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Coherence and Interaction in Confined Room-temperature Polariton Condensates with Frenkel Excitons

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Abstract

Strong light-matter coupling of a photon mode to tightly bound Frenkel excitons in organic materials has emerged as a versatile, room-temperature platform to study nonlinear many-particle physics and bosonic condensation. However, various aspects of the optical response of Frenkel excitons in this regime remained largely unexplored. Here, a hemispheric optical cavity filled with the fluorescent protein mCherry is utilized

to address two important questions. First, combining the high quality factor of the microcavity with a well-defined mode structure allows to address whether temporal coherence in such systems can be competitive with their low-temperature counterparts. To this end, a coherence time greater than 150 ps is evidenced via interferometry, which exceeds the polariton lifetime by two orders of magnitude. Second, the narrow linewidth of the device allows to reliably trace the emission energy of the condensate with increasing particle density and thus to establish a fundamental picture which quantitatively explains the core nonlinear processes. It is found that the blueshift of the Frenkel exciton-polaritons is largely dominated by the reduction of the Rabi splitting due to phase space filling effects, which is influenced by the redistribution of polaritons in the system. The highly coherent emission at ambient conditions establishes organics as promising room temperature polariton lasers and the detailed insights on the non-linearity are of great benefit towards implementing nonlinear polaritonic devices, optical switches and lattices based on exciton-polaritons at room temperature.

Keywords

polariton condensate, organic semiconductor, fluorescent protein, room-temperature, zero-dimensional, microcavity, strong coupling

Introduction

Strong coupling between excitons and photons inside a microcavity leads to the formation of cavity polaritons, hybrid light-matter quasiparticles.¹ In the low density limit, typically considered in experiments, exciton-polaritons obey bosonic statistics, and thus can undergo a dynamic condensation above a critical particle density due to stimulated processes into a low energy state.² In the condensed phase, polaritons emit coherent light without requiring population inversion. This process, which was termed polariton lasing, can exhibit a largely

decreased threshold as compared to that of conventional photon lasers.³ While the signatures of long range order and first order spatial coherence are routinely observed in polaritonic condensates,^{4,5} a pronounced temporal coherence only became accessible by utilizing noise-free pump-lasers,^{6,7} or engineering of a spatial confinement for the system.^{8–11}

In the conventional case of GaAs-based microcavity systems, the nonlinear properties originate from the admixture of Wannier-Mott type excitons with large spatial extension. They can interact with each other via the short- and long-range exchange interaction of the excitons,^{12,13} leading to an intrinsic non-linearity. This non-linearity has been established as a powerful tool to dynamically manipulate cavity polaritons and their condensates^{14,15} at ultra-fast time scales,¹⁶ and in complex architectures.¹⁷ Furthermore, it has recently been established as a tool to generate non-classical polariton states via the quantum blockade.^{18,19}

Utilization of organic materials in the context of strong light-matter coupling holds enormous potential, as they provide extremely robust polaritons at ambient conditions²⁰ and exhibit large coupling strengths up to 1 eV.²¹ However, signatures of polaritonic condensation and lasing were only reported in a small group of materials hosting tightly bound Frenkel excitons, including melt-grown single crystalline anthracene,²² polymers,^{23,24} fluorescent proteins²⁵ and yellow emitting dyes.²⁶ In a similar manner, polaritonic condensates at ambient conditions were discussed based on wide-bandgap semiconductors, including GaN^{27–29} and ZnO^{30,31} as well as inorganic perovskites.³² While in these studies the non-linear behavior in the strong coupling limit was reported, the explanation of the associated coherence of the emitted light and the nature of the interaction processes requires further investigation, both from experimental and theoretical side.

Here, we provide a joint experimental-theoretical study, which allows for a detailed description of the nonlinear response in the organic material-based system. This became possible by utilizing a high quality factor hemispheric cavity filled with the red fluorescent protein mCherry.³³ The unique molecular structure of mCherry proteins allows us to conduct the experiment under quasi-CW condition in the condensation process. While in most of the re-

ports devoted to polariton condensation with organic materials, optical pumping with short laser pulses (sub-10 ps) was required to circumvent exciton-exciton annihilation at high excitation densities,²⁴ due to the molecular structure fluorescent mCherry can tolerate strongly extended laser pulses. Here, the chromophore is surrounded by a β -barrel (Fig. 1a, inset) which protects the chromophore from the environment. In addition, the barrel-structure effectively reduces concentration-induced exciton-exciton annihilation, even in their solid state and suppresses biomolecular quenching at high excitation densities.²⁵

