

Molecular Energy Transfer Inside Optical Microresonators in the Strong Coupling Regime

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Abstract

In this work, energy transfer in the strong light-matter coupling regime is investigated. For this purpose, a donor-acceptor pair of J-aggregated dyes is spin-coated onto the mirrors of a tunable Fabry-Pérot microresonator. Donor-acceptor separations are systematically increased from direct contact up to 11 μm . White-light transmission spectra reveal that the system operates in the strong coupling regime and hybrid light-matter states (polaritons) are formed. Fitting a phenomenological Hamiltonian allows for determination of cavity distances and coupling energies. The theoretical analysis shows that certain hybrid polaritons contain contributions from both dyes, connecting donor and acceptor.

Fluorescence spectra are recorded to investigate the occurrence of energy transfer if donor and acceptor are strongly coupled to the same microcavity. The shapes of the fluorescence spectra show efficient energy transfer from donor to acceptor for all investigated distances which range from 0 to 11 μm . Within the same measurement, the energy transfer efficiency appears to be independent of donor-acceptor separation. The observed fluorescence features are well explained by a phenomenological Hamiltonian, which models the emerging polariton modes, and rate equations, which model the respective fluorescence intensities.

Zusammenfassung

In dieser Arbeit wird Energietransfer unter dem Einfluss starker Licht-Materie-Wechselwirkung untersucht. Zu diesem Zweck wird ein Donor-Akzeptor-Paar aus J-aggregierten Farbstoffen mittels Rotationsbeschichtung auf die Spiegel eines durchstimmbaren Fabry-Pérot-Mikroresonators aufgebracht. Die Abstände zwischen Donor und Akzeptor werden systematisch erhöht, von direktem Kontakt bis auf 11 μm . Weißlichttransmissionsspektren zeigen, dass das System im Regime starker Kopplung operiert, so dass sich hybride Licht-Materie-Zustände (Polaritonen) herausbilden. Durch das Fitting eines phänomenologischen Hamilton-Operators lassen sich die Abstände im Resonator und die Kopplungsenergien bestimmen. Die theoretische Analyse zeigt, dass bestimmte hybride Polaritonen Beiträge beider Farbstoffe enthalten, sodass Donor und Akzeptor verbunden werden.

Fluoreszenzspektren werden aufgenommen, um das Auftreten von Energietransfer zu untersuchen, wenn Donor und Akzeptor stark an denselben Mikroresonator gekoppelt sind. Die Spektren zeigen eine effiziente Energieübertragung vom Donor zum Akzeptor für alle untersuchten Abstände im Bereich von 0 bis 11 μm . Innerhalb derselben Messung scheint die Energietransfereffizienz unabhängig vom Abstand zwischen Donor und Akzeptor zu sein. Die beobachteten Fluoreszenzmerkmale lassen sich gut über einen phänomenologischen Hamilton-Operator erklären, der die entstehenden Polaritonmoden modelliert, sowie durch Ratengleichungen, die die jeweiligen Fluoreszenzintensitäten beschreiben.

List of Abbreviations

APD	avalanche photodiode
BRK	1-(3-Sulfopropyl)-2-(2-[1-(3-sulfopropyl)naphtho[1,2-d]thiazol-2(1H)ylidene]methyl-1-butenyl)naphtha[1,2-d]thiazoliumhydroxide
CCD	charge-coupled device
cw	continuous wave
DBR	distributed Bragg reflector
DOS	density of optical states
et al	<i>et alia</i>
etc	<i>et cetera</i>
FP	Fabry-Pérot
FRET	Förster resonance energy transfer
FWHM	full width at half maximum
HWHM	half width at half maximum
i.e.	<i>id est</i>
LDOS	local density of optical states
LP	longpass
NMR	nuclear magnetic resonance
PLDOS	partial (or projected) local density of optical states
PMET	polariton-mediated energy transfer
PVA	polyvinyl alcohol
QED	quantum electrodynamics
SERS	surface-enhanced Raman spectroscopy
TDBC	5,6-dichloro-2-[[5,6-dichloro-1-ethyl-3-(4-sulphobutyl)benzimidazol-2-ylidene]propenyl]-1-ethyl-3-(4-sulphobutyl)benzimidazolium hydroxide
TERS	tip-enhanced Raman spectroscopy

Chapter 1

List of Publications

1.1 Publications

This thesis is set up as a cumulative dissertation and summarizes the scientific results of the following two publications:

1. Kertzsch, Christoph, et al. “Global Spectral Analysis of Polaritonic Coupling of Multiple Organic Dyes to a Tunable Fabry-Pérot Resonator Operating with Mirror Separations up to 10 μm .” *Chemistry–A European Journal* 31.21 (2025): e202500344.
2. Kertzsch, Christoph, et al. “Polariton-Mediated Energy Transfer in a Tunable Optical Multimode Microcavity Exceeding 10 μm .” *Advanced Photonics Research* 7.1 (2026): e202500296.

The publications (including the respective Supporting Information files) are attached in Appendix B and C.

1.2 Further Publications

Further publications to which I have contributed during the research period but are not part of this thesis are:

1. Nosrati, Saeed, et al. “Controlling three-color forster resonance energy transfer in an optical Fabry-Pérot microcavity at low mode order.” *The Journal of Physical Chemistry C* 127.25 (2023): 12152-12159.
2. Bassler, Miriam C., et al. “Fluorescence lifetime imaging unravels the pathway of glioma cell death upon hypericin-induced photodynamic therapy.” *RSC chemical biology* 5.12 (2024): 1219-1231.

1.3 Conference Papers

Part of the results presented in this thesis were presented at the 24th International Conference on Transparent Optical Networks (ICTON) 2024, which resulted in the publication of two conference papers:

1. Kertzsch, Christoph, et al. “Strong coupling of organic semiconductors in a tuneable Fabry-Pérot microresonator.” 2024 24th International Conference on Transparent Optical Networks (ICTON). IEEE, 2024.
2. Kertzsch, Christoph, et al. “A tuneable Fabry-Pérot microcavity enables systematic investigation of strong light-matter coupling and energy transfer at distances of several μm .” 2024 24th International Conference on Transparent Optical Networks (ICTON). IEEE, 2024.

1.4 Scope of this Thesis and Personal Contributions

The aim of this thesis was to investigate the influence of optical microcavities on energy transfer phenomena. In particular, we investigated so-called Polariton-Mediated Energy Transfer (PMET) between thin films of J-aggregates strongly coupled to a tuneable Fabry-Pérot resonator. Results are published in peer-reviewed journals (see Section 1.1). For these works, I performed the principal part of the work, including data analysis and manuscript writing. Other contributors are:

- Jakob Keck, who helped with conceptualization and initial implementation of the experiment.
- Michael Mauch, as part of his Master’s thesis (which he did under the supervision of Jakob Keck and myself) [1]. He performed all the measurements and contributed significantly to the data analysis, in particular the development of the fitting procedure of the white-light transmission spectra.

See also the author contributions statements provided within the two publications.

Chapter 2

Introduction

Around 100 years after the formulation of quantum mechanics [2–9], research interest in quantum phenomena remains high and interesting results are regularly produced, as evidenced by the Nobel Prizes in Physics 2022 (for experiments with entangled photons, establishing the violation of Bell inequalities and pioneering quantum information science) and 2025 (for the discovery of macroscopic quantum mechanical tunnelling and energy quantisation in an electric circuit) as well as the United Nations General Assembly proclaiming 2025 as the International Year of Quantum Science and Technology. Some researchers go even further, claiming we are currently witnessing a “second quantum revolution” where the recent experimental demonstration of certain quantum mechanical effects paves the way for the development of new quantum technologies (quantum computing, quantum simulation, quantum sensing, quantum communication etc.) [10–15]. In this context, the exploration and utilization of quantum mechanical effects seems as promising as ever.

From the beginning, the study of light and light-matter interaction was of central importance within quantum mechanics¹ and has developed into a sophisticated research area. Within this research field, the development of new microfabrication techniques enabled the creation and investigation of small structures (on the order of magnitude of the investigated wavelengths) capable of confining light, which include Fabry-Pérot resonators, whispering gallery resonators, photonic crystals and plasmonic cavities. These structures, which are often called (optical) “microcavities” or “microresonators”, can significantly enhance the light field at certain resonance frequencies. Probably the most important results of these endeavors are surface-enhanced Raman spectroscopy (SERS) [18–21] and tip-enhanced Raman spectroscopy (TERS) [22–25], which utilize the strong (electric) field enhancement for Raman spectroscopy. Another approach is to use the strong light enhance-

¹One could argue that the development of quantum mechanics started with the observation of hydrogen spectral lines [16] and Planck’s treatment of black body radiation [17].

ment, which generally increases light-matter coupling, to explore different light-matter coupling regimes. In the so-called strong coupling regime, light-matter interaction is strongly enhanced compared to “free space” and the light- and matter-states become quantum mechanically entangled. This can drastically change certain material properties.

A material property where increased control is highly desirable is energy transfer. Energy transfer, which in this context refers to the transfer of excitation energy of (optically) excited species (primarily organic molecules), plays a crucial role in solar energy conversion, where energy often has to be transferred from highly absorbing species to “harnessing centers” (reaction centers, electrodes etc.), and device fabrication in general, where efficient energy transfer can be desirable or obstructive. Consequently, the exploration of microcavities as a tool for modifying energy transfer processes seems like a worthwhile endeavor. These would offer the advantage that the participating energy donors and acceptors do not have to be modified, but are “simply” placed in a different environment.

Recent works investigating energy transfer in the strong coupling regime suggest that there is an energy transfer mechanism emerging as a result of the hybridisation of light- and matter-states. Regarding this energy transfer mechanism, sometimes called “Polariton-Mediated Energy Transfer” (PMET), open questions remain:

- How does energy transfer efficiency depend on donor-acceptor separation? Previous works suggest that it might be independent of donor-acceptor separation.
- Is there a (practical) limit for the achievable donor-acceptor separations?
- Can PMET be realized in multi-mode cavities?

The goal of the experiments presented in this thesis was the study of energy transfer between molecular dyes which are strongly coupled to a tunable optical Fabry-Pérot microcavity (*i.e.* PMET). The tuning of the cavity allows for the investigation of a large range of donor-acceptor separations as well as the investigation of PMET under multi-mode conditions.

In Chapter 3, I provide the theoretical background necessary to understand this work, including

- a short summary on the quantum theory of light-matter interaction (Section 3.1),
- the physical properties of optical microcavities (Section 3.2), in particular Fabry-Pérot resonators (Section 3.2.1), and their coupling to optical transitions of matter (Sections 3.2.2 - 3.2.4),
- a summary of the literature on PMET (Section 3.3) and

- the modeling of strongly coupled multimode systems *via* phenomenological Hamiltonians (Section 3.4).

In Chapter 4, I summarize the results from the two publications mentioned in Section 1.1, including a short description of the most important experimental procedures (Section 4.1).

Chapter 3

Theoretical Background

In this Chapter, the theoretical and experimental foundations underlying the presented results are outlined. I assume that the reader has a certain familiarity with quantum mechanics. Nevertheless, I shortly summarize a few important concepts in the quantum description of light-matter interaction which are of particular relevance for this work in Section 3.1.

The following Section 3.2 deals with optical microcavities (in particular Fabry-Pérot resonators, the used cavity geometry) and their coupling to optical transitions of matter. Here, I derive important Equations for the phenomena emerging in the weak coupling (Section 3.2.3) and strong coupling (Section 3.2.4) regime.

The next two Sections deal with phenomena directly related to the presented work: Section 3.3 summarizes the scientific literature specifically dealing with energy transfer in the strong coupling. In Section 3.4, I discuss a problem central to the evaluation of the obtained data sets, namely the modeling of strongly coupled multimode systems *via* phenomenological Hamiltonians.

3.1 Light-Matter Interaction

The study of the interaction between light and matter is one of the oldest research endeavours, dating back to antiquity [26, 27]. Consequently, this research field has produced a plethora of theoretical frameworks with many “outdated” theories retaining relevance in certain situations (see, for example, [28]).

For the purposes of this work, it is necessary to explain the observed phenomena within a quantum-mechanical framework. Quantum theories of light-matter interaction can be classified in two regards:

- A rigorously quantum-mechanical treatment would require the quantization of both light and matter. However, many phenomena of light-matter interaction can be explained by quantizing only the matter

part while describing the light as a “classical” electromagnetic field. Therefore, the (additional) quantization of the light field is often called “second quantization”.

- When treating the postulated Hamiltonian, there are often approximation methods that can be applied. Here, a common approach is to treat the light-matter interaction term as a perturbation within quantum-mechanical perturbation theory. Furthermore, the so-called dipole approximation and rotating wave approximation are commonly used simplifications.

3.1.1 Second Quantization

When quantizing the light field (see, for example, [29–31]), the light field is conceived as a set of electromagnetic modes (characterized *via* a wavevector and polarization), where each mode is described as a quantum harmonic oscillator. Here, the number of excitations (the number of photons) in each mode is the central property of interest. Consequently, the quantum-mechanical states (sometimes called “Fock states”) are characterized by the number of photons in each considered mode. Furthermore, so-called raising and lowering (or creation and annihilation) operators,¹ which increase / decrease photon numbers, are of central importance.

Important results from second quantization are:

- Zero-point energy: The ground state of the electromagnetic field (photon number of 0) possesses a finite energy of $\frac{\hbar\omega}{2}$ (where $\hbar$ is the reduced Planck’s constant and ω is the angular frequency of the considered electromagnetic mode). This has physical consequences, for example the Casimir effect, the Lamb shift and spontaneous emission.
- Density of optical states (DOS):² Since the electromagnetic field is described as a set of discrete modes, the concept of a mode density emerges. This number density of optical states, which generally varies with frequency and position, is directly related to certain phenomena (see Section 3.1.2).

3.1.2 Density of Optical States

In a fully quantum-mechanical framework, the electromagnetic field is described as a set of modes, characterized by frequency and polarization, which are then occupied by certain numbers of photons [29, 30, 32]. Consequently, the number of available electromagnetic modes at a certain position in space is an important property for describing electromagnetic phenomena.

¹Often labeled $a^{(\dagger)}$.

²Sometimes also called optical mode density or light density of states.

When discussing the optical mode density, there are three (increasingly detailed) quantities of interest [32]:

- The density of optical states (DOS) $\rho(\omega)$ is the number density of optical states per unit volume and per unit frequency.
- The local density of states (LDOS) $\rho_l(r, \omega)$ includes a contribution from each mode in proportion to its electric field intensity at the point of interest r . Consequently, it accounts for local variations of the electric field in space.
- The partial (or projected) local density of states (PLDOS) $\rho_p(e_d, r, \omega)$ includes a contribution from each mode in proportion to its electric field strength projected along the (dipole) direction e_d at the point of interest r . Therefore, it is sensitive to polarization effects (unlike the LDOS).

In a homogeneous environment, where the PLDOS is independent of both orientation and position, we have [32]

$$3\rho_p(e_d, r, \omega) = \rho_l(r, \omega) = \rho(\omega) = \frac{n^3\omega^2}{\pi^2c^3} \quad (3.1)$$

Here, n is the refractive index, c is the vacuum speed of light and ω is the angular frequency of the electromagnetic modes. The (P)LDOS can be calculated (or measured) for optical nanostructures (see, for example, [32–41]) and is a very useful property for capturing their influence on certain phenomena.

