Long-Range Transport of Organic Exciton-Polaritons Revealed by Ultrafast Microscopy

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Supporting Information

ABSTRACT: The excitations in organic materials are often described by Frenkel excitons, whose wave functions are tightly localized on the individual molecules, which results in short-range, nanoscale transport. However, under strong light-molecule coupling, new quantum states, known as cavity polaritons, are formed and the wave functions describing the coupled system extend over distances much larger than the molecular scale. Using time-resolved microscopy we directly show that this fundamental modification in the nature of the system induces long-range transport in organic materials and propagation over several microns. By following the motion of polaritons in real-time, we measure the propagation velocity of polaritons and we find that it is surprisingly lower than expected. Our approach sheds new light on the fundamental characteristics of polaritons and can provide critical information for the design of future organic-electronic devices, which will harness the polaritonic properties to overcome the poor conductance of organic materials.

KEYWORDS: polaritons, organic semiconductors, pump−probe microscopy, exciton transport

When dye molecules are embedded in optical microcavities, strong light−matter interaction can form composite photonic-excitonic excitations, known as cavity polaritons. Since the recent discovery that the rate of a chemical reaction changes under strong coupling, the potential of using strong coupling for tailoring material properties has been increasingly drawing interest. One of the most intriguing effects which takes place under strong coupling in organic systems is the coherent and collective coupling of a macroscopically large number of molecules to a single photonic mode of the cavity. As a result, the polaritonic wave functions become delocalized and extend over distances comparable to the optical wavelength. The extended nature of the polaritonic states and the collective coupling of molecular ensembles was first demonstrated by the observation of spatial coherence of spontaneous emission from molecular films strongly coupled to surface plasmons. Naturally, the creation of delocalized states in the coupled system should affect transport phenomena, and indeed, very recently, a large enhancement in the conductance of organic semiconductors has been demonstrated under strong coupling. Moreover, it was observed that spontaneous emission from molecular films strongly coupled to propagating surface waves extends far beyond the excitation spot.

While these pioneering experiments have shown that long-range effects can emerge from strong light−matter coupling, they relied on steady-state measurements and inferred the polariton transport properties from time-averaged quantities. Although the dynamics of organic strongly coupled systems have been extensively studied in the time-domain, all of these previous studies were limited to single-point detection, with any spatial dynamics remaining hidden. However, in order to fully reveal the transport mechanism of polaritons and the dynamics occurring during their propagation, a direct measurement of the polaritons’ motion is highly desirable. Here we employ ultrafast microscopy to study for the first time the evolution of polaritons in organic cavities in space and time simultaneously. We observe the expansion of a localized polariton cloud in real-time, providing direct proof of long-range transport effects.
range transport in molecular systems under strong coupling. Surprisingly, we find that the polariton velocity is slower than the group velocity anticipated from the polariton dispersion.

In our experiments we use a metallic microcavity containing TDBC J-aggregate molecules26 (see Methods for details). We tune the cavity thickness to 156 nm, such that its optical resonance matches the molecular absorption (590 nm) at an incident angle of $\theta = 45^\circ$ for transverse magnetic (TM) polarization. This gives rise to the formation of polaritonic states which have both mixed photonic/excitonic nature (i.e., similar weights of the two components) and nonzero in-plane momentum. We characterize our system by performing angle-resolved reflection spectroscopy, from which we extract the dispersion relation of the hybrid cavity. The results are presented in Figure 1, for both TM (Figure 1a) and TE (Figure 1b) polarization. As seen, the dispersion displays clear avoided-crossing behavior and the formation of upper- and lower-polariton branches, as expected for the strong coupling regime. In addition, we performed transfer-matrix simulations for the same structure (black lines in Figure 1a,b), which perfectly match the measurements, with a Rabi-splitting of 200 meV separating the polaritonic branches at resonance. Note that since the TE cavity modes have stronger dispersion than the TM modes, the resonance points are different for the two polarizations (i.e., in-plane momentum of $k_x = 7.5 \, \mu \text{m}^{-1}$ for TM polarization and $5.3 \, \mu \text{m}^{-1}$ for TE).