Further, the hemispherical cavity provides a sufficiently tight spatial confinement with very high quality factor.³⁴ This allows us to conduct our experiment in a single mode scenario. Under these conditions, we find strongly extended temporal coherence length exceeding 150 ps in the condensed phase. We further observe clear indications for both, the contribution of the power-dependent reduction of the Rabi splitting as well as the redistribution of polaritons in the system, and establish a microscopic model to explain the processes. In conventional semiconductor microcavities the main contribution of the blueshift of a polariton mode is assigned to the Coulomb exchange interaction of Wannier-Mott excitons¹² due to the overlap of the wavefunctions of different excitons. In organic materials such an overlap cannot be expected as a result of the strong localization of tightly bound Frenkel excitons. Here, we provide a theory which accounts for the phase space filling effects for the Frenkel excitons. It predicts a density-dependent reduction of the Rabi frequency, which consequently results in the blueshift for the lower polariton mode.

Cavity characterization

A sketch of the studied device is shown in Fig. 1a. The system consists of a thin (few hundred nanometers) film of mCherry embedded in a microcavity formed by two distributed Bragg reflectors (DBRs) each consisting of 10.5 alternating pairs of SiO₂- and TiO₂-layers and a stopband ranging from 1.67 eV (741 nm) to 2.31 eV (536 nm) with reflectivity $\geq 99.9\%$

Figure 1: (a) Illustration of the microcavity containing a thin film of mCherry. Inset: Schematic image (side view) of the molecular structure of mCherry. The chromophore (violet) is surrounded by an 11-stranded β -barrel. The image was generated using JMol 14.28.3. (b) Absorption (orange line) and emission (red line) spectra of a mCherry film with predominant absorption transition at 2.112 eV (orange dashed line, X). (c) False-color photoluminescence spectrum of a planar area of the device shows two lower polariton branches (LP1, LP2) and an upper polariton branch (UP, magnified in intensity by a factor of 10 for clarity). The position of the polariton branches can nicely be reproduced using a coupled oscillator model (black dashed lines) with a coupling strength g of 133 meV and two longitudinal photon modes (C1,C2, gray dashed lines) inside the cavity.

between 1.90 eV (653 nm) and 2.13 eV (582 nm). For this configuration the mode quality factor exceeds $Q = 2.5 \times 10^4$ theoretically and $Q = 7.5 \times 10^3$ experimentally. Prior to coating the top DBR, we prepared a plateau-like area on the glass substrate with depth and diameter of about $500 \mu\text{m}$ and $4000 \mu\text{m}$ by wet chemical etching. On this plateau, we have defined lens-shaped indentations using ion beam milling.^{35,36} These hemi-ellipsoidal dimples have diameters ranging from $2 \mu\text{m}$ to $12 \mu\text{m}$ and depths between 100 nm and 650 nm, and the shape of the micro-lenses yields to effective radii of curvature R_C that ranges between $2 \mu\text{m}$ and $360 \mu\text{m}$. The layer of mCherry is then sandwiched between the two DBRs. Details of the microcavity fabrication can be found in the method section.

Fig. 1b shows the absorption (orange line) and emission (red line) spectra of mCherry. The absorption of mCherry exhibits a predominant transition at 2.112 eV (587 nm, orange dashed line, X), whereas the emission has its maximum at 2.003 eV (619 nm) with a second smaller maximum at 1.829 eV (678 nm).

In Fig. 1c we plot a false-color photoluminescence (PL) spectrum from the planar area next to the array of lenses. To highlight the behavior of the two-dimensional upper polariton mode, the intensity of the upper area is magnified by a factor of 10 compared to the lower one. For a zero in-plane wave vector $k_{\parallel} = 0$ the polariton mode peaks are located at $E_{UP} = 2.209 \text{ eV}$, $E_{LP1} = 1.994 \text{ eV}$ and $E_{LP2} = 1.724 \text{ eV}$ with linewidths of $w_{UP} = 5.9 \text{ meV}$, $w_{LP1} = 9.3 \text{ meV}$ and $w_{LP2} = 7.4 \text{ meV}$. By iteratively calculating the uncoupled photonic modes inside the cavity using transfer-matrix method (gray dotted lines, C1 and C2 are the two longitudinal modes in the cavity) and fitting with a coupled oscillator model (black dashed lines, LP1, LP2 and UP) the positions and the curvatures of the measured polariton dispersions can be nicely reproduced. The cavity parameters can be estimated from the fitting model, which gives an optical cavity length of $1.14 \mu\text{m}$ and a coupling strength g of 133 meV (Rabi frequency of $\hbar\Omega_R = 2g = 266 \text{ meV}$).