One of the most important effects directly related to the (P)LDOS is the modification of the spontaneous emission rate $\Gamma^{\text{sp.em.}}$ (first described theoretically by Purcell in 1946 [42] and experimentally by Drexhage in 1968 [43, 44]), which can be directly related to the PLDOS [32]:

$$\Gamma^{\text{sp.em.}} = \frac{\pi\omega\vec{\mu}^2}{\hbar\varepsilon_0\varepsilon}\rho_p(e_d, r, \omega) \quad (3.2)$$

Here, ω and $\vec{\mu}$ are the angular frequency and transition dipole moment, respectively, of the optical transition. $\hbar$ is the reduced Planck's constant, ε_0 is the vacuum permittivity and ε is the permittivity of the medium. We see that the spontaneous emission rate is directly proportional to the PLDOS $\rho_p(e_d, r, \omega)$. This phenomenon is discussed in further detail in Section 3.2.3.

3.2 Optical Microcavities

Generally, optical microcavities are small structures capable of confining light [31]. These include Fabry-Pérot resonators, whispering gallery resonators, photonic crystals and plasmonic cavities [31, 45]. All four confinement methods show a size-dependent resonance frequency spectrum. Consequently, if the dimensions of the confining structure are below or close to

the wavelength of visible light (*i.e.* a few hundred nm), resonances appear in the visible part of the electromagnetic spectrum.

Optical microcavities are often characterized *via* the Q -factor, which is defined as the ratio of a resonant cavity frequency (ω_c) to the linewidth (full width at half maximum, FWHM) of the cavity mode ($\delta\omega_c$) [30, 31, 46]:

$$Q = \frac{\omega_c}{\delta\omega_c} \quad (3.3)$$

which is a measure for the energy decay. To be more precise, Q^{-1} is the fraction of energy lost in a single round-trip / transit (if such a concept can be applied to the considered cavity) [31, 46]. It is also related to the photon lifetime τ_{cav} / photon decay rate $\frac{1}{\tau_{cav}}$ of the cavity *via* [30, 31]

$$\tau_{cav} = \frac{Q}{\omega_c} \quad (3.4)$$

For this work, we utilized a tunable Fabry-Pérot resonator, whose physics will be further explored in the next Section.

3.2.1 Fabry-Pérot Resonator

A Fabry-Pérot resonator³ [46, 47] consists of two plane-parallel mirrors, separated by a distance L_{cav} (see Figure 3.1). Its optical properties can be calculated by analyzing plane-wave illumination of the system. Here, repeated back-and-forth reflections between the two mirrors and the resulting interferences have to be considered (for detailed derivations, see for example [28, 30, 46]). The resulting transmission spectrum shows distinct maxima (which correspond to minima in the reflection spectrum) when the round-trip phase shift of the incoming light, which is determined by its wavelength and the optical path length of the resonator, equals an integer multiple of 2π . Consequently, resonance peaks occur for

$$nL_{cav} = m \frac{\lambda_m}{2} \quad (3.5)$$

or alternatively

$$\omega_m = m \frac{\pi c}{nL_{cav}}. \quad (3.6)$$

Here, $m = 1, 2, 3, \dots$ is the mode number, λ_m and ω_m are the wavelength and angular frequency, respectively, of the resonance peaks, n is the refractive index inside the resonator, L_{cav} is the distance between the two plane-parallel mirrors (making nL_{cav} the optical path length of the resonator) and c is

³Often also called Fabry-Pérot interferometer or Fabry-Pérot etalon.

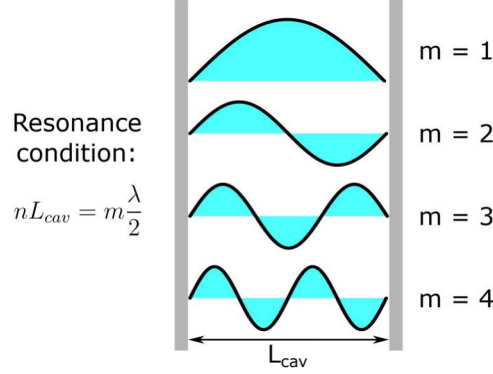


Figure 3.1: Pictorial representation of a Fabry-Pérot resonator consisting of two Ag mirrors separated by L_{cav} . Inside the resonator, the electromagnetic field amplitude for the first four resonance conditions is depicted.

the vacuum speed of light.⁴ Equation 3.5 also offers a quite intuitive interpretation of the resonance condition: Resonant wavelengths, when sketched inside the resonator as in Figure 3.1, must have nodes at the mirror surfaces.

Another important quantity that can be derived from the aforementioned calculations is the so-called Finesse F of the Fabry-Pérot resonator. It is defined as the ratio of the free spectral range⁵ ($\Delta\omega_c$) to the linewidth of the cavity (FWHM $\delta\omega_c$) and is determined by the reflectivities of the two mirrors ($R_{1/2}$) [30]:

$$F = \frac{\Delta\omega_c}{\delta\omega_c} = \frac{\pi (R_1 R_2)^{1/4}}{1 - \sqrt{R_1 R_2}} \quad (3.8)$$

Therefore, a high Finesse results in sharp resonance peaks. It is related to the Q -factor *via*

$$Q = \frac{\omega_c}{\Delta\omega_c} F \quad (3.9)$$

One should note that for an increasing mirror separation, the Q -factor increases (due to the increasing round-trip length) while the Finesse stays constant.

For mirrors, usually either metal mirrors (Ag, Al) or distributed Bragg reflectors (DBR) are used. Metal mirrors have the advantage of high reflectivity across the visible spectrum, making them operatable at different mirror distances. Bragg reflectors offer ultra-high reflectivities at specific frequencies. For the work presented here, we utilized a tunable Fabry-Pérot

⁴If one also considers the angle of incidence θ , equation 3.6 becomes [31]

$$\omega_m = m \frac{\pi c}{L_{cav} \sqrt{n^2 - \sin^2 \theta}} \quad (3.7)$$

⁵The frequency separation between successive cavity modes.

resonator with Ag mirrors where we control the mirror separation *via* piezo-actuators.

3.2.2 Exciton-Cavity Coupling

When an optical emitter is placed inside a microcavity in such a way that it can absorb photons from and emit photons into the cavity modes, we can expect that its optical properties change compared to free space. Here, one distinguishes two different coupling regimes [30, 31]:

- In the weak coupling regime, the interaction between emitter and radiation field is perturbative and spontaneous emission from the emitter is irreversible. Changes in the optical properties of the emitter are due to changes in the electromagnetic environment inside the cavity compared to free space (namely the local density of optical states, see Section 3.1.2).
- If, on the other hand, reabsorption of emitted photons takes place, we reach the strong coupling regime. Here, the confinement of the photons inside the cavity has to be very efficient, meaning that competing dissipation / damping processes, which remove photons from the system, have to be effectively suppressed. If this can be achieved and the probability of reabsorption of a photon is higher than the probability of it escaping the cavity, a perturbative description of the system breaks down and mixed light-matter eigenstates emerge.

The interaction between exciton and cavity is usually quantified *via* a coupling energy $\hbar g$ (and corresponding angular frequency g and time-scale $\frac{2\pi}{g}$). Comparing this time-scale to the photon decay channels of the system, namely the photon decay rate of the cavity κ ⁶ and the non-resonant decay rate of the emitter γ , we have a criterion for determining the coupling regime:

$$\begin{aligned} g \ll (\kappa, \gamma) &\Rightarrow \text{weak coupling} \\ g \gg (\kappa, \gamma) &\Rightarrow \text{strong coupling} \end{aligned}$$

A short remark on historical context: Light-matter interaction inside optical resonators was first studied using atoms in microwave cavities (for some reviews on this topic, see [48–50]). Therefore, much of the physics was first developed in this context, which shaped terminology.⁷ Since then, coupling between matter and cavities has been studied for many different materials and many different cavity systems (see, for example, [45, 51]). The main focus of this work is the coupling between organic molecules and a Fabry-Pérot resonator.

⁶ $\kappa = \frac{1}{\tau_{cav}} = \frac{\omega_c}{Q}$, see Equation 3.4

⁷For example, optical transitions of matter are often denoted “atoms”.

The experiments presented in this work were performed in the strong coupling regime. But since the transition between weak and strong coupling is not sharp and weak coupling effect might play an (additional) role in the performed experiments, I will also shortly discuss the physics of weak coupling (Section 3.2.3) before moving on to strong coupling (Section 3.2.4).

3.2.3 Weak Coupling: Modifying the Electromagnetic Environment

In the weak coupling regime, the main effect is a modification of the spontaneous emission rate of an emitter enclosed in a cavity (see also Section 3.1.2). This effect was first described by Purcell in 1946 [42] (in the context of nuclear magnetic resonance (NMR) spectroscopy) and is therefore known as Purcell effect.

Derivation of the Purcell effect is rather straightforward: As shown in Equation 3.2, the spontaneous emission rate is directly linked to the PLDOS. The effect of an enclosing cavity on an emitter can be conceived as a change of the PLDOS compared to free space (where the PLDOS is usually increased at the cavity resonances). Detailed calculations reveal that there are four aspects that govern the modification of the spontaneous emission rate [30, 31]:

- Parameters of the cavity, namely Q -factor, cavity volume V_{cav} , resonance wavelength λ_c and refractive index n . These are summarized in the so-called Purcell factor F_P :

$$F_P = \frac{3Q \left(\frac{\lambda_c}{n}\right)^3}{4\pi^2 V_{cav}} \quad (3.10)$$

Since the following three terms are normalized, the Purcell factor gives the maximum spontaneous emission enhancement the cavity can provide.

- Detuning between emitter frequency ω_e and cavity mode. If one assumes a Lorentzian line shape for the cavity mode (with center angular frequency ω_c and half width at half maximum (HWHM) $\Delta\omega_c$), one gets:

$$\frac{\Delta\omega_c^2}{4(\omega_e - \omega_c)^2 + \Delta\omega_c^2} \quad (3.11)$$

This term shows that we have the maximum emission enhancement at resonance ($\omega_e = \omega_c$) and that we can suppress spontaneous emission at large detunings.

- Dipole orientation with respect to the electric field. Since the electric dipole operator and electric field operator are vectors, we have a

normalized dipole orientation factor:

$$\xi^2 = \left(\frac{|\vec{\mu} \cdot \vec{E}|}{|\vec{\mu}| |\vec{E}|} \right)^2 \quad (3.12)$$

Here, $\vec{\mu}$ and $\vec{E}$ are the transition dipole moment and electric field vectors, respectively. For random orientation of the dipoles, we have $\xi^2 = \frac{1}{3}$.

- Electric field strength at the position of the emitter. Since the electric field within a microcavity is usually spatially modulated, the placement of the emitter with respect to nodes and antinodes is important. Therefore, we get a factor

$$\frac{|E(r_e)|^2}{|E_{max}|^2} \quad (3.13)$$

where $E(r_e)$ is the electric field at the position of the emitter and E_{max} is the maximum electric field of the cavity mode.

In total, we have

$$\frac{\Gamma^{cav}}{\Gamma^{free\ space}} = \frac{3Q \left(\frac{\lambda_e}{n}\right)^3}{4\pi^2 V_{cav}} \frac{\Delta\omega_c^2}{4(\omega_e - \omega_c)^2 + \Delta\omega_c^2} \xi^2 \frac{|E(r_e)|^2}{|E_{max}|^2} \quad (3.14)$$

for the modification of the spontaneous emission rate inside a cavity.

Explicit calculations with planar metal cavities show that for these systems, one expects a maximum fluorescence rate enhancement of 3 whereas the cavity resonance is actually slightly red-shifted compared to the fluorescence transition [52].

3.2.4 Strong Coupling: Generating Hybrid Light-Matter States

The Jaynes-Cummings model: Interaction of a two-level system with a single optical mode

Much of the physics of strong coupling can be understood by investigating a fully quantum-mechanical model, introduced by Jaynes and Cummings in 1963 [53]. The Jaynes-Cummings model describes the interaction of a two-level atom with a single quantized mode of the optical field (for detailed derivations and discussions of the model, see for example [31, 54–57]). Consequently, the Jaynes-Cummings Hamiltonian contains three terms:

- H_{TLS} : The energy of the atom. Since it is approximated as a two-level system, its Hamiltonian reads

$$H_{TLS} = \frac{\hbar\omega_A}{2} (\sigma_z + 1), \quad (3.15)$$

where $\hbar\omega_A$ is the energy separation between the two levels (where $\hbar$ is the reduced Planck's constant and ω_A the angular frequency characterizing the transition) and σ_z is the Pauli z -matrix. Often, a factor of $\frac{\hbar\omega_A}{2}$ is added such that the ground (excited) state energy of the atom corresponds to $E = 0$ ($E = \hbar\omega_A$).

- H_{OF} : The energy of the optical field inside the cavity. Since only a single mode is considered, it is given by

$$H_{OF} = \hbar\omega_c \left(a^\dagger a + \frac{1}{2} \right), \quad (3.16)$$

where ω_c is the angular frequency of the cavity mode and $a^\dagger a$ is the photon number operator.

- H_{int} : The coupling energy between atom and optical mode:

$$H_{int} = \hbar g_0 \left(\sigma^+ a + \sigma^- a^\dagger \right) \quad (3.17)$$

with the coupling energy $\hbar g_0$ given by

$$\hbar g_0 = \sqrt{\frac{\hbar\omega_c}{2\varepsilon_0 V}} \mu, \quad (3.18)$$

which is derived using the dipole approximation⁸ and rotating wave approximation.⁹ Here, $a^\dagger$ (a) is the photon creation (annihilation) operator for the optical mode, σ^+ (σ^-) is the raising (lowering) operator for the two-level system. Consequently, $\sigma^+ a$ describes absorption of a photon by the two-level system and $\sigma^- a^\dagger$ describes emission of the two-level system into the optical mode. ε_0 is the vacuum permittivity, V is the cavity volume and μ is the transition dipole moment of the atom (not considering polarization effects).

In total, the Jaynes-Cummings Hamiltonian reads:

$$H_{JC} = \frac{\hbar\omega_A}{2} (\sigma_z + 1) + \hbar\omega_c \left(a^\dagger a + \frac{1}{2} \right) + \hbar g_0 \left(\sigma^+ a + \sigma^- a^\dagger \right) \quad (3.19)$$

The quantum-mechanical states of the system are characterized by the state of the atom and the number of photons in the optical mode. Therefore, we have

$$|g(e)\rangle \otimes |n\rangle = |g(e), n\rangle \quad (3.20)$$

⁸Neglecting the variation of the electric field across the length scale of the atom. This means that the interaction energy can be described as the coupling of a dipole moment to the electric field: $\hbar g_0 \approx \vec{\mu} \cdot \vec{E}$, which corresponds to the classical energy of a dipole in an electric field. For simplicity, I neglect the vector character of μ and $E = \sqrt{\frac{\hbar\omega_c}{2\varepsilon_0 V}}$ in equation 3.18.

⁹Neglecting fast-oscillating terms.

as the system states (here, $\otimes$ signifies that we are constructing the product space of $|g(e)\rangle$ and $|n\rangle$). Immediately, we have $|g, 0\rangle$ as the ground state with the ground state energy $E_{GS} = \frac{\hbar\omega_c}{2}$ corresponding to the zero-point energy of the electromagnetic field.