In order to study the spatial dynamics of cavity polaritons we constructed a time-resolved imaging system, based on wide-field, two-color transient absorption microscopy29,30 and operated in reflection mode (see Methods). Transient absorption is frequently used for time-resolved spectroscopy and it provides temporal information about the excited state population. Here, we incorporated imaging capabilities into the system in order to acquire both temporal and spatial information. Briefly, the cavity sample is excited nonresonantly by a focused 520 nm laser pulse, creating a localized spot of polaritons. The probe beam, passing through a variable delay line, is then launched onto the sample at $45^\circ$, covering a large area around the excited spot. The reflected probe beam is imaged onto a camera and the transient reflection $\Delta R/R$ (see Methods) is recorded. In this way our system captures the spatial distribution of the polaritons as a function of the time-delay $\tau$, following their excitation by the pump pulse.

The results of the pump-probe microscopy are presented in Figure 2. First, we performed the measurements on a control sample, consisting of a polymer layer doped with TDBC molecules and deposited on a silver mirror. Figure 2a shows the transient reflection image at $\tau = 0$, that is, when the pump and probe pulses are temporally overlapping. The image represents the molecular excitons’ distribution in the film, and it corresponds to the shape of the circular pump beam, with a diameter of $\sim 3 \, \mu \text{m}$ fwhm. When the probe beam is delayed by $\tau = 9$ psec (Figure 2b), the signal decreases due to the decay of the exciton population, but its spatial distribution remains similar. This is expected, since the diffusion length of the excitons (several nanometers) is much smaller than both the excited spot and the resolution of the imaging system. In sharp contrast, when we perform the same measurement on the cavity sample, in which polaritons are excited, we observe a very different behavior: for a TM-polarized probe the polariton spot, having a similar distribution at $\tau = 0$ (Figure 2c), expands in the horizontal direction, reaching a width of $6 \, \mu \text{m}$ after 7 psec, as seen in Figure 2d. The appearance of a change in the probe reflection away from the pumped area clearly demonstrates the motion of polaritons in the sample, and confirms that micron-scale transport of polaritons indeed takes place.

![Figure 1. Polariton dispersion for TM (a) and TE (b) polarizations, acquired via angle-resolved reflection microscopy (false-color maps) and by transfer-matrix simulations (solid black lines). The white dashed lines mark the dispersion of free photons with an incident angle of $45^\circ$ and the in-plane momentum is related to the angle of incidence by $k_x = \frac{2\pi \sin \theta}{\lambda}$.](image1)

![Figure 2. Spatial distribution of excitons in a film of bare molecules at zero time delay (a) and at a delay of $\tau = 9$ ps (b) between the pump and probe pulses. (c–f) Polariton distribution measured in the cavity sample for TM and TE polarization at zero time delay (c, e) and after 7 ps of evolution (d, f), demonstrating the expansion of the excited polariton cloud. The arrow in (a) marks the in-plane momentum component of the probe beam in all measurements, and the color bars indicate the magnitude of the transient-reflection signal in $10^{-3}$.](image2)
place in the organic cavity. Note that the expansion occurs to the right, which is due to the oblique incident angle of the probe. Since there is no inherent directionality in the planar cavity and the polaritons are excited nonresonantly, the lower polariton branch is isotropically populated in phase space, and expansion should occur in all directions. However, due to momentum conservation, the probe beam selects only a subpopulation of excited polaritons, having an in-plane momentum set by the transverse component of the probe wave-vector. This results in the apparent directional transport observed in Figure 2d, in a manner similar to fluorescence imaging experiments, where Fourier-space filtering has been used to interrogate a particular direction of polaritons. Interestingly, this directionality also excludes the possibility that the observed signal results from other nonlocal effects, such as thermal nonlinearity, which would lead to isotropic behavior. For a TE-polarized probe we obtain similar results (Figure 2e for $\tau = 0$ and Figure 2f for $\tau = 7$ psec); however, the expansion is more moderate compared to the TM case.