Spectral properties of the polariton condensate

Next, we provide a detailed power-dependent study of confined polaritonic modes, associated with the lower polariton branch LP1. We utilized a tunable pulsed laser at a wavelength of 532 nm (tuned to the first Bragg minimum of the DBR structure), providing pulses with a length of 7 ns (repetition rate of 2 Hz), focused to the dimple area with a radius of curvature of $R_C = 16 \mu\text{m}$. This extended pulse length provides quasi steady-state conditions, since the lifetime of excitons in mCherry was previously found to be around 1 ns and the polaritonic lifetime ranges is around 1 ps. In Fig. 2a we show far-field resolved spectra recorded at different pump powers. Due to the three-dimensional confinement the emission appears dispersion-less. Compared to the spectrum in Fig. 1c the mode is slightly shifted to lower energies. This redshift is caused by the larger cavity length due to the dimple depth, which is partly compensated by the spectral blueshift provided by the optical confinement. The calculated optical cavity length in our dimple cavity is $1.21 \mu\text{m}$ which allows us to extract polaritonic fractions (calculated from the so-called Hopfield coefficients) corresponding to an admixture of 23.9% exciton and 76.1% photon in the confined LP1 mode (cavity-exciton detuning $\Delta = -66 \text{ meV}$). By changing the pump power from 0.50 nJ (left) over 1.00 nJ (center) to 3.16 nJ (right), we can witness a significant increase in the emission intensity and a progressive energy shift of our confined mode.

The hallmarks of a zero-dimensional polariton laser are illustrated in Figs. 2,3. The threshold behavior of our device is best reflected via the input-output representation depicted in Fig. 2b. Here, we find a significant non-linear increase of the emitted intensity at a pump power of 0.78 nJ/pulse, which is accompanied by a collapse of the linewidth from $300 \mu\text{eV}$ approaching the resolution limit of our optical spectrometer ($180 \mu\text{eV}$).

Additional proof of the polariton condensation in our system is provided by polarization measurements. Previously, it was found that condensates in planar microcavities^{4,37,38} and confined structures^{39,40} spontaneously acquire a linear polarization, which is usually pinned to some axis defining the anisotropy of the system. In our structure, below threshold, we find

Figure 2: Excitation power-dependent analysis of the device at the position of a dimple with radius of curvature of $R_C = 16 \mu\text{m}$. (a) Far-field resolved spectra for pump powers below the condensation threshold (left, $P=0.6 P_{th}$), right above the threshold (center, $P=1.3 P_{th}$) and far past the threshold (right, $P=4.1 P_{th}$). A significant increase in the intensity and a blueshift of the confined, dispersionless mode is clearly visible. (b) Integrated emission intensity (black filled circles) versus excitation energy. The threshold at $P=0.78 \text{ nJ/pulse}$ indicates the onset of polariton condensation of the confined mode. At the same pump power the linewidth collapses to the resolution limit of the spectrometer ($180 \mu\text{eV}$, red dashed line). The gray dotted lines indicate the excitation powers of the spectra shown in (a). (c) Waterfall plot of the PL intensity for different pump powers showing a significant blueshift below threshold which continues with a reduced slope after threshold.

a degree of linear polarization of 0.27(1) (see Fig. 3a), which indicates a slight anisotropy of our hemispheric microcavity. Once the threshold is crossed, our condensate acquires a strong degree of linear polarization in excess of 0.95(3), which indicates the efficient relaxation of our system in the lowest, symmetry-split mode. While the strong increase of linear polarization in a weakly split polaritonic resonance is a strong indicator of highly efficient bosonic final state stimulation, it further indicates the possibility to engineer the polarization properties in our hemispheric cavities. This will become of particular interest in coupled cavity structures, where the control of the polariton pseudospin has been identified as a viable quantity in ultra-fast on chip simulation approaches.⁴¹

Figure 3: Polarization-dependent normalized intensities of the hemispherical microcavity below condensation threshold (a) and above (b). The black lines are fits to determine the degree of linear polarization of 0.27(1) below and 0.95(3) above threshold, respectively.

