contribution obtained by diagonalizing linear molecular chains comprising of hundreds of monomers.[18] Each molecule within the linear chain is coupled with the rest via dipole-dipole interactions, which yield collective excitonic states localized at specific segments of the linear chain. Static disorder is taken into account by considering energy fluctuations with Gaussian

distribution.[19,20] For simplicity, we only consider the coupling of the lowest exciton eigenstate in the Lifshitz tail of the J-band of each aggregate to the photonic microcavity mode, which dominates the oscillator strength.[18] We then transform into extended polariton eigenstates and include the higher energy uncoupled Frenkel excitons[4] via their interaction with the phonons, which couples all polariton and ER states. The equation of motion for the LP populations couples to phonon-assisted density matrices, which, similar to Ref. 17, were treated in the steady state after introducing their dephasing time that relaxes the energy conservation condition.[17] We thus derive a master equation that also includes nonlinear and quantum kinetic effects, which we solved here within the linear and Born approximations.[17] The details of our derivation will be published elsewhere. The phonon energies used in our simulations were extracted from the measured J-aggregate Raman spectra (Fig. 3(c)). As seen in Fig. 2, we thus attain excellent agreement between theory and experiment for the PL emission. Using the values of the unknown exciton-phonon coupling strengths inferred from the PL, we then obtained the time-dependence of the LP populations, which determines the temporal PL dynamics. We thus accomplish polariton population build-up times on the order of hundreds of femtoseconds from delocalized
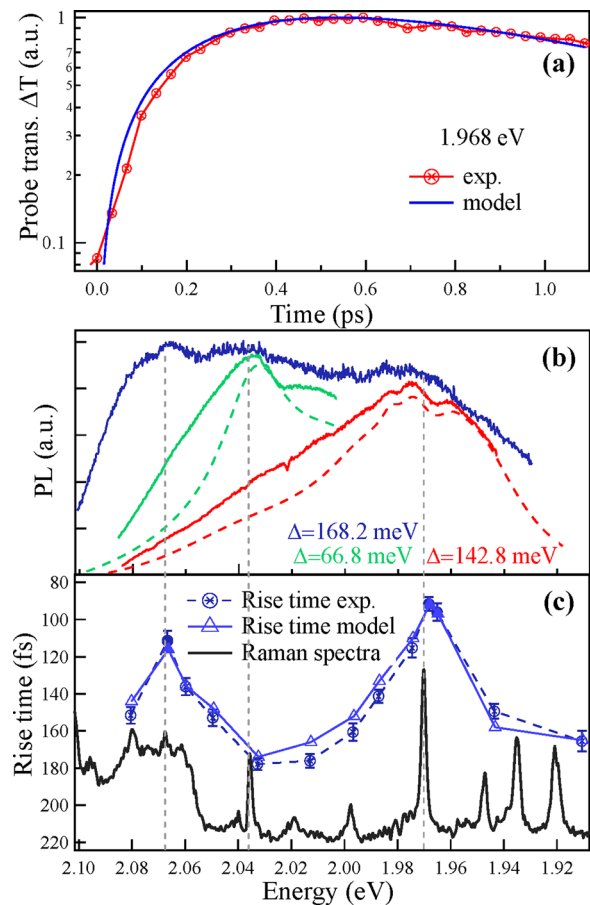
FIG. 3. (Color online) (a) Temporal changes in probe transmission reflecting real polariton population at vibronic resonance of 1.968 eV; measured (circles) and modelled (solid line). (b) Experimental (solid lines) and modelled (dashed lines) angle integrated PL intensity for different exciton-cavity mode detunings showing peaked emission when resonance condition is met. (c) Measured and modelled ER to LP rise time values at different energies. J-aggregate Raman spectra are superimposed for comparison confirming fast build-up time at resonances.
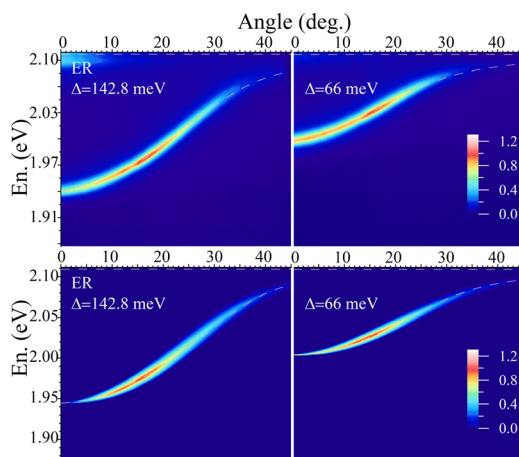
FIG. 2. (Color online) Normalized contour plots of the angular PL intensity for two different detunings. Upper panel: experimental lower polariton branch PL images. Lower panel: modelled steady state polariton emission. Dashed lines indicate the bare cavity mode dispersions and exciton reservoir energy.

bright exciton states, followed by a slower decay on the ps timescale reflecting the overall reduction of ER population (Fig. 3(a)).

To confirm our conjecture of the relevant scattering mechanism in the time domain, we probe, using sub-35 fs time resolution, the LP population dynamics by performing transient pump-probe spectroscopy and we compare this with the theoretical predictions for the parameters extracted from the static PL. The rise time and subsequent relaxation dynamics of a non-resonantly excited population was extracted from the changes in the probe transmission at various time delays. Here, we excited the system using 1.5 mW, non-resonant, 400 nm, sub-100 fs pump pulses at a 250 kHz rate. A 0.2 mW probe beam was then continuously adjusted in resonance with the polariton dispersion. We thus obtained the dynamics of the real polariton populations along the LP branch. The LP branch population build-up times due to exciton-phonon scattering are obtained by fitting the rise times of the measured transmission signals when varying the probe energy between 1.91 eV and 2.08 eV, whereas signal decay reflects the scattering rate from all ER states to LP branch. The results of the fits, together with the modelled rise time values, are shown in Fig. 3(c). For comparison, the Raman spectra of the spin-coated J-aggregate film, scaled to the energy of the ER at 2.118 eV, is also shown. Remarkably, from rise time fitting, we find that relaxation into specific polariton states along the LP dispersion is significantly enhanced when the resonance conditions for selected discrete vibrational modes are met. In addition, the nontrivial dependence of the polariton population build-up time on probe energy along the LP branch proves that the rise time is not associated with the duration of the pump pulse which creates initial exciton reservoir population. Furthermore, it can be seen that the energies of the angle integrated PL maxima (Fig. 3(b)) coincide with the Raman peak positions. Interestingly, only vibrational modes with energies smaller than the polariton "trap" depth are activated depending on the sample detuning conditions. The observed relative broadening of the PL, as compared to the sharp Raman peaks, originates from the intrinsic on-site energetic disorder of the J-aggregate Frenkel excitons,[21,22] confirmed by our theory.

In conclusion, we report on a resonant ultrafast exciton-discrete phonon scattering mechanism that enhances the relaxation to the LP branch of a J-aggregate organic microcavity. The engineering of this phonon-assisted relaxation channel in J-aggregate microcavities could ultimately lower the threshold for achieving stimulated polariton amplification and lasing, by overcoming the obstacle of non-radiative exciton-exciton annihilation effects.[23]

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