In order to reveal the propagation dynamics of the polaritons we repeated the measurements at several intermediate time-delays, as shown in the 2-D images in Figure S1. Figure 3a,b shows the normalized horizontal cross sections of the polariton cloud (obtained by averaging the transient reflection distribution over 3 $\mu$m around its maximum) for increasing delay time values, with TM and TE polarization, respectively (for the data before normalization, see Figure S2). Once again, one can clearly see the gradual broadening of the polariton cloud following its excitation. In Figure 3c we plot the width of the polariton cloud (see Supporting Information for details) as a function of the delay time, from which we estimate the expansion velocities to be $0.4 \pm 0.1$ $\mu$m/psec for the TM case and $0.16 \pm 0.1$ $\mu$m/psec for TE polarization. In an additional set of measurements (see Figure S3), we observed similar expansion when probing the polariton dynamics. However, when the probe wavelength was tuned to the energy of the uncoupled states in the same cavity (around 590 nm), the recorded spot maintained its shape over 7 psec, as observed in the bare-molecule film.

The observed expansion velocities can be compared with the group velocities extracted from the measured dispersion curves for the lower polariton branch at 45°, which gives values of 26.3 and 25.7 $\mu$m/psec for TM and TE polarizations, respectively (see Figure S4). Clearly, the expansion velocity measured in our experiments is significantly lower than anticipated, suggesting that the transport of polaritons does not occur through a simple ballistic process. This could be a result of the inherently disordered nature of molecular films, which is manifested in the properties of the polaritons through their excitonic component and limits their spatial extent. Interestingly, for the TE polaritons, which are measured off-resonance and have a larger excitonic component (82% compared to 55%, see Figure S4) the reduction in the measured velocity is more pronounced, indicating that the slow velocity measured in our experiments is indeed related to the underlying properties of the molecular excitons. These observed propagation velocities are also much slower than those reported in ref 19, in which organic molecules were coupled to Bloch surface waves in dielectric structures. Those hybrid structures, which were fabricated by physical vapor deposition techniques, are much more ordered than the metal–polymer cavities used in our experiments, and the polaritons are subjected to a significantly lower degree of disorder and losses in the metal. As a result, the propagation distances of the polaritons in such structures are much longer,19 and the propagation velocities will naturally be closer to the group velocity, as determined by the dispersion relation of the system.

It is interesting to note that in recent theoretical work31 it was predicted that under certain circumstances the dark (uncoupled) states of the strongly coupled system may inherit the delocalized nature of the polaritonic modes, which should give rise to an additional mechanism by which strong coupling can lead to long-range transport. However, such delocalization is not expected to occur in systems for which the spectrum is continuous31 (such as planar cavities or with surface-plasmons) and, therefore, should not contribute to the expansion we observed in our experiments. Furthermore, the difference in the measured velocity for the TM and TE polarizations (Figure 3c) and the fact that we do not observe any expansion when probing the uncoupled states (Figure S3) provide strong indications that the expansion is directly related to the motion of polaritons in the system. Nevertheless, the influence of the dark states on the transport and spatiotemporal dynamics in strongly coupled systems may very well prove to be important, and our approach provides the possibility of studying such effects in the future.