Optical nonlinearities in our system become extremely pronounced after reaching the threshold, as it can be seen from the energy-trace of the position of the emission maximum well-captured in the waterfall plot in Fig. 2c. We observe that the mode experiences a well developed blueshift below the condensation threshold, which smoothly changes its slope at threshold and progressively continues up to several tens of the threshold power. This behavior was systematically captured by investigating various hemispheric cavities providing different mode confinements. To quantify the different mode volumes, which result from the different geometries, we performed finite-difference time-domain (FDTD) calculations using the commercial software "Lumerical FDTD solutions" and the mode volume $V_{EM} = \frac{\int d\mathbf{r} \epsilon \mathbf{E}(\mathbf{r})^2}{\max(\epsilon \mathbf{E}(\mathbf{r})^2)}$ with ϵ being a dielectric permittivity and $\mathbf{E}(\mathbf{r})$ being the strength of the electrical field at

point $\mathbf{r}$. Empirically, we find that while the general trend of the blueshift scaling with input power is universal (steep slope before the threshold P_{th} , followed by reduced slope after P_{th}), the magnitude of the shift strongly depends on the mode volume.

In conventional semiconductor microcavities several mechanisms can lead to the blueshift of a polariton mode.⁴² It is generally believed that the main impact is provided by the Coulomb exchange interaction of Wannier-Mott excitons,¹² which can be efficient only if there is a substantial overlap of the wavefunctions of different excitons. In organic materials such overlap cannot be expected as in this case the tightly bound Frenkel excitons are strongly localized. The average separation between chromophores is estimated to be ~ 2.5 nm, defined by the barrel size. If we consider mCherry molecules to have a dipole moment of ~ 1 nm times the electron charge, the nonlinear shift per particle for unstructured dipoles at room temperature is of the order of 10^{-8} meV, being too small to describe the findings. To explain the origin of the blueshift in the organic cavity under study we provide a theory which accounts for the phase space filling effects for the Frenkel excitons. It predicts the density-dependent decrease of the Rabi frequency and consequently leads to the blueshift for the lower polariton mode.

Theoretical description of the blueshift in organic semiconductors

Theoretically, the system can be described using Frenkel exciton operators $\hat{X}_n^\dagger = \hat{a}_n^\dagger \hat{b}_n^\dagger$, represented by a tightly bound electron-hole pair ($\hat{a}_n$ and $\hat{b}_n$ being electron/hole annihilation operators) localized at an atomic site n .⁴³ The system Hamiltonian can be written as the sum of free energies for the cavity mode and Frenkel excitons, which are strongly coupled due to light-matter interaction $\hat{\mathcal{H}}_{\text{coupl}}$ (see Supporting Information, S1, for the detailed description).

The latter reads as

$$\hat{\mathcal{H}}_{\text{coupl}} = \sum_{\mathbf{k}} g_{\mathbf{k}} (\hat{X}_{\mathbf{k}}^{\dagger} \hat{c}_{\mathbf{k}} + h.c.), \quad (1)$$

where the Fourier transformed version of the Frenkel exciton operator was used, $\hat{c}_{\mathbf{k}}$ is a cavity photon annihilation operator (bosonic), and the light-matter coupling constant $g_{\mathbf{k}}$ was defined at the cavity photon wavevector $\mathbf{k}$. The behavior of the system can be described by the Heisenberg equation of motion for the operators $\langle \dot{\hat{X}}_{\mathbf{k}'} \rangle$ and $\langle \dot{\hat{c}}_{\mathbf{k}'} \rangle$. For the Frenkel exciton mode with momentum $\mathbf{k}'$ we get

$$i\hbar \langle \dot{\hat{X}}_{\mathbf{k}'} \rangle = [\hat{X}_{\mathbf{k}'}, \hat{\mathcal{H}}_{\text{coupl}}] = \sum_{\mathbf{k}} g_{\mathbf{k}} \hat{c}_{\mathbf{k}} [\hat{X}_{\mathbf{k}'}, \hat{X}_{\mathbf{k}}^{\dagger}], \quad (2)$$

where in general the commutator of Frenkel excitons does not correspond to a simple delta function, $[\hat{X}_{n'}, \hat{X}_n^{\dagger}] = \delta_{n',n} - \delta_{n',n}(\hat{a}_n^{\dagger} \hat{a}_n + \hat{b}_n^{\dagger} \hat{b}_n)$, and has mixed statistics.^{44,45} Importantly, the presence of the density-dependent term makes the light-matter coupling effectively nonlinear. Similarly, an equation of motion $\langle \dot{\hat{c}}_{\mathbf{k}'} \rangle$ for the cavity mode operator can be derived, and we note that here in the lowest order the term originating from $\hat{\mathcal{H}}_{\text{coupl}}$ remains density independent. Finally, the Rabi splitting as a function of the exciton number (related to the pump power), can be found from dispersions of polariton modes, for the state which in total contains N_{PL}^X Frenkel excitons coupled to light (Supporting Information, S1). Once we consider corrections in increasing order of N_{PL}^X , the renormalized Rabi frequency reads