A useful simplification for the remaining states is to consider the number of excitations in the system (the number of photons + 1 if the atom is in the excited state), which is conserved. For each excitation number, the problem reduces to a two-dimensional problem in the subspace $\{|e, n\rangle, |g, n+1\rangle\}$ (where $n = 0, 1, 2, \dots$ is the photon number with the atom in the excited state). Upon associating $|e, n\rangle \leftrightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|g, n+1\rangle \leftrightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ we can calculate an explicit representation of the Hamiltonian matrix in each subspace:

$$\begin{aligned}
(H)_n &= \begin{pmatrix} \langle e, n | H_{JC} | e, n \rangle & \langle e, n | H_{JC} | g, n+1 \rangle \\ \langle g, n+1 | H_{JC} | e, n \rangle & \langle g, n+1 | H_{JC} | g, n+1 \rangle \end{pmatrix} \\
&= \hbar \begin{pmatrix} (n + \frac{1}{2})\omega_c + \omega_A & g_0\sqrt{n+1} \\ g_0\sqrt{n+1} & (n + \frac{3}{2})\omega_c \end{pmatrix} \\
&= \left[n + \frac{1}{2} \right] \hbar\omega_c \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \hbar \begin{pmatrix} \omega_A & g_0\sqrt{n+1} \\ g_0\sqrt{n+1} & \omega_c \end{pmatrix} \\
&= \left[E_{GS} + (n+1)\hbar\omega_c + \frac{\Delta}{2} \right] \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\hbar}{2} \begin{pmatrix} \Delta & \Omega_n \\ \Omega_n & -\Delta \end{pmatrix}
\end{aligned} \tag{3.21}$$

where $\Delta \equiv \omega_A - \omega_c$ is the detuning between atomic transition and cavity mode and $\Omega_n \equiv 2g_0\sqrt{n+1}$ is the Rabi frequency for n photons ($n+1$ excitations).¹⁰

By solving the eigenvalue equations of $(H)_n$, we obtain

$$E_{\pm, n} = E_{GS} + \hbar \left[(n+1)\omega_c + \frac{\Delta}{2} \pm \frac{R_n}{2} \right] \tag{3.22}$$

for the energy eigenvalues and

$$\begin{aligned}
|+\rangle_n &= \sin \theta_n |e, n\rangle + \cos \theta_n |g, n+1\rangle \\
|-\rangle_n &= \cos \theta_n |e, n\rangle - \sin \theta_n |g, n+1\rangle
\end{aligned} \tag{3.23}$$

for the eigenvectors. Here,

$$R_n \equiv \sqrt{\Omega_n^2 + \Delta^2} = \sqrt{4g_0^2(n+1) + \Delta^2} \tag{3.24}$$

is the generalized Rabi frequency and

$$\begin{aligned}
\sin \theta_n &= \frac{\Omega_n}{\sqrt{(R_n - \Delta)^2 + \Omega_n^2}} \\
\cos \theta_n &= \frac{R_n - \Delta}{\sqrt{(R_n - \Delta)^2 + \Omega_n^2}}
\end{aligned} \tag{3.25}$$

¹⁰In the literature, the factor associated with the identity matrix in Equation 3.21 might differ due to different definitions of the ground state energy of the system E_{GS} .

are the normalized amplitudes of the eigenvectors.

Notice the following features of the obtained solution:

- If we turn off the coupling ($g_0 = 0$), we recover the solution for the uncoupled system.¹¹ Here, light and matter states are completely independent.
- For large detunings ($|\Delta| \gg \Omega_n$), we also recover the uncoupled solution.
- At resonance ($\Delta = 0$), we have

$$E_{\pm,n}^{\Delta=0} = E_{GS} + \hbar \left[(n+1) \omega_c \pm \frac{\Omega_n}{2} \right] \quad (3.26)$$

and

$$|\pm\rangle_n^{\Delta=0} = \frac{1}{\sqrt{2}} (|e, n\rangle \pm |g, n+1\rangle) \quad (3.27)$$

Here, the degeneracy of the uncoupled energy levels $|e, n\rangle$ and $|g, n+1\rangle$ is lifted and the new energy levels are now separated by $\hbar\Omega_n$. The eigenvectors are a linear combination of the uncoupled states, resulting in hybrid light-matter states, often called “polaritons”, where the state of the atom and the state of the photon mode are quantum-mechanically entangled. Experimentally, this results in so-called Rabi splitting where the previously degenerate peaks of cavity mode and molecular transition split into an upper and lower polariton (see Figure 3.2).

- If we consider the energies as a function of the detuning Δ , we observe so-called avoided (or anti) crossing.
- Furthermore, the eigenvectors can be used to quantify the entanglement / hybrid nature of the emerging states: As can be seen in Equation 3.23, the emerging polaritonic states can be decomposed into the eigenstates of the uncoupled system. The respective coefficients α_n , which quantify the contributions from the uncoupled states (enumerated *via* n) for each polariton,¹² can generally be derived from the normalized eigenvectors¹³ and we have $|\alpha_n|^2 \leq 1$ and $\sum_n |\alpha_n|^2 = 1$. For a two-dimensional problem, we have $|\alpha_1|^2 = |\alpha_2|^2 = \frac{1}{2}$ for maximum entanglement and $|\alpha_1|^2 = 1, |\alpha_2|^2 = 0$ for minimal entanglement. Often, these coefficients are called “Hopfield coefficients” (after John J. Hopfield, who coined the term “polariton”).

¹¹If the atom is in the ground state: $|g, n\rangle$ with energy $E = E_{GS} + n\hbar\omega_c$; if the atom is in the excited state: $|e, n\rangle$ with energy $E = E_{GS} + n\hbar\omega_c + \hbar\omega_A$.

¹²For Equation 3.23, we have $\alpha_n \in \{\cos \theta_n, \pm \sin \theta_n\}$.

¹³If the uncoupled states correspond to the trivial base vectors, the α_n -values directly correspond to entries in the eigenvectors. If not, the α_n -values can be obtained *via* the scalar product of the eigenvector and the respective uncoupled state vector.

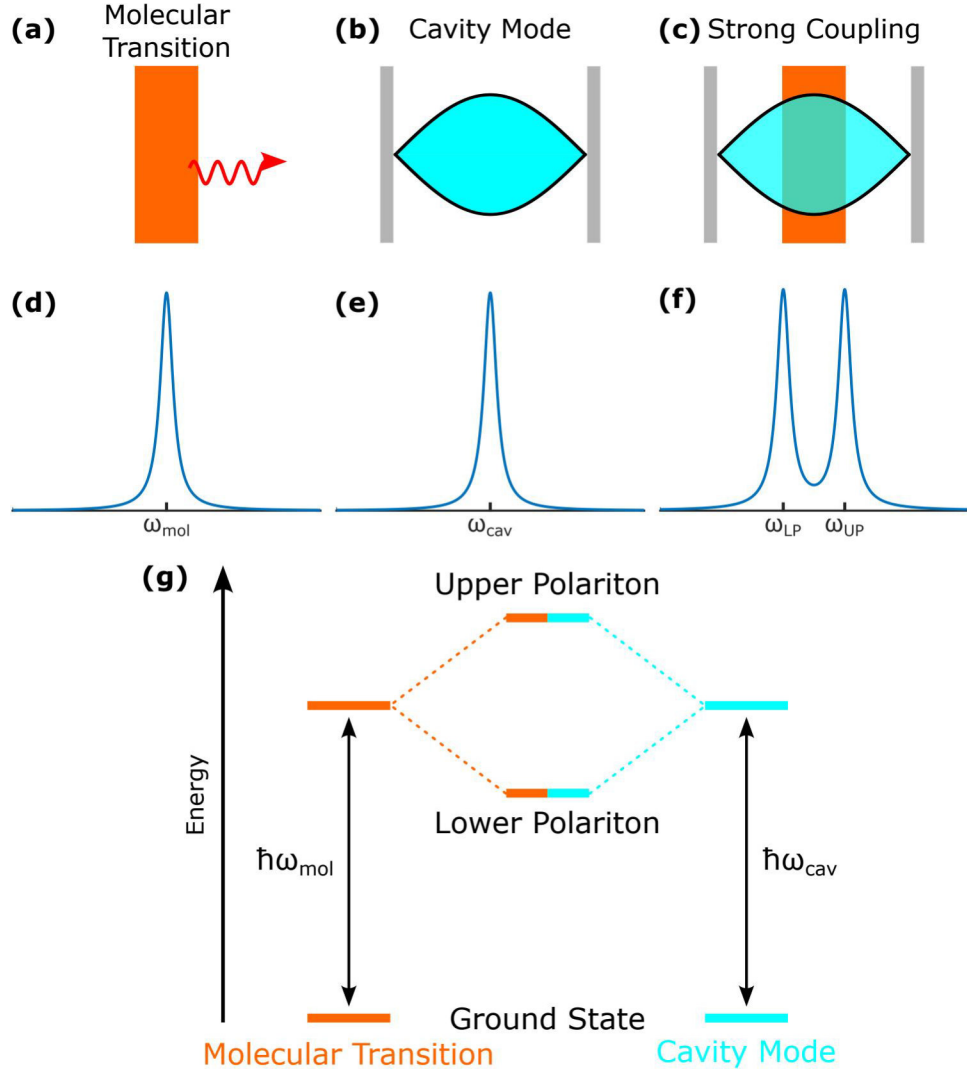


Figure 3.2: Pictorial representation of strong coupling: Molecules exhibiting an optical transition (a) are placed inside a Fabry-Pérot resonator (b), leading to the situation depicted in (c). In the strongly coupled system, the resonant uncoupled optical peaks (depicted in (d) and (e)) split into an upper and lower polaritonic peak (f). In (g), the situation from (c)/(f) is re-plotted in terms of energy levels. The use of two different colors (orange for the molecular transition and cyan for the cavity mode) hints at the mixed / hybrid nature of the emerging polaritons.

Extensions of the Jaynes-Cummings model: Interaction of N two-level systems with a single optical mode

Probably the most straightforward extension of the Jaynes-Cummings model is to include multiple atoms (coupling of a single optical mode with N identical two-level systems). Such models were developed by Dicke in 1954 [58] and by Tavis and Cummings in 1968 [59]. The difference between the two models is the rotating wave approximation, which is applied only in the Tavis-Cummings model, leading to the presence of additional terms in the Dicke model [57, 60, 61]. For more detailed discussions of these models, see [31, 57, 60, 62].

The main result is that the coupling energy in the Tavis-Cummings model $\hbar g^{TC}$ scales with the square root of the number of coupled emitters: [30, 31, 57]:

$$\hbar g^{TC} = \sqrt{N} \hbar g_0^{JC} \quad (3.28)$$

Here, N is the number of coupled emitters and $\hbar g_0^{JC}$ is the coupling energy of the corresponding Jaynes-Cummings model ($N = 1$).

Practical aspects for achieving strong coupling

From previous equations (3.18 and 3.28), we can immediately see that the following parameters have an influence on the coupling energy:

- The electric field inside the cavity, which should be high. This means strong field enhancement which corresponds to a high Q -factor.
- The cavity volume, which should be small.
- The dipole moment of the coupled emitter, which should be high.
- The number of coupled emitters, which should be large.

An additional aspect is the relative orientation between the electric field vector and the dipole moment of the emitter, which was neglected in equation 3.18. Upon considering the vector character of the two quantities, it becomes obvious that coupling is most efficient if the dipole moment of the emitter is aligned parallel to the electric field vector and vanishes if dipole moment and electric field vector are orthogonal.

Furthermore, the magnitude of the electromagnetic field is usually spatially modulated within the cavity. For the simplest case, an ideal Fabry-Pérot resonator, the electric field strength is modulated sinusoidally between the two mirror surfaces (see Figure 3.1). Therefore, positioning of the emitters with respect to the nodes and antinodes of the electric field is crucial for obtaining high coupling strengths, with the optimal position being an antinode [63–65].

In practice, one of the most common types of emitters used in the study of strong coupling are so-called J-aggregates. J-aggregates, discovered independently in the mid 1930s by Jelly [66, 67] and Scheibe [68, 69], are a class of organic molecules [70, 71]. Under certain conditions, these molecules self-aggregate which drastically modifies their optical properties compared to the monomers: Exciton coupling between the molecules leads to the formation of a collective, delocalized optical transition. A strong and narrow absorption / emission band (“J-band”) with very small Stokes shift emerges which is red-shifted compared to the monomers [72–74]. The J-band exhibits a strong oscillator strength, making J-aggregates suitable to achieve strong coupling with large coupling strengths at room temperature [75].

For this work, we utilized two J-aggregates: TDBC and BRK. The respective molecular structures and absorption / emission spectra (for the aggregated forms) are displayed in Figure 4.1.

Strong coupling and material properties

As shown above, strong light-matter coupling fundamentally changes quantum-mechanical properties compared to the uncoupled system by entangling light and matter states. Accordingly, it has garnered considerable attention in the context of material science, molecular chemistry and quantum photonics (for some recent reviews, see [76–85]). Especially noteworthy is the possibility of (drastically) changing certain material properties, including:

- Chemical reactivity (for exciton strong coupling [86–91], vibrational strong coupling [92–95] as well as strong coupling to plasmonic structures [96, 97])
- Charge transport [98–100]
- Exciton transport [100–103]
- Energy transfer (see Section 3.3)

3.3 Energy Transfer in the Strong Coupling Regime: Polariton-Mediated Energy Transfer (PMET)

Generally, modification of energy transfer under strong coupling has been reported for multiple different materials and cavity configurations (for recent reviews, see [84, 85]).

Here, I will focus on J-aggregated organic molecules coupled to Fabry-Pérot resonators. For such systems, the emergence of a new energy transfer mechanism was first reported by David Lidzey *et al.* in 2014 [104] and later reproduced by the same group [105] and the group of Thomas Ebberssen [106–108]. In these experiments, two different J-aggregates (an energy

donor and a red-shifted energy acceptor)¹⁴ were strongly coupled to the same microcavity. The resulting hybridization of light and matter states, which fundamentally changes the energy landscape of the system, leads to the emergence of a new energy transfer channel from donor to acceptor, dubbed “Polariton-Mediated Energy Transfer” (PMET). PMET shows the following features:

- The mechanism seems to be independent of donor-acceptor separation [81, 107].
- PMET was demonstrated for donor-acceptor separations of up to 2 μm [105], which is orders of magnitude larger than Förster- or Dexter-type mechanisms.

As a point of comparison, a short discussion of Förster Resonance Energy Transfer (FRET), arguably the most important energy transfer mechanism for organic molecules, is provided in Appendix A.

In certain regards, however, the aforementioned experiments were limited:

- Fabry-Pérot microcavities were constructed by successive thin film preparation steps. This resulted in rigid Fabry-Pérot resonators with fixed distances between the mirrors as well as the donor- and acceptor-containing layers.
- Consequently, tuning of the cavity modes was only possible by performing angle-resolved measurements.
- Usually, only a single cavity mode interacted with the excitonic transitions of the J-aggregates.