In order to compare the overall kinetics to previously reported data, we integrate the recorded signal of $\Delta R/R$ over the whole image to obtain the total polariton population as a function of time, as presented in Figure 3d. We find that the
probed polariton population (circles for TM polarization and triangles for TE) decays with a half-life time of ∼3 psec for both polarizations. This decay is slightly slower than that of bare molecules (rectangles in Figure 3d), and it is consistent with previous fluorescence lifetime and transient absorption measurements conducted on similar systems.26 Interestingly, our spatially resolved measurements shed new light on the lifetime of the polaritons themselves.26,27 This notion is once established that this effect is associated with an inherently long lifetime of the polaritons themselves.26,27.27 These slower decay rates were initially explained by invoking a slow energy transfer process from the uncoupled-exciton reservoir into the lower polariton branch,12,25 however, recent time-resolved experiments have established that the propaga-tion velocity of polaritons in low-Q cavities should be dominated by the short cavity lifetime and therefore very short (∼50 fsec), the typical lifetimes observed in time-resolved experiments are several pico-seconds.26−28 This notion is once again reinforced by our spatially resolved measurements: as the generated population in the exciton reservoir is unlikely to migrate in the sample, the appearance of a signal a few microns away from the initial excitation spot and only several picoseconds after the excitation pulse can only be attributed to a lower polariton lifetime, on a picosecond time-scale.

In conclusion, using ultrafast time-resolved microscopy we were able to follow the motion of polaritons in real time, providing the first direct observation of long-range transport in organic materials under strong coupling. These measurements reveal that the propagation velocity of polaritons is in the range of 0.2−0.4 μm/psec, which is considerably slower than predicted by the polariton dispersion, suggesting that in organic microcavities the transport is not purely ballistic. This discrepancy becomes larger when the polaritons have a larger excitonic component, indicating that this behavior originates from the disordered nature of the molecules. As we demonstrated here, our time-resolved microscopy technique opens new possibilities to explore the spatiotemporal dynamics of organic strongly coupled systems and to reveal the underlying processes governing transport in such systems. Most importantly, our results provide direct evidence that strong coupling of molecular excitons to extended photonic modes brings the energy transport from nanometric dimensions into the micron scale. As demonstrated recently, this huge enhancement in the transport properties of such hybrid molecular-photonic structures can be exploited to tailor and to improve the performance of organic-electronics devices.

**METHODS**

**Sample Preparation.** The TDBC-cavity structure was prepared by first sputtering a 30 nm thick Ag layer on a precleared microscope coverslip (0.17 mm thick). Then a polymer film doped with J-aggregate molecules (TDBC) (5,6-dichloro-2-[[5,6-dichloro-1-ethyl-3-(4-sulphobutyl)-benzimidazol-2-ylidene][propenyl]-1-ethyl-3-(4-sulphobutyl)benzimidazolium hydroxide, inner salt, sodium salt, Few Chemicals) was deposited using spin-coating (810 rpm) to form a layer of ∼159 nm. The polymer/dye solution was prepared by dissolving poly(vinyl alcohol) (PVA, molar weight 205000) in water (5 wt %) at 90 °C for several hours, cooling to room temperature and mixing with an equal amount of 0.5 wt % water solution of TDBC. The mixture was filtered with a 0.2 μm nylon membrane filter prior to spin coating. Finally, sputtering a second layer of Ag (30 nm) completed the cavity structure, yielding an empty cavity Q-factor of ∼30. A control sample of bare molecules was prepared in a similar manner, with a ∼150 nm thick PVA/TDBC layer deposited on a single 30 nm thick Ag mirror.

**Dispersion Measurements by Angle-Resolved Reflectometry.** A halogen lamp was used to generate a collimated white-light beam, which was then focused on the sample by an objective (Olympus, 60×, N.A. 0.9), such that a broad distribution of angles simultaneously sampled the cavity structure. The beam was then reflected by the cavity back into the objective and the intensity distribution at the back focal plane of the objective was imaged onto the entrance slit of an imaging spectrometer (IsoPlane SCT320, Princeton Instruments). Using this configuration, the angle-resolved reflection spectrum can be measured with a single shot and the polariton dispersion, appearing as a dip in the reflection, can be conveniently extracted.14 A polarizer was placed in front of the spectrometer to allow the separate measurements of TE or TM polarizations, and a silver mirror was used as a reference for the reflection spectrum.