$$g(N_{\text{PL}}^X) = g(0) \sqrt{1 - \frac{N_{\text{PL}}^X}{N_s}}, \quad (3)$$

where by $g(0)$ we explicitly denote the low density coupling term at zero $\mathbf{k}$. In practice, experiments are usually limited to low excitation regime $N_{\text{PL}}^X/N_s \ll 1$ where Eq. (3) can be expanded into series, with the first order being relevant for the nonlinear coefficient estimate. Taking the lower polariton branch, its blueshift as a function of the exciton number is then

given by

$$\Delta E_L(N_{\text{PL}}^X) = \frac{g^2(0)}{\sqrt{\Delta^2 + 4g^2(0)}} \frac{N_{\text{PL}}^X}{N_s}, \quad (4)$$

where Δ is the cavity-exciton detuning. The blueshift value is therefore larger for samples with increased Rabi frequency, has a detuning dependence and is inversely proportional to the number of available Frenkel exciton sites N_s . The exciton density dependence of the light-matter coupling introduces the optically nonlinear behavior, which was observed experimentally.

We can now apply the microscopic theory to the experiment and compare the results. For this, the measured value of the total number of excitons is required. In general, it is a non-trivial function of the pump power, as it can depend much on scattering processes,^{46,47} leading to a non-radiative decay or a redistribution into modes outside of the light cone. At the same time, we can try to extract this quantity from the PL measurements, where we observe the linear increase before the threshold and the weaker increase after the condensation point. Note, that the blueshift given by Eq. (4) increases linearly with the number of excitons, while originating from the exciton-photon coupling term. Thus, the effective Hamiltonian describing the process is $\sum_{\mathbf{k}, \mathbf{k}'} \hat{c}_{\mathbf{k}}^\dagger \hat{X}_{\mathbf{k}} \hat{X}_{\mathbf{k}'}^\dagger \hat{X}_{\mathbf{k}'} + h.c.$. At the same time, to compare it with the Kerr-type nonlinearity for excitons, typically coming from the Coulomb exchange, we can assign an equivalent Hamiltonian for interacting excitons in the bosonized picture, characterized by the operators $[\hat{x}_{\mathbf{k}}, \hat{x}_{\mathbf{k}'}^\dagger] = \delta_{\mathbf{k}, \mathbf{k}'}$ with the interaction Hamiltonian given by

$$\hat{H}_{int} = \frac{\hbar u}{2} \hat{x}^\dagger \hat{x}^\dagger \hat{x} \hat{x}, \quad (5)$$

where the effective interaction constant reads

$$\hbar u = \frac{g^2(0)}{N_s \sqrt{\Delta^2 + 4g^2(0)}}, \quad (6)$$

and we considered the exciton to be in the lowest mode $\hat{x}_0 =: \hat{x}$.

To test the validity of the proposed mechanism, we compare the theory to experiments

performed using three mCherry samples put into different optical resonators. The first resonator s2 corresponds to the device already presented in Fig. 2, while the other two have either a hemisphere with smaller diameter ($2\mu\text{m}$, s1) or a deeper hemisphere (650 nm , s3). These configurations lead to different radii of curvature and electromagnetic mode volumes. The corresponding electromagnetic mode volumes were estimated by FDTD calculations as $V_{\text{EM}}^{(\text{s1})} = 0.172\mu\text{m}^3$, $V_{\text{EM}}^{(\text{s2})} = 0.591\mu\text{m}^3$ and $V_{\text{EM}}^{(\text{s3})} = 1.874\mu\text{m}^3$. Let us consider only

Figure 4: Excitation power-dependent blueshift for different sample geometries and therefore different mode volumes. The experimental data (symbols) and the model derived in this paper (lines) show very good accordance. The fits were performed using Eq. (4) and Eq. (9) with shared parameters for the 'filling factor' (connected via the mode volume) and the fitting coefficients β_P and c_P .