For these reasons, we wanted to expand on these previous works and perform measurements with a tunable Fabry-Pérot microcavity at large mirror separations (several μm). This enables us to

1. systematically study the system as a function of donor-acceptor separation,
2. investigate situations where multiple cavity modes interact simultaneously with the excitonic transitions of the J-aggregates and
3. explore the (practically realizable) upper limit of donor-acceptor separations for which PMET occurs.

¹⁴All five works used the J-aggregate TDBC as energy donor. For the energy acceptor, [104, 105] used the J-aggregate NK-2707, [106–108] used the J-aggregate BRK.

3.4 Strong Coupling in Multimode Systems: Phenomenological Hamiltonians

To properly model the emerging polariton modes in a strongly coupled system with multiple different excitons and multiple cavity modes, a phenomenological Hamiltonian, which is essentially a sensible extension of the Jaynes-Cummings Hamiltonian (Equation 3.21), is highly desirable.

In the literature, there are two different “schemes” for constructing an appropriate phenomenological Hamiltonian. For the “coupled” mode (used, for example, in [109–114]), the excitons couple to each cavity mode simultaneously. For the “decoupled” mode (used, for example, in [105, 115]), the excitons couple independently to each cavity mode. As an example, for 2 excitons (labeled A and B) and N cavity modes, we would have

$$H_{coupled} = \begin{pmatrix} E_A & 0 & \hbar g_A & \hbar g_A & \dots & \hbar g_A \\ 0 & E_B & \hbar g_B & \hbar g_B & \dots & \hbar g_B \\ \hbar g_A & \hbar g_B & E_{cav,1} & 0 & \dots & 0 \\ \hbar g_A & \hbar g_B & 0 & E_{cav,2} & & 0 \\ \vdots & \vdots & \vdots & & \ddots & 0 \\ \hbar g_A & \hbar g_B & 0 & 0 & 0 & E_{cav,N} \end{pmatrix}_{(N+2) \times (N+2)} \quad (3.29)$$

and

$$H_{decoupled} = \begin{pmatrix} E_{cav,1} & \hbar g_A & \hbar g_B & 0 & 0 & 0 & \dots & 0 & 0 & 0 \\ \hbar g_A & E_A & 0 & 0 & 0 & 0 & \dots & 0 & 0 & 0 \\ \hbar g_B & 0 & E_B & 0 & 0 & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & 0 & E_{cav,2} & \hbar g_A & \hbar g_B & & & & \\ 0 & 0 & 0 & \hbar g_A & E_A & 0 & & & & \\ 0 & 0 & 0 & \hbar g_B & 0 & E_B & & & & \\ \vdots & \vdots & \vdots & & & & \ddots & & & \\ 0 & 0 & 0 & & & & & E_{cav,N} & \hbar g_A & \hbar g_B \\ 0 & 0 & 0 & & & & & \hbar g_A & E_A & 0 \\ 0 & 0 & 0 & & & & & \hbar g_B & 0 & E_B \end{pmatrix}_{(3N \times 3N)} \quad (3.30)$$

where E_{cav} are the energies of the cavity modes,¹⁵ $E_{A/B}$ are the energies of the excitons and $\hbar g_{A/B}$ are the coupling energies for a certain exciton (which are assumed to be the same for all cavity modes).

Works dealing directly with the problem are unfortunately not conclusive: In [116], the decoupled Hamiltonian is generally recommended, while in [117, 118], a transition between the coupled and decoupled Hamiltonian, which depends on the oscillator strength of the excitons, is proposed.

¹⁵Here, we will use the energies of an ideal Fabry-Pérot resonator: $E_{cav,m} = m \frac{\pi \hbar c}{n L_{cav}}$, which is derived by multiplying Equation 3.6 with $\hbar$.

Irrespective of the chosen form of the Hamiltonian, its eigenvectors can be used to calculate Hopfield coefficients which indicate the relative contributions of excitons and the cavity modes for each polariton (as mentioned in Section 3.2.4). As an example, $H_{coupled}$ with the two J-aggregates TDBC and BRK as excitons and N cavity modes (which corresponds to the experimental system investigated in this work) yields the following eigenvalue equation:

$$\begin{pmatrix} E_{TDBC} & 0 & \hbar g_{TDBC} & \hbar g_{TDBC} & \dots & \hbar g_{TDBC} \\ 0 & E_{BRK} & \hbar g_{BRK} & \hbar g_{BRK} & \dots & \hbar g_{BRK} \\ \hbar g_{TDBC} & \hbar g_{BRK} & E_{cav,1} & 0 & \dots & 0 \\ \hbar g_{TDBC} & \hbar g_{BRK} & 0 & E_{cav,2} & & 0 \\ \vdots & \vdots & \vdots & & \ddots & 0 \\ \hbar g_{TDBC} & \hbar g_{BRK} & 0 & 0 & 0 & E_{cav,N} \end{pmatrix} \cdot \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \\ \vdots \\ \alpha_{N+2} \end{pmatrix} = E_{pol} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \\ \vdots \\ \alpha_{N+2} \end{pmatrix} \quad (3.31)$$

For the two excitons, it is immediately obvious that their contributions are captured by the first two entries of the eigenvectors. Consequently, we have

$$|\alpha^{TDBC}|^2 = |\alpha_1|^2 \quad (3.32)$$

and

$$|\alpha^{BRK}|^2 = |\alpha_2|^2. \quad (3.33)$$

To keep the number of coefficients reasonable, we decided to condense the contributions from the cavity modes into a single coefficient:

$$|\alpha^{light}|^2 = \sum_{i=3}^{N+2} |\alpha_i|^2 \quad (3.34)$$

For $H_{decoupled}$, the procedure is analogous. Due to the decoupling of the modes, however, one has to perform appropriate summations for all three coefficients. If the Hamiltonian is set up according to Equation 3.30 (where $A \leftrightarrow$ TDBC and $B \leftrightarrow$ BRK), we have:

$$\begin{aligned} |\alpha^{TDBC}|^2 &= |\alpha_2|^2 + |\alpha_5|^2 + |\alpha_8|^2 + \dots \\ |\alpha^{BRK}|^2 &= |\alpha_3|^2 + |\alpha_6|^2 + |\alpha_9|^2 + \dots \\ |\alpha^{light}|^2 &= |\alpha_1|^2 + |\alpha_4|^2 + |\alpha_7|^2 + \dots \end{aligned} \quad (3.35)$$

Chapter 4

PMET at Large Distances: Results & Discussion

In this Chapter, I summarize the results presented in the two publications mentioned in Section 1.1 [119, 120] (see Appendix B and C, respectively). The goal of these works was to investigate Polariton-Mediated Energy Transfer (PMET, see Section 3.3) inside a tunable Fabry-Pérot resonator at large mirror separations.

For this purpose, we developed an experimental platform to perform white-light transmission and fluorescence measurements on a tunable Fabry-Pérot resonator whose optical modes are simultaneously strongly coupled to two different J-aggregates, the energy donor TDBC and the energy acceptor BRK, which I describe in Section 4.1. This includes the construction of tunable Fabry-Pérot resonators (Section 4.1.1), the implementation of optical measurements (Section 4.1.2) and a description of the measurement procedure and investigated sample configurations (Section 4.1.3).

Measurements were performed on four different cavity-J-aggregate configurations which served as the experimental foundation for both publications: In [119] (Appendix B), white-light transmission measurements were used to characterize the system by fitting a phenomenological Hamiltonian to the observed transmission peaks, which is presented in Section 4.2. In [120] (Appendix C), the corresponding fluorescence measurements (which were taken within the same measurement cycles as the white-light transmission measurements) were analyzed, which is presented in the following five Sections: To exclude energy transfer without cavity, we performed appropriate fluorescence control measurements, which are presented in Section 4.3. In Section 4.4, the effect of the laser excitation efficiency on the total fluorescence signal is investigated. Section 4.5 looks for trends in energy transfer efficiency. Furthermore, we fitted the phenomenological Hamiltonian $H_{coupled}$ to the experimental fluorescence maxima (Section 4.6) and developed a model based on rate equations to explain the observed fluores-

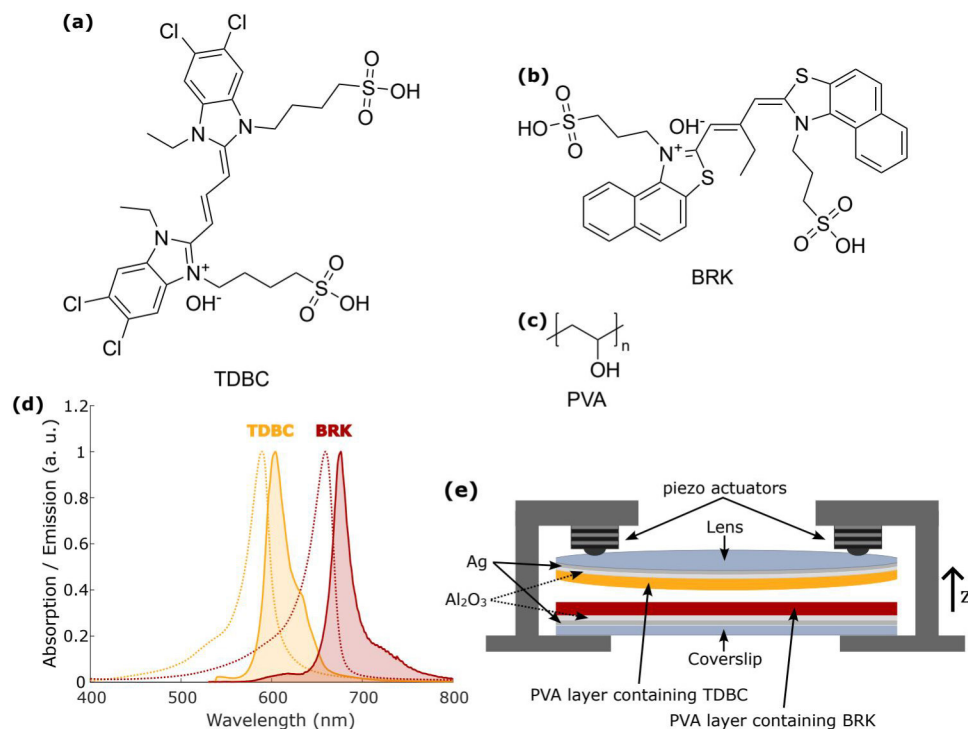


Figure 4.1: Molecular structures of the used J-aggregates (TDBC in (a) and BRK in (b)) and the polymer PVA used for spin-coating (in (c)). (d) Free space absorption (dashed lines) and emission spectra (532 nm excitation; solid lines) of TDBC (orange) and BRK (red). (e) Sketch of the tunable Fabry-Pérot resonator. (d) and (e) are adapted from [120].

cence intensities (Section 4.7).

In the last Section of this Chapter (Section 4.8), I provide a short summary and conclusion.

4.1 Experimental Procedures

4.1.1 Construction of Tunable Fabry-Pérot Resonators

Optical resonators were prepared similar to previous works of our group (for the most recent examples, see [65, 121–124]): Mirrors were constructed by subsequently coating cleaned glass substrates with Cr, Ag and lastly Al₂O₃ using electron beam evaporation. Here, Cr serves as an adhesive layer, Ag as the mirror and Al₂O₃ as a spacer layer. As glass substrates, we used a coverslip for the bottom mirror and a plano-convex lens for the top mirror. The use of a plano-convex lens instead of a coverslip solves the problem of

aligning the two mirrors: When approaching the coated plano-convex lens towards the coated coverslip, a Fabry-Pérot cavity is formed at the position of the apex of the convex lens, where the surface is in good approximation parallel to the bottom mirror. Under a light microscope, this can be observed *via* the appearance of Newton’s rings at the corresponding position. This is in practice much easier than aligning two flat surfaces where tilt between the mirrors is a big problem (especially if one of the mirrors has to be movable).

To introduce the sample into the resonator, polymer solutions containing the J-aggregate TDBC or BRK (see Figure 4.1) were spin-coated onto the spacer layers of the mirrors. The Fabry-Pérot resonator was then assembled by placing the mirrors in a cage system. Here, the back mirror was coupled to a piezo-actuator, which enabled precise control and modification of the mirror separation. The resulting structure is depicted in Figure 4.1 (e).

The assembled resonators were placed into a confocal microscope for optical measurements. Here, the resonators could be moved in the plane perpendicular to the optical axis for the purpose of moving the center of the Newton’s rings into the focus of the objective lens. This was achieved either by directly imaging the Newton’s rings *via* a camera or by observing the cavity transmission peaks, which shift to the blue when moving the optical focus into the center of the Newton’s rings, with a spectrometer.

Further details on the construction of the used resonators are provided in the experimental sections of the publications (see Appendices B and C).

4.1.2 Optical Measurements Using a Custom-Built Confocal Microscope

Optical measurements were performed with a custom-built confocal microscope, as depicted in Figure 4.2. Here, the same objective lens is used to focus the excitation laser onto the sample and for detection of the emitted light. Pinholes are placed in the excitation and detection path (in conjugated focal planes) to increase optical resolution and contrast [125–127]. Samples are mounted on a piezo-stage to enable positioning in the plane perpendicular to the optical axis. In the detection path, light is guided either into a spectrometer or onto avalanche photo diodes (APD) for single photon detection. A long-pass filter is used to block scattered laser light.

To enable white-light transmission measurements, we placed a white-light source behind the sample. Here, the longpass filter and pinhole in the detection path were usually removed.

For fluorescence measurements, a 532 nm continuous wave (cw) laser was used. At this wavelength, absorption by the energy donor (TDBC) is significantly larger compared to the energy acceptor (BRK) (see Figure 4.1 (d)). Furthermore, we placed a camera behind the sample (replacing the white-light source) to detect the laser light transmitted through the cavity.

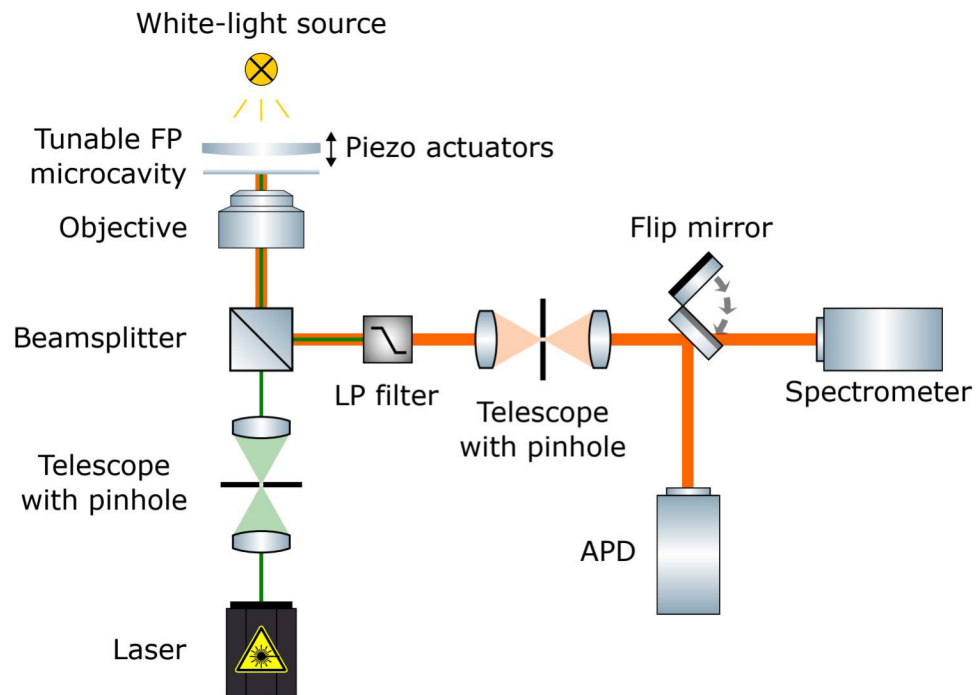


Figure 4.2: Conceptual sketch of the used confocal microscopes. The laser beam path is shown in green and the detection light path in orange. The same objective is used for excitation and detection of the sample. Pinholes in the laser and detection path are used to improve optical resolution and contrast. Used abbreviations: APD (avalanche photo diode), FP (Fabry-Pérot), LP (longpass).