**Pump−Probe Microscopy.** A sketch of the pump−probe microscopy system is presented in Figure 4. In our experiments we used a pulsed laser amplifier (Spitfire Ace) operated at 500 Hz with 80 fs pulses and a wavelength of 800 nm. To generate the pump beam, part of the amplifier output was sent into an optical parametric amplifier (Topas, Light Conversion) which converted the pulse wavelength to 520 nm. The pump beam was passed through an optical chopper to reduce its repetition rate to 250 Hz and then focused onto the sample at normal incidence by a 60× objective (Olympus, N.A. 0.90). We note that the pump was injected into the cavity through the glass substrate side. Another part of the amplifier output was used for the probe beam: the 800 nm beam was sent through a computer-controlled delay stage, which was used to control the time-difference between the excitation and probe pulses and then focused onto a Sapphire plate in which pulses of

![Figure 4. Schematic diagram of the pump−probe microscopy setup. WP, half-wavelength waveplate; L1, lens (150 mm); L2, lens (50.8 mm); SPF, short-pass filter (700 nm); BPF, band-pass filter (655 ± 20 nm), mounted on a rotation stage; L3, lens (125 mm); L4, Nikon camera lens (50 mm); LPF, long-pass filter (580 nm); OPA, optical parametric amplifier.](image-url)
continuous white light (CWL) were generated. A variable neutral density filter and an iris were placed before the focusing lens and were used to optimize the stability of the generated CWL. Then, the CWL beam was collimated and passed through a 700 nm short-pass filter to remove any residual 800 nm light, and a band-pass filter (655 ± 20 nm), which was used to limit the energy span of the probed states. We used the angle-dependence of the filter transmittance to tune the wavelength of the probe according to the measured sample and the spectral region interrogated (590 nm for the bare-molecule film and 617 and 610 nm for the cavity measurements with TM and TE polarizations, respectively). The collimated beam was then refocused on the sample at an incident angle of 45°, and we aligned it such that the center of the probe and pump beams coincided at the plane of the sample. The reflected probe beam was imaged through a 580 nm long-pass filter (to block the scattered pump) from the sample to a scientific CMOS camera (Zyla 4.2, Andor) using a camera lens (Nikkor 50 mm F/1.2 AiS, Nikon) and with a magnification of 52. We limited the field of view of the camera to a square of height and width of 128 × 128 pixels, such that the whole area probed on the sample was 16 × 16 μm², being completely illuminated by the probe beam, which had an overall diameter of 100 μm. In that way, we made sure that the probed area was uniformly illuminated by the probe beam and that the measurements were less sensitive to small changes in the pump–probe spatial overlap. The camera acquisition time was set to 1.2 ms, and the camera was synchronized with the laser amplifier, such that each consecutive pair of acquisitions captured the probe image following a pump pulse (the “pumped” image, I⁺) and then a probe image without excitation ("unpumped" image, I₀). From these two intensity distributions the relative transient reflection can be obtained, being defined as $\frac{\Delta R}{R} = \frac{I^+ - I_0}{I_0} = \frac{I^+}{I_0} - 1$, where $\frac{I^+}{I_0}$ is the pixel-wise ratio of the two captured intensity distributions. In order to reduce noise, which is primarily due to intensity fluctuations of the probe beam, we recorded a long sequence of image pairs (typically using averaging times of 10–240 s, with 250 images-pairs per second), calculated the transient reflection for each pair separately and finally averaged over the whole sequence. Further reduction of noise was obtained by convoluting the resulting images with a Gaussian window of 5 pixels fwhm (corresponding to ~0.7 μm in the image), resulting in a final noise level of 3 × 10⁻⁴ in $\Delta R/R$, with an averaging time of 10 s. In our measurements we have verified that the recorded signal scales linearly with the pump intensity, without any change in the overall shape of the spot, which ensures that the excitation is monophotonic.

**ASSOCIATED CONTENT**

☐ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.7b01332.

Supplementary transient-reflection data, calculated polariton group velocities and excitonic weights, and details on the calculation of polariton-distribution width (PDF).

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