the dominant light-matter coupling, which occurs between excitons and the C_1 mode, and estimate the ratio between blueshifts for samples s1 and s2 using Eq. (4). The Rabi coupling at low excitation power corresponds to

$$g(0) = |\mathbf{d}_X \cdot \mathbf{E}| \sqrt{N_s} = |\mathbf{d}_X \cdot \mathbf{e}_{\text{EM}}| \sqrt{\frac{\hbar \omega_{c,0}}{2\varepsilon_0 V_{\text{EM}}}} \sqrt{n_s V_s}, \quad (7)$$

where $\mathbf{d}_X$ denotes the dipole moment for Frenkel excitons (assumed to be pointing the same direction) and $\mathbf{E}$ is the electric field for the cavity mode, directed along the vector $\mathbf{e}_{\text{EM}}$. Here, ε_0 is the vacuum permittivity, n_s is the density of the molecules available for the coupling and situated in volume V_s . From Eq. (7) one can see that in the crude approximation of the full volume of the EM mode being filled with mCherry molecules, $V_{\text{EM}} = V_s$, the Rabi

frequency is volume-independent and has only weak energy dependence for the two samples, which can be safely neglected. This then can explain equal Rabi frequencies for samples of different volume. We consider the same excitation conditions (i.e. number of generated excitons) as in the performed experiment. The ratio of blueshifts for different cavities reads

$$\frac{\Delta E_L^{(s2)}}{\Delta E_L^{(s1)}} = \left(\frac{g^{(s2)}}{g^{(s1)}} \right)^2 \frac{\sqrt{\Delta_{s1}^2 + (2g^{(s1)})^2}}{\sqrt{\Delta_{s2}^2 + (2g^{(s2)})^2}} \times \frac{V_s^{(s1)}}{V_s^{(s2)}}. \quad (8)$$

The analysis of Eq. (8) gives a prefactor coming from the ratio of the coupling parameters, times the dominant term corresponding to the ratio of available Frenkel exciton states. For the considered case of equal Rabi frequencies, $\Omega_X^{(s2)} = \Omega_X^{(s1)} = 266 \text{ meV}$, and detunings of $\Delta_{s1} = -97 \text{ meV}$, $\Delta_{s2} = -66 \text{ meV}$, the prefactor is close-to-unity. Considering that each mode volume is filled with molecules and couples to light ($V_s^{(s1)} = V_{\text{EM}}^{(s1)}$ and $V_s^{(s2)} = V_{\text{EM}}^{(s2)}$), the ratio of detunings is $\mathcal{R}_{\text{theory}} = \Delta E_L^{(s2)} / \Delta E_L^{(s1)} = 3.55$ and stays the same for equal pump (exciton population). Finally, let us consider the exciton number dependence as a function of pump power P , motivated by the experimental findings. The reasoning comes from the observed PL data where the growth of the intensity before and after the threshold has different rates. This is parametrized by the function

$$\frac{N_X(P)}{N_X(P_{th})} = \frac{\tanh(\beta_P P / P_{th}) + c_P P / P_{th}}{\tanh(\beta_P) + c_P}, \quad (9)$$

where β_P and c_P are dimensionless coefficients. The hyperbolic tangent in the numerator is responsible for the linear growth at small powers. Using the determined values for the Rabi splitting, detuning and mode volumes, the plotted data shown in Fig. 4 can simultaneously be fitted using Eq. (4) and Eq. (9) and shared parameters for the 'filling factor' (which is connected via the mode volumes for the different samples) and the coefficients β_P and c_P . In addition, we have used an offset for each data set to account for the blueshift for lower excitation powers. The fits for all three data sets are in very good agreement, even though several approximations were taken. The extracted filling factor at threshold is 1.1% for

the s2 sample, which corresponds to a few tens of thousands of molecules, and the fitting coefficients are $\beta_P = 1.3$ and $c_P = 5.5 \times 10^{-3}$.

First-order Coherence properties and interaction strength of the polariton condensate

The confinement, provided by the hemispheric microcavity, results in a mono-mode condensate and provides ideal conditions to study the temporal coherence of the emitted light in greater detail. The first-order correlation function $g^{(1)}(\tau)$ describes the temporal phase coherence. The following measurements were performed on the resonator s3 (see Supporting Information S2 for more details). From the linewidth a temporal coherence length above threshold of at least 7 ps can be estimated, yet, with a clear limitation by the instrument resolution for all data points above threshold. To analyze the coherence build up more in detail we measured the temporal coherence using a Michelson interferometer in mirror-retro-reflector configuration. Since the mirror is mounted on a piezo stage as well as on a motorized linear stage, we can change the delay time τ between the two arms of the interferometer. Exemplary interference fringes are shown in Fig. 5a and Fig. 5b, which signify coherence throughout the mode in the dimple cavity. Importantly, by varying the delay time in our interferometer, we can analyze the decay of the fringe amplitude and fitting the fringe patterns we deduce $g^{(1)}(\tau)$ over τ^{48} and therewith the coherence time τ_c .