Further details of the experimental setup are presented in the experimental sections of the publications (see Appendices B and C).

4.1.3 Sample Preparation and Measurement Procedure

Optical resonators were prepared as described in Section 4.1.1. Measurements were performed with four different cavity configurations. Here, different polymer solutions were spin-coated onto the mirrors of the Fabry-Pérot resonator:

- 2M-D: The donor (TDBC) spin-coated onto the top mirror (the coated lens).
- 2M-A: The acceptor (BRK) spin-coated onto the bottom mirror (the coated coverslip).
- 2M-DA: The donor spin-coated onto the top mirror and the acceptor spin-coated onto the bottom mirror. To ensure comparability, the same coated mirrors as in 2M-D and 2M-A were used. For this configuration, we performed two measurements (labeled 2M-DA-I and 2M-DA-II) at different mirror separations, respectively.
- 1M-DA: To exclude the possibility of energy transfer without cavity, we exchanged the bottom mirror for a pristine coverslip (spin-coated with the donor). Here, we only performed fluorescence measurements.

For measurements, a Fabry-Pérot resonator was assembled (see Figure 4.1 (e)) and placed into the confocal microscope such that the optical focus spot was in the center of the Newton’s rings (see Section 4.1.2). At the start of a measurement, we brought the top mirror into contact with the bottom mirror. We then step-wise increased the mirror separation *via* the piezo-actuator coupled to the back mirror. After each voltage step, we measured an optical spectrum (white-light transmission or fluorescence) until the full range of the piezo-actuators was used. Since we had to adjust the optical setup when switching between the two measurement modes,¹ we first took a series of transmission measurements and subsequently took a series of fluorescence measurements over the same voltage range. Here, the *xy*-position of the cavity remained unchanged. The achieved mirror separations differed slightly between the two measurements (see Table 4.1 and Section 4.6). For the configuration with both donor and acceptor (2M-DA), we recorded a second series of transmission and fluorescence spectra at larger mirror separations. Here, we used μm -screws to manually move the back mirror to the approximate end-point of the first measurement.

¹Replacing the white-light source behind the Fabry-Pérot resonator with a camera and inserting longpass filters.

Table 4.1: Optical path length nL_{cav} calculated from the fits of $H_{coupled}$ to the transmission peaks and fluorescence maxima for all four cavity configurations.

	Range of nL_{cav} (μm)	
	Transmission measurement	Fluorescence measurement
2M-D	2.456 ... 7.850	3.403 ... 8.704
2M-A	1.138 ... 7.040	0.690 ... 6.495
2M-DA-I	1.433 ... 7.210	1.426 ... 7.026
2M-DA-II	7.260 ... 12.800	7.322 ... 12.860

Analysis of the obtained spectra (see Sections 4.2 and 4.6) reveals the achieved mirror separations for all measurements, which are summarized in Table 4.1. The obtained values show that during a single measurement, the piezo-actuators increase the mirror separation by approximately 5 μm .

In the following Sections, the results of the white-light transmission and fluorescence measurements are summarized and discussed. Here, I will focus on the measurements 2M-DA-I and 2M-DA-II where PMET was observed.²

4.2 System Characterization *via* Analysis of Transmission Spectra

First, we analyzed the transmission measurements to extract important system parameters, namely the coupling energies $\hbar g$ and cavity length nL_{cav} . For this purpose, we developed a fitting routine in MATLAB where we fit each obtained spectrum in a series to a phenomenological Hamiltonian. For each spectrum, we get the cavity length³ and coupling energies. We then smoothed the resulting curves; for the cavity lengths, we used a simple smoothing function, for the coupling energy, we manually adjusted the parameter A in $\hbar g = A \cdot (nL_{cav})^{-1/2}$. The respective curves for the obtained cavity lengths and coupling energies are provided in the Supporting Information of [119] in Appendix B. For 2M-DA-I, transmission spectra and the calculated fit to $H_{coupled}$ are shown in Figure 4.3.

The most important results from this analysis are:

- The obtained curves for the cavity length show a slightly faster than linear increase over the course of the measurements. This reflects the expected voltage-displacement behaviour of the piezo-actuators, which were not feedback-controlled. If the mirrors touched at the start of

²The measurements with only one J-aggregate (2M-D and 2M-A) mainly served as reference measurements and additional data sets to test and validate the developed analysis procedures. For the respective analyses, see the publications in Appendix B and C.

³In this context, the cavity length refers to the optical path length of the cavity, which is the mirror separation times the refractive index.

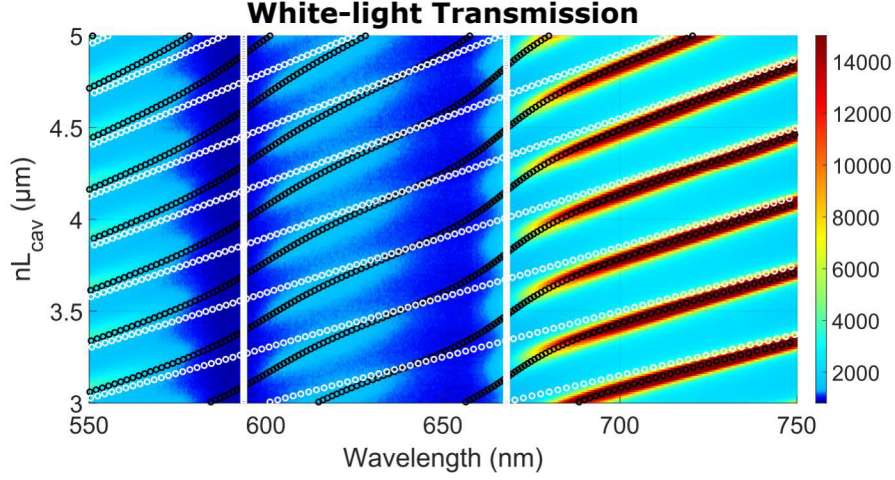


Figure 4.3: White-light transmission spectra for 2M-DA-I as false-color map. Black circles show the fits to $H_{coupled}$. For comparison, white circles show the corresponding uncoupled excitons and cavity modes. Spectra are plotted against the cavity distances from the fits. Adapted from [119].

the measurement, we observed only very small changes in the cavity lengths of the first few spectra.

- The obtained coupling energies (at least 30 meV throughout all measurements and distances) suggest that we reached the strong coupling regime for all investigated distances. This is also apparent from the progression of the transmission maxima which show clear deviations from the linear progression one would expect for an uncoupled Fabry-Pérot resonator (see Figure 4.3).
- Since it was not clear which phenomenological Hamiltonian had to be used, we tested both $H_{coupled}$ and $H_{decoupled}$. We obtained significantly better agreement with the experimental data when using $H_{coupled}$ (see the Supporting Information of [119] in Appendix B). This agrees rather well with the results from [118]: Here, the coupling behaviour of differently concentrated TDBC thin films strongly coupled to a Fabry-Pérot resonator was investigated. It was found that $H_{coupled}$ matched experimental data better for low-concentration stock solutions⁴ (1 and 2 wt%). For high-concentration stock solutions (4 and 6 wt%), however, a transition to $H_{decoupled}$ was observed. We have used 1 wt% stock solutions for both J-aggregates.
- The obtained coupling energies decrease with increasing cavity length

⁴Concentration of the J-aggregate TDBC in the polymer solution used for spin-coating.

as $\hbar g \propto (nL_{cav})^{-1/2}$. This is the expected behaviour if the only influence on the coupling energy is the cavity volume (see Equation 3.18).

- Additionally, we observed small oscillations in the obtained coupling energy-cavity length curves which are most likely due to a subtlety of the Hamiltonian: To keep the number of fit parameters reasonable, we assumed the coupling energy between an exciton and the cavity modes to be the same for all cavity modes. This means that we perform an effective averaging of the coupling energies if there are multiple cavity modes on resonance simultaneously. If now the coupling energies of different cavity modes differ in a systematic way as a function of cavity length, this would result in oscillations of the averaged coupling energies. We identified two possible sources for such differences: (1) The spectral width of the excitonic transitions and (2) the influence of the electric field strength of the cavity modes at the spatial position of the exciton layers. Both phenomena would lead to an additional dependence of the coupling energy on the exact spectral position of the cavity modes. However, the resulting oscillations in the coupling energy-cavity length curves were generally small (especially at large cavity lengths where the averaging of the coupling energies is pronounced) and it was not necessary to take these into account to obtain excellent fits of the phenomenological Hamiltonian to the measured transmission peaks.
- Using the fit results, we also calculated the Hopfield coefficients for the emerging polariton modes. We specifically looked for so-called “hybrid polaritons” which contain contributions from both donor and acceptor. We found that for most cavity configurations of 2M-DA-I and 2M-DA-II, there was at least one hybrid polariton with energy in between the free space exciton energies with at least two percent excitonic contribution from both donor and acceptor (see, for example, Figure 4.6). The only exceptions occurred at the start of 2M-DA-I for situations where there were no cavity modes present with energy in between the free space exciton energies. These situations disappeared with decreasing free spectral range at higher cavity distances.

To summarize, the analysis of the measured series of transmission spectra shows that we reached the strong coupling regime for all investigated measurement configurations. Hybrid polaritons, which are most likely crucial for enabling PMET, were present throughout 2M-DA-I and 2M-DA-II. Furthermore, we clarified the correct form of the phenomenological Hamiltonian and the behaviour of the coupling energies as a function of cavity length.

4.3 Comparison of Energy Transfer in Strongly Coupled and “Free Space” Systems

Next, we analyzed the fluorescence measurements to investigate energy transfer from donor to acceptor. As a preliminary step, we had to check if there is significant energy transfer without the optical cavity. For this purpose, we prepared an additional “Fabry-Pérot resonator” (labeled 1M-DA-I) where we have exchanged the lower mirror for a pristine glass coverslip. Apart from this, sample preparation and measurement procedure were identical to 2M-DA-I. The resulting series of fluorescence spectra (see Appendix C) is clearly dominated by donor fluorescence.⁵ Acceptor fluorescence, on the other hand, is very weak. This is to be expected since the donor has a significantly stronger absorption at the laser excitation wavelength (532 nm) compared to the acceptor (see Figure 4.1 (d)). We conclude that there is no significant energy transfer from donor to acceptor without the cavity.

For the measurements performed with fully assembled Fabry-Pérot resonators, we generally observe rather complex patterns with multiple fluorescence peaks which change both in wavelength and intensity with increasing cavity length (see Figure 4.4).

To get a general impression of the fluorescence behaviour, we summed and normalized the obtained series of fluorescence spectra and compared them to the free space fluorescence peaks (see Figure 4.4 (b)).⁶ We can immediately deduce some useful information:

- If the dyes are enclosed inside the cavity, fluorescence is generally red-shifted compared to the “free space” fluorescence peaks (see Figure 4.4 and Appendix C). Literature dealing with the emission properties of strongly coupled J-aggregates [64, 128–134] suggests that for a single excitonic transition coupled to a single cavity mode (resulting in the formation of an upper and lower polariton⁷), the emission spectrum is dominated by the lower polariton and the reservoir of uncoupled molecules (exciton reservoir)⁸ [64, 109, 133]. The upper polariton, on the other hand, is usually not observed due to fast non-radiative decay towards the lower polariton and the exciton reservoir [129–131]. For a graphical representation of this situation, see Figure 4.5. Consequently, the observation of red-shifted fluorescence in our system

⁵Here, the donor fluorescence is slightly blue-shifted compared to the reference peak. This is due to absorption by the acceptor since donor fluorescence has to pass through the acceptor layer to be detected.

⁶The weak modulations of the cyan line from 700 to 800 nm in Figure 4.4 (b) are due to fringing effects caused by the coating of the CCD camera in the spectrometer, which become visible at high intensities.

⁷“Upper” and “lower” with respect to the energy of the uncoupled excitons.

⁸Literature shows that most organic molecules remain uncoupled [131–133, 135].

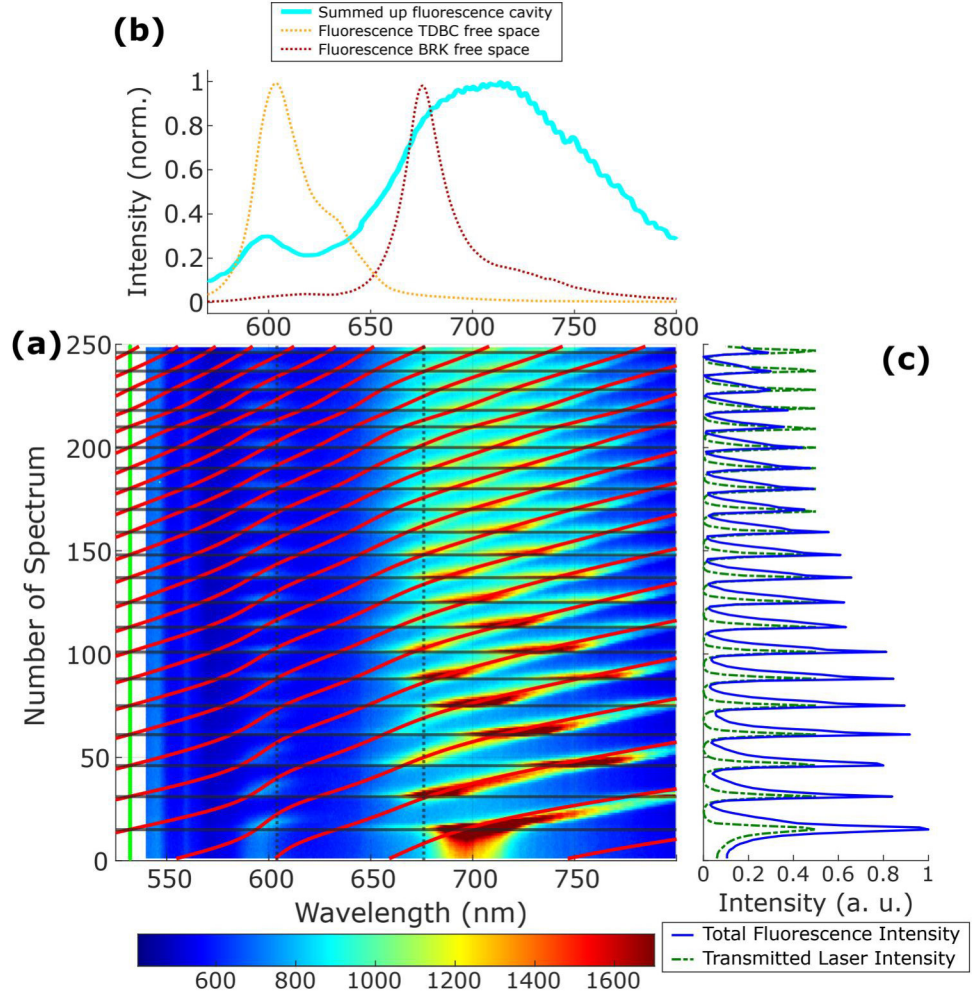


Figure 4.4: (a) False-color maps displaying fluorescence spectra for 2M-DA-I. Here, spectra were taken consecutively while stepwise increasing the cavity length. Vertical black dotted lines represent the free space TDBC and BRK fluorescence maxima (604 and 676 nm, respectively). The horizontal black lines mark maxima in the total fluorescence signal. The vertical green line at 532 nm represents the excitation laser wavelength. Red lines represent the polariton modes from our phenomenological Hamiltonian model $H_{coupled}$, which we fitted to the fluorescence maxima. (b) Fluorescence spectra for 2M-DA-I, summed and normalized, as solid cyan line. For comparison, we also show the free space fluorescence spectra of TDBC (orange dotted line) and BRK (red dotted line). The x -axis is aligned to the x -axis of (a). (c) Spectrally integrated fluorescence intensity (blue line) and transmitted laser intensity (green line) as a function of spectrum number for 2M-DA-I. One can clearly see the correlation between the transmitted laser intensity and the peak fluorescence intensities. The y -axis is aligned to the y -axis of (a). Adapted from [120].

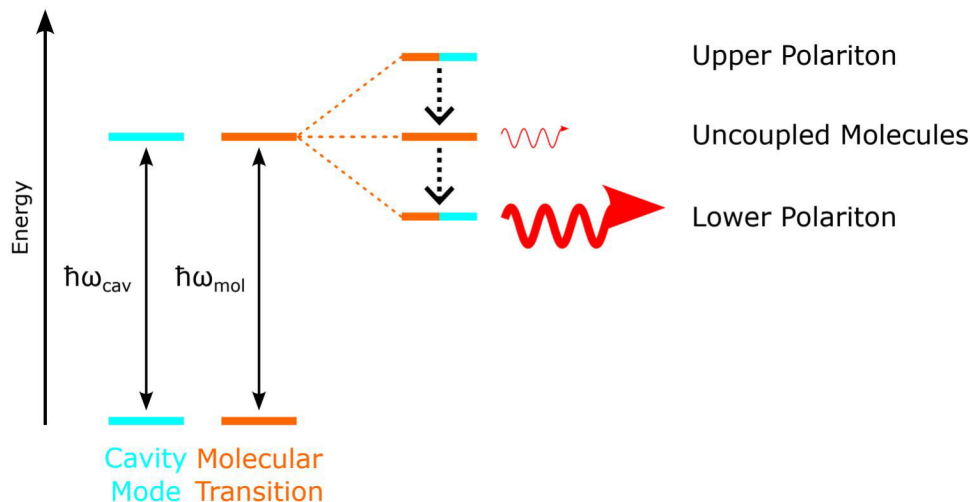


Figure 4.5: Expected fluorescence characteristics of a system consisting of a single cavity mode strongly coupled to a single molecular transition. The width of the red arrows corresponds to the expected fluorescence intensity.

coincides with the existing literature suggests that fluorescence originates from lower polaritons.

- When comparing the relative fluorescence intensities of donor and acceptor in 1M-DA-I and 2M-DA-I, acceptor fluorescence is significantly increased upon insertion of the lower Ag mirror. This implies that there is an efficient energy transfer process from donor to acceptor that only occurs under strong coupling conditions.
- Compared to the free space spectra the averaged fluorescence spectra, especially for the acceptor, are broadened significantly. This is due to the shifting of the individual polariton modes to the red with increasing cavity length.

4.4 Influence of the Excitation Efficiency on the Total Fluorescence Intensity

Next, to understand the measured fluorescence patterns in more detail, we investigated the modulations in the total fluorescence intensity. For this purpose, we had measured the transmitted laser intensity for each voltage step *via* a camera placed behind the top mirror of the cavity. Here, we expect peaks when the cavity is on resonance with the excitation laser (532 nm). We compared the obtained curves with the total (spectrally integrated) fluorescence intensity (as functions of spectrum number, see Figure 4.4 (c)).

We see that the peak positions are highly correlated. From a theoretical perspective, this is to be expected since the number of photons inside the resonator able to induce fluorescence is maximal if there is a cavity mode resonant with the excitation laser.

We conclude that the main factor which determines the fluorescence intensity is the excitation efficiency which depends on the resonance between the optical resonances of the cavity and the excitation laser. We observed maximum fluorescence when there was a cavity mode resonant with the excitation laser (at 532 nm).

It is noteworthy that one can use the information that maxima in the transmitted laser intensity / total fluorescence intensity can be used as a “spectroscopic ruler” for the mirror separation since these can be related to resonance conditions which are directly related to the cavity length (see Section 4.6 where we exploit this fact).

Another phenomenon apparent in the total fluorescence intensity curves is a continuous decrease. This is most likely due to photobleaching of the organic dyes. Additionally, we suspect that the coupling efficiency between excitation laser and cavity decreases as the k -vector distribution of resonant cavity modes narrows with increasing cavity length.

4.5 Energy Transfer Efficiency

For energy transfer processes, the donor-acceptor distance dependence is of particular interest. Therefore, we investigated changes in the energy transfer efficiency, manifested in the donor/acceptor fluorescence ratio, over the course of the measurements. Comparing individual fluorescence spectra, however, is rather difficult due to the total intensity fluctuations. To compensate, we performed a kind of moving average where we averaged the fluorescence spectra over two modulation periods (from a maximum in the total fluorescence to the maximum after the next one). We then calculated the BRK to TDBC intensity ratios,⁹ which remained approximately constant within 2M-DA-I and 2M-DA-II, respectively (corresponding Figures are provided in Appendix C). This confirms previous assumptions that PMET is independent of donor-acceptor separation [81, 107]. Differences between the two measurements are most likely due to inhomogeneities in the spin-coated films. Because we manually moved the upper mirror *via* the μ m-screws between 2M-DA-I and 2M-DA-II, we cannot guarantee that both measurements were performed at identical spatial positions.

To reiterate, PMET was present for all investigated cavity lengths (see Table 4.1) in 2M-DA-I and 2M-DA-II, which corresponds to donor-acceptor separations ranging from 0 to 11 μ m,¹⁰ with no visible breakdown in energy

⁹Here, we obtained a value of approximately 4.5 for 2M-DA-I and 3.8 for 2M-DA-II.

¹⁰A short discussion on the exact relationship between optical path length and the

efficiency / acceptor fluorescence.

4.6 Fitting of Polariton Modes to Fluorescence Maxima

We already proposed that fluorescence primarily originates from certain radiative polaritons. Therefore, we can gain much insight by fitting our theoretical model ($H_{coupled}$) to the fluorescence maxima. Unfortunately, we cannot simply carry over the results from the fits to the transmission measurements due to offsets of the achieved cavity distances. We identified two causes for these discrepancies:

1. Heating of the cavity by the white-light source during transmission measurements and
2. hysteresis of the piezo actuators.

Consequently, we developed a new fitting procedure which takes the coupling energy-cavity distance relationships derived from the transmission measurements but recalculates the cavity distances. For this purpose, we use the finding that maxima in the total fluorescence intensity correspond to resonances between the excitation laser and a cavity mode. Details are provided in Appendix C. Using this procedure, we achieve excellent agreement between calculated polariton modes and measured fluorescence maxima (see Figure 4.4 (a) for 2M-DA-I). This confirms that a majority of the observed fluorescence originates from certain radiative polaritons.

4.7 Modeling Polariton Populations and Fluorescence Intensities Using Rate Equations

With these results in mind, we now have a close look at the fluorescence spectra of donor-acceptor systems strongly coupled to the Fabry-Pérot resonator (2M-DA-I/II, see Figures 4.4 and 4.6 (b)). These generally show the following features: A small fluorescence peak is visible around 600 nm, while the vast majority of fluorescence intensity originates from a broad band around 680 - 780 nm, which is superimposed by sharp spikes. The spectral positions of these spikes are well described by the fitted polariton modes. We therefore conclude that fluorescence primarily originates from certain radiative polaritons, which are generally lower in energy than the uncoupled acceptor exciton. Especially at higher cavity lengths (which corresponds to a small free spectral range of the optical modes), the individual polariton peaks start to merge to form a broad fluorescence feature.

separation between donor and acceptor layer is provided in Appendix B.

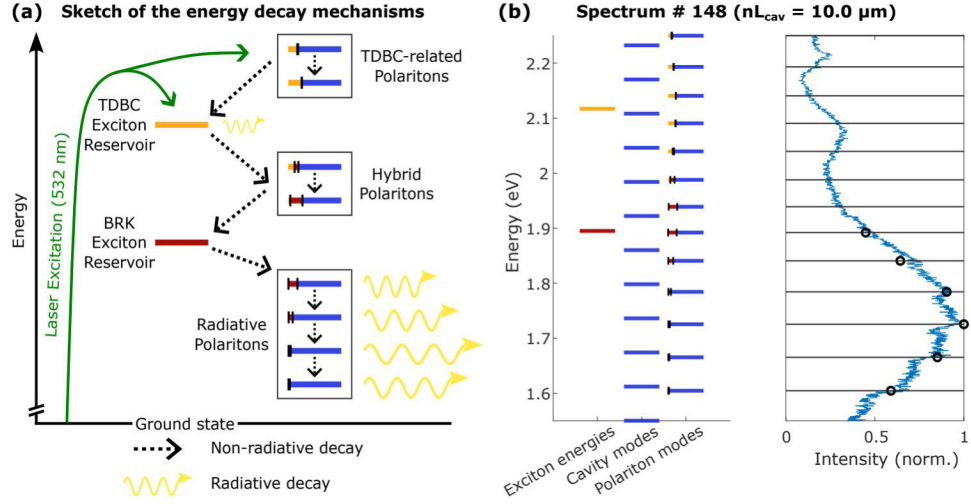


Figure 4.6: (a) Sketch of the energy decay mechanisms for the strongly coupled cavity containing donor and acceptor (2M-DA-I/II). (b) Fluorescence spectrum # 148 and corresponding best fit to $H_{coupled}$ from 2M-DA-II (for this spectrum, $nL_{cav} = 10 \mu m$). In the left panel of (b), we show the energies resulting from the fit of our model to the fluorescence false-color map. For reference, the left and middle columns show the uncoupled energies of TDBC (orange) and BRK (red) together with the uncoupled cavity modes (blue). In the right column the resulting polariton modes are displayed. Here, we indicate the respective light and matter fractions by the length of the differently colored sections of the lines for each polariton mode ($|\alpha^{TDBC}|^2$ in orange, $|\alpha^{BRK}|^2$ in red, and $|\alpha^{light}|^2$ in blue). In the right panel of (b), the corresponding fluorescence spectrum (# 148 from 2M-DA-II) is shown (with the same y -axis as the left panels, which corresponds to the wavelength range of 550-800 nm). Horizontal black lines correspond to the energies of the polariton modes. Black circles show the results for the polariton emission intensities from our rate equation model. The small peak at 2.2 eV is an artifact from the laser system. Adapted from [120].

The small peak at 600 nm, on the other hand, most likely originates from the reservoir of uncoupled donor molecules since the peak does not spectrally shift as would be expected for polaritons. Additionally, comparison of the 600 nm fluorescence feature with the other measurements supports this hypothesis: It strongly resembles 1M-DA-I, where the corresponding fluorescence originates from uncoupled TDBC, whereas it differs significantly from 2M-D, where the fluorescence originates from TDBC-polaritons.

We offer the following interpretation, which is also graphically depicted in Figure 4.6 (a): Excitation by the 532 nm laser should populate the reservoir of uncoupled donor molecules (most organic molecules remain uncoupled [131–133,135]), either *via* direct excitation (see absorption spectra of TCBC, Figure 4.1 (d)) or fast non-radiative decay from directly excited (resonant) polaritons (as reported previously [129–131]). Part of the population then decays radiatively, generating the small fluorescence peak at 600 nm.

Most of the population, however, decays non-radiatively, leading to a local minimum of the fluorescence intensity for energies between the two exciton reservoirs. Here, fast non-radiative decay processes towards the acceptor exciton reservoir most likely play an important role for suppressing radiative decay. Crucially, the presence of hybrid polaritons, which connect donor- and acceptor-related states, enables population transfer from the (initially excited) energy donor to the energy acceptor. For polaritons with lower energy than the acceptor exciton reservoir, fast non-radiative decay to an exciton reservoir is no longer available and the polaritons become radiative. This leads to the formation of the fluorescence feature between 680 - 780 nm, where the fluorescence intensity is maximal around 720 nm. For these radiative polaritons, we propose that the individual fluorescence intensities are the result of an increasing radiative rate due to an increasing photonic character (increasing $|\alpha^{light}|^2$) competing with a decrease in occupancy with lower polariton energy, respectively.

To further investigate this point, we modelled the fluorescence intensities of the radiative polaritons *via* the following set of rate equations:¹¹

$$\begin{aligned}
\frac{dN_1}{dt} &= \Phi - k_{nrad}|\alpha_1^{BRK}|^2 N_1 - k_{rad}|\alpha_1^{light}|^2 N_1 \\
\frac{dN_2}{dt} &= k_{nrad}|\alpha_1^{BRK}|^2 N_1 - k_{nrad}|\alpha_2^{BRK}|^2 N_2 - k_{rad}|\alpha_2^{light}|^2 N_2 \\
\frac{dN_3}{dt} &= k_{nrad}|\alpha_2^{BRK}|^2 N_2 - k_{nrad}|\alpha_3^{BRK}|^2 N_3 - k_{rad}|\alpha_3^{light}|^2 N_3 \\
&\vdots
\end{aligned} \tag{4.1}$$

Here, we describe the populations N_i of radiative polaritons $i = 1, 2, \dots$ with energy between 1.895 and 1.55 eV (within the broad fluorescence feature).

¹¹Similar approaches have been used in [104, 128, 129, 132–134].

For the highest polariton ($i = 1$), we assume a constant pumping rate Φ . Additionally, we assume two decay channels for each polariton:

1. Non-radiative decay $k_{nrad}|\alpha_i^{BRK}|^2 N_i$ to the next lower polariton due to exciton-exciton scattering. It is proportional to the exciton fraction of the polariton¹² and populates the next lower lying ($i + 1$) polariton.
2. Radiative decay $k_{rad}|\alpha_i^{light}|^2 N_i$ which is proportional to the light fraction of the polariton.

Furthermore, we assume that the rate constants k_{nrad} and k_{rad} are the same for all polaritons, respectively. For the following analysis, we chose to only focus on the relative (normalized) polariton fluorescence intensities due to the strong modulations of the total fluorescence intensity during measurements.