Below threshold a coherence time of $\tau_c = (1.5 \pm 0.1)$ ps was determined, which already shows the capability of the device due to the high quality three-dimensional confinement. Above threshold we observe different behavior of $g^{(1)}(\tau)$ for different occupancies of the condensate. At the pump power of $P = 1.4 P_{th}$, which corresponds to a mean occupancy of $\tilde{n}=7.6$ polaritons (see also section S2 of the Supporting Information), the decay of $g^{(1)}(\tau)$ can largely be described by an exponential decay of $g^{(1)}(\tau) \sim \exp(-\tau/\tau_c)$ (see Fig. 5c). The single exponential decay indicates single-mode condensation as well as predominant intrinsic

Figure 5: First-order coherence properties of the polariton condensate. (a) Real-space interference image of the condensate near zero delay time for a pump power of $P = 1.4 P_{th}$. (b) Fringe pattern of the data received by integrating the marked area shown in (a) in y -direction (black dots). The red line is a fit using equation (10) to obtain $g^{(1)}(\tau)$. (c,d) Measured first-order coherence $g^{(1)}(\tau)$ for different delay times (black dots), exponential fits (orange solid lines) and Gaussian fits (red dashed lines) for a pump power of $P = 1.4 P_{th}$ (c) and $P = 4.4 P_{th}$ (d), respectively. (e) Temporal coherence τ_c of the polariton condensate versus the mean occupancy $\tilde{n}$. The black curve is calculated using Eq. (S22) and the fitting parameters in Fig. S2 (see Supplementary Information).

dephasing of the condensate.⁴⁸

For an increased number of polaritons in the condensate $\tilde{n}=64$ ($P = 4.4 P_{th}$) the shape of the decay changes from a predominantly exponential to a predominantly Gaussian decay $g^{(1)}(\tau) \sim \exp(-\tau^2/\tau_c^2)$ (see Fig. 5d). The Gaussian broadening of $g^{(1)}(\tau)$ has previously been associated with interaction induced energy variations due to number fluctuations in the condensate^{7,48,49} and can be described using single-mode matter-wave laser theory.^{49–51} Here, single particle decay processes and effective interactions are treated simultaneously (see also Supporting Information S3 for details), while the limiting case of weak effective interaction can be described by $g^{(1)}(\tau) \sim \exp(-\tau/\tau_c)$, and the Gaussian broadening can be described by the interaction constant u via $\exp(-\tau^2/\tau_c^2) = \exp(-2\tilde{n}u^2\tau^2)$. In our case, as it was already discussed, Coulomb-based exciton-exciton interactions are absent and the nonlinearity originates from the quenching of the Rabi splitting. However, according to Eq. (4) in bosonized picture the latter can be reduced to an effective polariton-polariton interaction with the characteristic constant u given by Eq. (6). Using the theory provided in literature,^{48–51} both curves can be simultaneously fitted with shared parameters for the decay rate of the polariton ground state, a gain saturation number and the effective interaction constant u (see section S3). With the deduced parameters, the coherence time τ_c dependent on the mean polariton occupancy $\tilde{n}$ can be calculated (black curve in Fig. 5e) and a coherence time of (160 ± 8) ps was found for the measurement shown in Fig. 5c. We note, that the coherence time of 160 ps is unprecedented in any room-temperature polariton condensate and reflects the maturity of our device. The values reported so far have been limited to a few ps in planar ($\approx 1 - 2$ ps)^{23,52} and confined (≈ 1 ps)⁵³ organic samples as well as in planar GaN (≈ 0.7 ps or ≈ 2.8 ps electrically driven)^{27,29} and ZnO nanowires (≈ 1.2 ps).³¹

From the fit in Fig. 5e we can extract $u = (1.6 \pm 0.2) \cdot 10^{-3} \text{ ps}^{-1}$ or $\hbar u V_c = (2.0 \pm 0.2) \mu\text{eV} \times \mu\text{m}^3$ per polariton in the condensate. Here, the previous determined mode volume ($V_{EM}^{(s3)} = 1.874 \mu\text{m}^3$) was used as the volume of the condensate V_c . This value can be compared with the analysis provided by tracing the condensate energy with pump power, yielding a

value of $\hbar u V_c = (2.7_{-1.1}^{+2.5}) \mu\text{eV} \times \mu\text{m}^3$ per polariton for the samples s1–s3 (see Supporting Information S2), which is in excellent agreement.

Conclusion

With our work, we addressed two of the most significant questions in room-temperature polaritonics: The question of coherence, as well as the origin of interaction provided by tightly bound Frenkel excitons in the strong coupling regime. This study became feasible by implementing a high quality factor hemispheric, single mode microcavity, filled with mCherry proteins that can be driven under quasi equilibrium conditions.

Our core finding reflects that it is possible to obtain very long coherence times in excess of 150 ps in room-temperature polaritonic condensates. Furthermore, the energy shift of localized Frenkel exciton polaritons is widely dominated by the quasi-two level structure of the excitons, yielding a progressive reduction of the Rabi splitting also above threshold. We analyze, that this shift acts analogously to a Coulomb exchange interaction with a strength of approx. $(2.0 \pm 0.2) \mu\text{eV} \times \mu\text{m}^3 / \text{polariton}$.

While our finding of highly coherent condensation at ambient conditions addresses the suitability of organic polaritonics regarding their utilization as highly coherent room temperature polariton lasers, shedding light on the non-linearity will be of great benefit towards implementing non-linear devices, optical switches and lattices based on exciton-polaritons at room temperature.

Methods

Sample preparation

Prior to sputtering DBR layers onto the substrates (quartz slides, area 1 cm^2 , thickness 0.5 mm, roughness $< 1 \text{ nm RMS}$), lens-shaped dimples were written into one of the sub-

strates using ion beam milling (FEI Helios NanoLab DualBeam). Afterwards, 10.5 pairs of alternating SiO₂ (108 nm)/TiO₂ (62 nm) layers were deposited using ion beam deposition (Nordiko 3000) onto the substrates. Highly concentrated (175 g/liter) solution of mCherry ($\approx 6 \mu\text{l}$) was spin-coated onto the distributed Bragg reflector with the lens-shaped indentations. The structure was capped with an identical mirror (without indentations) to form the microcavity. To realize a nearly constant film thickness, the mCherry solution dried out over 48 hours under a constant pressure of 0.25 N/cm^2 (equally distributed over the top DBR).

Sample characterization

The sample was excited either by the 532 nm line of a continuous-wave diode laser that is resonant with the first Bragg minimum of the top mirror for pre-characterization or by a wavelength-tunable optical parametric oscillator system with ns-pulses tuned to 532 nm for the experiments in the non-linear regime. The excitation beam was focussed onto the sample surface (spot size $\approx 3.6 \mu\text{m}$ in diameter) using a high-NA objective (50x, NA=0.42) in front of the sample. The emission was collected in reflection geometry through the same objective, filtered by using a 550 nm longpass filter, monitored onto the entrance slit of a 500 mm spectrometer and recorded with a peltier-cooled EMCCD (Andor Newton 971). This configuration leads to a spectral resolution of about $180 \mu\text{eV}$ for energies around 2 eV. Most measurements were performed in Fourier imaging configuration with a Fourier lens collecting the angle-dependent information in the back-focal plane of the microscope. The absorption spectrum was measured in transmission configuration using a collimated white light source that was focused onto the backside of a thin film of mCherry coated on a quartz slide. The transmitted light was then collected and recorded with the previously described objective and spectrometer, respectively.

For the measurements of the coherence properties of the condensate a Michelson interferometer in mirror-retro-reflector configuration was used. Here, the real-space image from the microcavity is split by a 50:50 beam splitter into two arms. One arm is directed towards

a plane mirror which is mounted on a piezo-controlled linear stage which itself is mounted on a linear long-travel motorized translation stage. The other arm is directed onto a cube corner retro-reflector reflecting the image back to the beam splitter. Passing the same beam splitter, the image (from the mirror) and the point reflected image (from the retro-reflector) interfere with each other. At the output of the beam splitter a high-resolution imaging CCD camera ($6.5\ \mu\text{m}$ pixel size) records the interference patterns. The visibility of the interference fringes for two interfering beam profiles $I_1(x)$ and $I_2(x)$ is given by⁴⁸

$$I(x, \tau) = I_1(x) + I_2(x) + 2|g^{(1)}(\tau)|\sqrt{I_1(x)I_2(x)}\cos\left(\frac{2\pi\theta}{\lambda_0}x + \phi\right) \quad (10)$$

with λ_0 the wavelength of the lasing mode and ϕ , θ , τ the phase difference, angle, and time delay between $I_1(x)$ and $I_2(x)$.

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Supporting Information Available

Extended theoretical description of the blueshift in organic semiconductors (S1), nonlinearity of the samples s1-s3 and excitation power-dependent analysis of the device s3 (S2), and additional information on the first-order coherence (S3).

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