For an individual fluorescence spectrum, we can now use the results from the fit of $H_{coupled}$ to the false-color fluorescence maps to calculate the number of radiative polaritons and their respective Hopfield coefficients $|\alpha_i^{BRK}|^2$ and $|\alpha_i^{light}|^2$. We then assume an arbitrary pumping rate Φ and solve for the polariton populations N_i under steady-state conditions $\frac{dN_i}{dt} = 0$. Fluorescence intensities of the polaritons are calculated *via* $I_i = N_i k_{rad} |\alpha_i^{light}|^2$ and normalized. Results can then be plotted on top of the experimental fluorescence spectrum, as shown in Figure 4.6 (b).

The only free parameter is the ratio between non-radiative decay constant and radiative decay constant $\frac{k_{nrad}}{k_{rad}}$, which determines the spectral position of the fluorescence intensity maximum. We tested different ratios and obtained the best agreement with the experimental fluorescence spectra of 2M-DA-II for $\frac{k_{nrad}}{k_{rad}} = 40$. This agrees rather well with published ratios which are between 2 [128] and 100 [64].

4.8 Summary and Conclusion

To summarize the results presented in this Chapter, we investigated PMET in a tunable Fabry-Pérot resonator with mirror separations between 1.5 and 12 μm . Evaluation of white-light transmission measurements revealed that we were operating in the strong coupling regime and that hybrid polaritons, which contain exciton contributions from both donor and acceptor, were present throughout.

We offer the following mechanistic explanation for PMET: Fast non-radiative decay towards the exciton reservoirs in the presence of hybrid polaritons enables efficient energy transfer from (initially excited) donor-related to acceptor-related states. Radiative emission occurs from polaritons with lower energy than the acceptor exciton reservoir. The respective

¹²For radiative polaritons, this equals the BRK fraction. The TDBC fraction is negligible.

relative intensities result from the interplay between the photonic character of the polariton, which increases radiative emission, and the depletion of occupancy with decreasing energy. Therefore, the presence of hybrid polaritons and a large ratio between non-radiative and radiative decay constant are most likely crucial for enabling PMET.

Efficient PMET was observed for all investigated distances (0 up to 11 μm separation between donor and acceptor layer) with an efficiency seemingly constant within the same measurement. This result is quite striking, signifying a substantial increase in the maximum reported donor-acceptor separation for PMET (which was previously 2 μm [105]) and corroborates the assumption that PMET is independent of donor-acceptor distance [81, 107]. Since we did not observe a breakdown of PMET during our measurements, it remains unclear where the (practically realizable) upper limit for donor-acceptor distance lies.

Now, one may ask how PMET related to other energy transfer mechanisms like FRET.¹³ We indeed found an analogy: Both processes are only possible if there is an energetic overlap between donor and acceptor (a non-zero overlap integral for FRET and the presence of hybrid polaritons for PMET). The main difference is the donor-acceptor distance dependence: FRET is strongly distance-dependent, whereas PMET seems to be distance-independent.

In this context, one may also ask if the term “energy transfer” is an appropriate characterization of PMET. For “conventional” energy transfer processes like FRET, excitation energy is transferred from a spatially localized donor to a spatially localized acceptor. For PMET, where energy flows between polaritons which are delocalized within the optical cavity, one could argue that no spatial transfer of energy takes place. Therefore, a more appropriate description of PMET might be “spectral engineering of hybrid light-matter systems”. Basically, appropriate naming of the phenomenon depends on the aspect the researcher wants to stress. We decided to stick with “Polariton-Mediated Energy Transfer” since it was already established in the literature.

¹³Förster Resonance Energy Transfer, see Appendix A

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Appendix A

Förster Resonance Energy Transfer (FRET)

A.1 Essential Equations and Historical Context

Arguably the most important energy transfer mechanism for organic molecules is Förster Resonance Energy Transfer (FRET),¹ where an excited donor D transfers its energy to an unexcited, red-shifted acceptor A *via* dipole-dipole interaction. The effect was first successfully described by Theodor Förster in the late 1940s [136–140] (for some nice accounts on the historical development of FRET theory, see [141–143]; for a viewpoint article on Förster’s life, see [144, 145]). His main results are summarized below. For the rate of energy transfer, we have

$$k_{ET} = \frac{1}{\tau_D^0} \left(\frac{R_0}{R} \right)^6 \quad (\text{A.1})$$

and for the efficiency of energy transfer, we have

$$E = \frac{k_{ET}}{k_{ET} + \frac{1}{\tau_D^0}} = \frac{1}{\left(\frac{R}{R_0} \right)^6 + 1} \quad (\text{A.2})$$

Here, τ_D^0 is the fluorescence lifetime of the donor in the absence of the acceptor, R is the distance between donor and acceptor and R_0 is the so-called Förster-radius, which characterizes the length scale for FRET in a given system (for $R = R_0$, $E = 50\%$). It is defined as²

$$R_0^6 = \frac{9000 \ln 10}{128\pi^5} \frac{\kappa^2 \Phi_D^0}{n^4 N_A} J_\nu \quad (\text{A.3})$$

¹Sometimes also called Fluorescence Resonance Energy Transfer, Resonance Energy Transfer (RET) or Electronic Energy Transfer (EET).

²To get the correct numerical factor, one has to explicitly consider the units of the overlap integral J and the Avogadro constant. For clarification, see [146]. Here, I assumed $[J] = \text{M}^{-1}\text{cm}^{-1}$ and $[N_A] = \text{mol}^{-1}$.

Here, Φ_D^0 is the quantum efficiency of the donor in the absence of the acceptor, n is the (average) refractive index of the medium and N_A is the Avogadro constant. J_ν is the spectral overlap integral between the emission of the donor and the absorption of the acceptor:

$$J_\nu = \int_0^\infty f_{norm}^D(\nu) \varepsilon^A(\nu) \frac{d\nu}{\nu^4} \quad (\text{A.4})$$

Here, f_{norm}^D is the normalized emission spectrum³ of the donor and ε^A is the extinction coefficient of the acceptor, both expressed as functions of the wavenumber ν . κ is an orientation factor defined as

$$\kappa = \cos \theta_{DA} - 3 \cos \theta_D \cos \theta_A \quad (\text{A.5})$$

where θ_{DA} is the angle between the transition moment vectors of donor and acceptor and θ_D and θ_A are the angles between these respective vectors and the vector connecting donor and acceptor. κ^2 can take on values between 0 and 4. For random orientations / freely rotating molecules, $\kappa^2 = \frac{2}{3}$.

From these equations, we can derive the main features of FRET:

- The molecular properties governing FRET are the spectral characteristics of the molecules (emission spectrum of the donor and absorption spectrum of the acceptor) and their relative orientation.
- FRET strongly depends on the donor-acceptor separation.
- Experimentally, FRET manifests itself in a reduced fluorescence lifetime of the donor (since an additional non-radiative decay channel emerges) and an increase in acceptor emission.
- In practice, efficient FRET usually occurs for donor-acceptor separations of approximately 1-10 nm. This enables scientists to utilize FRET for the study of protein-protein interactions, where the occurrence of FRET between fluorescent proteins is used as an indicator for interaction.

For his quantum-mechanical derivation [137] Förster used theories developed by Dirac [147, 148], which nowadays would be identified as time-dependent quantum perturbation theory and Fermi's golden rule [149].

A.2 Derivation of FRET within molecular QED

In 1989, Andrews showed that FRET can be incorporated into a unified theory within molecular quantum electrodynamics (QED), for which FRET

³Meaning that $\int_0^\infty f_{norm}^D(\nu) d\nu = 1$.

and radiative energy transfer⁴ are the short-range and long-range approximations, respectively [150]. In this section, I will provide a short summary of the respective derivation. For more detailed treatments, see [151–155].

As a starting point, the QED Hamiltonian for a system containing a single donor molecule (D) and a single acceptor molecule (A) coupled to the radiation field can be written as:

$$H = H_{mol}^D + H_{mol}^A + H_{rad} + H_{int}^D + H_{int}^A \quad (\text{A.6})$$

Here, $H_{mol}^{D/A}$ are the Hamiltonians of the unperturbed molecules and H_{rad} is the Hamiltonian of the radiation field. Consequently, the system states are characterized by the state of the donor and the acceptor (in the simplest case, donor and acceptor are approximated as a two-level system with a ground (gr) and an excited (ex) state) as well as the photon numbers of the optical modes (characterized by a wavevector $\vec{k}$ and a polarization ξ).

The key terms for describing energy transfer are the interaction terms $H_{int}^{D/A}$, which describe the interaction between the respective molecule and the electromagnetic field. These are perturbative in nature because the light-molecule interactions are generally weak compared to the Coulombic energies within the molecules. In the dipole approximation, the interaction between the molecules and the electromagnetic field is determined by the transition dipole moment of the donor (acceptor) times the electric field. Expressed *via* the corresponding quantum-mechanical operators, we have

$$H_{int} = H_{int}^D + H_{int}^A = -\varepsilon_0^{-1} \vec{\mu}^D \cdot \vec{d}^\perp(\vec{R}_D) - \varepsilon_0^{-1} \vec{\mu}^A \cdot \vec{d}^\perp(\vec{R}_A) \quad (\text{A.7})$$

Here, ε_0 is the vacuum permittivity and $\vec{\mu}^{D/A}$ are the electric-dipole operators of the donor / acceptor, which act on matter states. $\vec{d}^\perp(\vec{R})$, evaluated at the position of the donor $\vec{R}_D$ or the acceptor $\vec{R}_A$, is the displacement electric field operator, which acts on photon number states. It can be written as

$$\vec{d}^\perp(\vec{R}) = i \sum_{\vec{k}, \xi} \sqrt{\frac{\hbar c k \varepsilon_0}{2V}} \left\{ \vec{e}^{(\xi)}(\vec{k}) a^{(\xi)}(\vec{k}) e^{i\vec{k} \cdot \vec{R}} - \vec{e}^{*(\xi)}(\vec{k}) a^{\dagger(\xi)}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}} \right\} \quad (\text{A.8})$$

Here, i is the imaginary unit, $\hbar$ is the reduced Planck constant and c is the vacuum speed of light. The sum is over all photon modes, which are characterized by a wavevector $\vec{k}$ and a polarization vector $\vec{e}^{(\xi)}(\vec{k})$. * marks the complex conjugate. $a^{(\xi)}(\vec{k})$ and $a^{\dagger(\xi)}(\vec{k})$ are the annihilation and creation operators for a photon of wavevector $\vec{k}$ and polarization ξ . V is an arbitrary quantization volume.⁵

⁴Emission and reabsorption of a photon.

⁵The volume of the quantization box necessary to define the field operators in QED.

The time-dependent perturbation series for the probability amplitude / matrix element for the transition from an initial (i) to a final (f) state M_{fi} reads

$$M_{fi} = \langle f | H_{int} | i \rangle + \sum_r \frac{\langle f | H_{int} | r \rangle \langle r | H_{int} | i \rangle}{E_i - E_r} + \dots \quad (\text{A.9})$$

The first term of the perturbation series describes emission and absorption of photons. For the process we are interested in, namely the transition

$$D^* + A \rightarrow D + A^* \\ |D^{ex}, A^{gr}; 0\rangle_i \rightarrow |D^{gr}, A^{ex}; 0\rangle_f$$

(* denotes that the molecule is in the excited state), the leading term is the second-order term. Here, the sum is over all system states except i and f . However, only two states ($|D^{gr}, A^{gr}; 1\rangle$ and $|D^{ex}, A^{ex}; 1\rangle$) generate matrix elements $\neq 0$.

Here, a more intuitive explanation of the process arises: The energy transfer process is mediated *via* virtual photons, represented by the two intermediate states, which are created / annihilated at the donor / acceptor, accompanied by a transition $gr \rightarrow ex$ / $ex \rightarrow gr$.

Now, one has to calculate the four matrix elements and evaluate the resulting expressions, which includes computing the sum over all polarizations and k -vectors [156, 157]. The end result is

$$M_{fi} = \mu_i^D V_{ij}(k, R) \mu_j^A \quad (\text{A.10})$$

which is expressed *via* the transition dipole moments of the molecules

$$\mu^D = \langle D^{gr} | \vec{\mu} | D^{ex} \rangle \\ \mu^A = \langle A^{ex} | \vec{\mu} | A^{gr} \rangle \quad (\text{A.11})$$

and the so-called coupling tensor

$$V_{ij}(k, \vec{R}) = \frac{e^{ikR}}{4\pi\epsilon_0 R^3} \left\{ (1 - ikR) (\delta_{ij} - 3\hat{R}_i \hat{R}_j) - (kR)^2 (\delta_{ij} - \hat{R}_i \hat{R}_j) \right\} \quad (\text{A.12})$$

To connect this result to experimentally accessible quantities, one can, in the simplest case, use Fermi's golden rule⁶ and perform a rotational average to obtain the energy transfer rate Γ :

$$\Gamma \propto (\mu^D)^2 (\mu^A)^2 \frac{1}{(4\pi\epsilon_0 R^3)^2} \left[3 + (kR)^2 + (kR)^4 \right] \quad (\text{A.13})$$

Notice the following features:

⁶ $\Gamma = \frac{2\pi}{\hbar} |M_{fi}|^2 \rho_f$, where ρ_f is the density of acceptor final states.

- The spectral characteristics of donor and acceptor enter into the transfer rate *via* the transition dipole moments.
- The result can be decomposed into three regimes with different distance-dependences (R^{-6} , R^{-4} and R^{-2}).
- We see the R^{-6} distance dependence for $R \rightarrow 0$ and the R^{-2} distance dependence for $R \rightarrow \infty$, recovering Förster's result at small distances and radiative energy transfer at large distances.

Upon performing the exact calculations, including the connection between the transition dipole moments and the optical spectra and explicitly considering the orientation dependence, one can recover Förster's results exactly at small distances ($R \lesssim 100$ nm) [150, 151].

Appendix B

**First Publication: Global
Spectral Analysis of
Polaritonic Coupling of
Multiple Organic Dyes to a
Tunable Fabry-Pérot
Resonator Operating with
Mirror Separations up to 10
 μm**

Global Spectral Analysis of Polaritonic Coupling of Multiple Organic Dyes to a Tunable Fabry-Pérot Resonator Operating with Mirror Separations up to 10 μm

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We study strong optical coupling and the formation of hybrid polaritons by a donor-acceptor pair of J-aggregated dyes separated by up to 11 μm in a tunable Fabry-Pérot resonator. Fitting a phenomenological Hamiltonian to the white light transmission spectra of different cavity-J-aggregate-configurations, for which several hundred spectra were recorded

sequentially as function of cavity length, allows us to determine coupling energies as a function of the effective cavity distances. The theoretical analysis shows that certain hybrid polaritons contain contributions from both dyes, making this system a promising platform for polariton-mediated energy transfer at very large distances.

Introduction

After the first demonstration of strong coupling in organic molecules embedded in an optical resonator, which was achieved by Lidzey *et al.* in 1998,^[1] hybrid light-matter states called (cavity) polaritons have created considerable attention since they possess new characteristics that are not found in either the original exciton or the optical mode. As a result, material properties such as energy transfer,^[2–9] transport processes,^[10–15] or chemical reactivity,^[16–21] may undergo significant changes.^[22–27] These states can emerge if an optically active material, characterized by its excitonic transitions, is enclosed in an optical Fabry-Pérot (FP) microcavity. If the energy exchange between the excitons and the optical modes of the microcavity is faster than competing dissipation processes, *i. e.* is reversible, the system is said to be strongly coupled and new eigenstates are formed.

In previous works, cavities were typically constructed by successive thin film preparation steps (substrate – Ag mirror – active layer – spacer layer – active layer – Ag mirror), resulting in rigid FP resonators with fixed distances between the two mirrors. For such systems, the energy of the cavity modes can be tuned by varying the incidence angle of the radiation and performing angle-resolved measurements, which exploit the parabolic dispersion relation $E(k)$ of the cavity modes.^[28] We, on the other hand, use an open FP resonator with tunable mirror

separation.^[29–38] This enables us to increase the mirror distance continuously by several μm during a single measurement and to investigate the system's behaviour as a function of cavity length at mirror separations exceeding 10 μm , which is much larger than previously reported.

If several different excitons are coupled to the same microcavity, the resulting hybridisation has been shown to enable "Polariton-mediated energy transfer" (PMET)^[2–6] at much larger distances (up to 2 μm ^[6]) than conceivable *via* dipole-dipole interactions (Förster^[39]) or electronic exchange (Dexter^[40]), which are inherently short-ranged. For the mechanistic explanation of PMET, previous authors stressed the importance of "hybrid polaritons"^[2–6] which contain significant contributions from both excitonic constituents.

In this work, we study the formation of strong coupling and hybrid polaritons by a donor-acceptor pair of J-aggregated dyes separated by up to 11 μm in a tunable FP resonator. Thin films containing the well-known J-aggregates TDBC as energy donor and BRK as energy acceptor were deposited on top of the adjacent mirrors (film thickness 500–600 nm, see SI), as sketched in Figure 1(a). J-aggregates are organic molecules with very favourable optical properties due to supramolecular self-organization,^[41] such as intense and narrow J-bands and a small Stokes shift as shown in Figure 1(b) by the TDBC and BRK absorption and emission spectra, making them ideal for achieving strong coupling at room temperature.^[42] We present experimental white light transmission spectra as a function of the mirror separation up to 12 μm for different cavity-J-aggregate configurations, which were successfully fitted by a phenomenological Hamiltonian, which allowed us to determine the coupling energies as a function of the effective optical cavity length.

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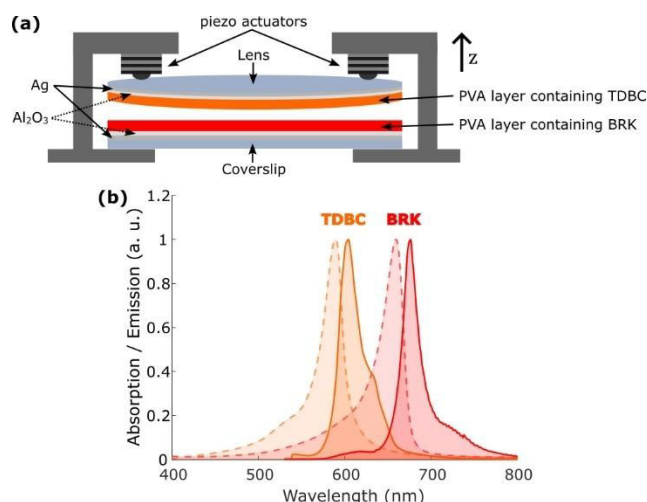


Figure 1. (a) Sketch of the tunable FP resonator. (b) Free space absorption (dashed lines) and emission spectra (solid lines) of the two J-aggregates TDBC (orange) and BRK (red).

Results and Discussion

Transmission Measurements

We prepared three different cavity-J-aggregate-configurations: the donor TDBC on the top mirror (2M-D), the acceptor BRK on the bottom mirror (2M-A), and a donor-acceptor configuration with TDBC on the top mirror and at the same time BRK on the bottom mirror (2M-DA-I). To ensure comparability we used the

same coated mirrors for all three configurations. After setting up a certain configuration, we brought the top mirror into contact with the bottom mirror. Then, we used the piezo actuators to stepwise move the upper mirror in the z-direction by gradually decreasing the applied voltage, which increased the cavity distance, until the minimum voltage was reached giving a mirror separation of about 5 μm . Following each voltage step, we recorded a transmission spectrum. For the configuration involving both J-aggregates (2M-DA-I), we moved the upper mirror to the approximate endpoint of the first measurement using μm -screws to increase the starting cavity distance. We then performed a second scan, moving the piezo actuators over the whole voltage span a second time at larger distances of approximately 5–10 μm (2M-DA-II).

In Figure 2, we present the series of transmission spectra plotted as false-color maps. Here we only show smaller sections for better visibility. The complete false-color maps are provided in the SI. For strongly coupled J-aggregate thin films, usually only a small fraction of the aggregates couples to the light field while most remain uncoupled.^[43–46] Hence, the transmission around the present excitonic transitions (TDBC and/or BRK) is very low, which is due to absorption by uncoupled molecules. The absolute intensities of the transmission peaks change with wavelength. This is mainly due to the spectrum of the used white light source, which we did not correct for.

From the progression of the transmission maxima, it is already evident that we are operating in the strong coupling regime since the transmission maxima do not follow straight lines as would be expected for an uncoupled cavity (see

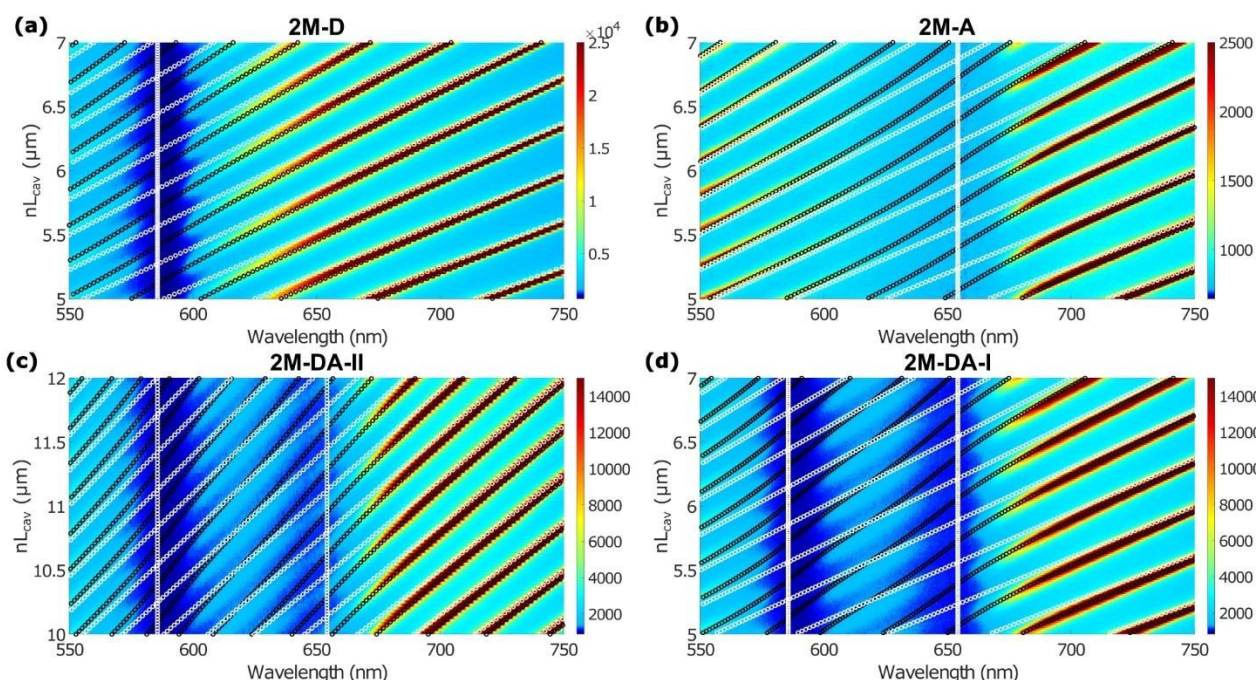


Figure 2. Transmission spectra plotted as false-color maps for different cavity-J-aggregate-configurations: Only TDBC in (a), only BRK in (b), both TDBC and BRK in (c) and (d). Black circles show the fits to H_{coupled} . For comparison, white circles show the corresponding uncoupled excitons and cavity modes. The spectra are plotted against the cavity distances from the fits. Here, we only show cutouts of the obtained maps for better visibility. Maps showing the entire cavity tuning range are provided in the SI.

Equation (1) and Figure S2) but show clear bending near the excitonic transitions.

Theoretical Model

The spectral evolution of the transmission spectra as a function of the cavity length can be interpreted in terms of a theoretical model based on strong exciton-photon coupling. For this purpose, we have developed a procedure to fit the experimentally obtained transmission maxima by the phenomenological Hamiltonian outlined below. The results from the fits are plotted as black circles in Figure 2. The phenomenological Hamiltonian contains the exciton energies of the J-aggregates E_{TDBC} and E_{BRK} as well as the photon energies of the cavity modes as diagonal elements, determined via

$$E_{cav,m} = m \frac{\pi \hbar c}{nL_{cav}} \text{ with } m = 1, 2, 3, \dots, \quad (1)$$

where m is the mode number, $\hbar$ is the reduced Planck's constant, c is the vacuum speed of light, and nL_{cav} is the optical path length. The exciton-photon coupling energies $\hbar g_{TDBC}$ and $\hbar g_{BRK}$ which correspond to one half of the Rabi splitting energy are introduced as off-diagonal elements. For the exciton energies we choose $E_{TDBC} = 2.117$ eV (corresponding to 585.59 nm) and $E_{BRK} = 1.895$ eV (corresponding to 654.29 nm) which are the absorption maxima of TDBC and BRK, determined from Lorentzian fits to the free space absorption spectra (see Figure 1(b)). We chose these values since it was demonstrated that for systems incorporating porphyrins for which absorption and emission are clearly distinguishable (large Stokes shift), strong coupling was achieved with the absorption band.^[1,47] The optical path length and the relevant coupling energies are treated as parameters, which are fitted to the experimental data.

The different energies are arranged in a Hamiltonian matrix (labelled " $H_{coupled}$ ", left most matrix in Equation (2)). The energies of the resulting polariton modes are then simply the eigenvalues of this matrix.

The hybrid light-matter states are characterized by coefficients, which indicate the fraction or relative contribution of the cavity modes and the excitons (sometimes called "Hopfield coefficients"). To obtain these coefficients, we explicitly write down the eigenvalue equation for $H_{coupled}$:

$$\begin{pmatrix} E_{TDBC} & 0 & \hbar g_{TDBC} & \hbar g_{TDBC} & \hbar g_{TDBC} \\ 0 & E_{BRK} & \hbar g_{BRK} & \hbar g_{BRK} & \dots & \hbar g_{BRK} \\ \hbar g_{TDBC} & \hbar g_{BRK} & E_{cav,1} & 0 & 0 \\ \hbar g_{TDBC} & \hbar g_{BRK} & 0 & E_{cav,2} & 0 \\ \vdots & & & \ddots & 0 \\ \hbar g_{TDBC} & \hbar g_{BRK} & 0 & 0 & 0 & E_{cav,N} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \\ \vdots \\ \alpha_{N+2} \end{pmatrix} = E_{pol} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \\ \vdots \\ \alpha_{N+2} \end{pmatrix} \quad (2)$$

Here, the vector with entries α_i is the eigenvector and E_{pol} is the eigenvalue, which corresponds to the energy of a certain polariton mode. N is the number of considered cavity modes. By solving this equation, one obtains $N+2$ eigenvalues E_{pol} with associated eigenvectors (α_i).

For the uncoupled system, $\hbar g_{TDBC} = \hbar g_{BRK} = 0$ and $H_{coupled}$ becomes a diagonal matrix. Consequently, the eigenvalues are just the diagonal elements E_{TDBC} , E_{BRK} , $E_{cav,1}$, ..., $E_{cav,N}$ and the eigenvectors are just the trivial base vectors. Therefore, each α_i directly relates to an eigenvector in the uncoupled basis and can be associated with a certain exciton transition or cavity mode: $\alpha_1 \leftrightarrow E_{TDBC}$, $\alpha_2 \leftrightarrow E_{BRK}$, $\alpha_3 \leftrightarrow E_{cav,1}$, $\alpha_4 \leftrightarrow E_{cav,2}$, ...

The eigenvectors are normalized such that the absolute values squared $|\alpha_i|^2$ are a good measure for the contribution of the different constituents of the polariton ($0 \leq |\alpha_i|^2 \leq 1$ and $\sum_i |\alpha_i|^2 = 1$).

In our system, we have two exciton parts (the two J-aggregates TDBC and BRK), which are characterized by the first two entries of the eigenvectors:

$$\begin{aligned} |\alpha^{TDBC}|^2 &= |\alpha_1|^2 \\ |\alpha^{BRK}|^2 &= |\alpha_2|^2 \end{aligned} \quad (3)$$

For the light part, we look at the remaining vector elements and sum them up for simplicity:

$$|\alpha^{light}|^2 = \sum_{i=3}^{N+2} |\alpha_i|^2 \quad (4)$$

Fitting Procedure

To fit the transmission spectra by the phenomenological Hamiltonian, we have developed a fitting procedure in MATLAB (details are provided in the SI) which allows us to fit the entire series of transmission spectra as a function of increasing mirror separation with the effective optical path lengths of the cavity and the coupling energies as fit parameters. The resulting polariton modes are shown as black circles in Figure 2. The cavity lengths increase slightly faster than linear over the course of the entire series of spectra for all investigated cavity configurations (see Figure S4) while the coupling energies $\hbar g$ decrease with increasing cavity length (see Figure S5) as expected for a Fabry-Pérot resonator with cavity volume V .^[48,49]

$$\hbar g = \sqrt{\frac{\hbar \omega}{2\epsilon_0 V}} \mu. \quad (5)$$

Here, μ is the transition dipole moment of the embedded material, ω is the angular frequency of the cavity mode, and ϵ_0 is the vacuum permittivity. Assuming $V \propto nL_{cav}$, we expect a decrease of the coupling energy as $\hbar g = A \cdot (nL_{cav})^{-1/2}$, where A is a material-dependent constant which we treated as a fit parameter. By adjusting A , we can describe the obtained coupling energies with very good agreement for distances

> 3.5 μm . Small systematic deviations we observe in the obtained curves (Figure S5) are discussed in the SI. The values for the coupling strength and for the optical path lengths obtained from the fits are listed in Table 1.

In Table 1, we also calculated the distances between the J-aggregate containing layers for 2M-DA-I and 2M-DA-II by assuming that the mirrors touched at the start of 2M-DA-I (for further discussion on this point, see the SI).

There is some debate in the literature regarding the appropriate Hamiltonian for strongly coupled multimode cavities. Some works^[6,50] recommend the “decoupled” Hamiltonian $H_{\text{decoupled}}$ where each cavity mode is coupled to the excitons independently (see SI). Alternatively, a transition between $H_{\text{decoupled}}$ and the “coupled” Hamiltonian H_{coupled} (left most matrix in Equation (2)) where the excitons couple with each cavity mode simultaneously is proposed depending on the oscillator strength of the active layer.^[51,52]

Therefore, we have fitted both Hamiltonians to the transmission data using the procedure outlined above and found significantly better agreement for H_{coupled} (more details are provided in the SI). This result is consistent with the findings of Georgiou *et al.* who have investigated strong coupling of spin coated thin films containing TDBC in an optical microcavity.^[51] They observed for low-concentration TDBC solutions (1 and 2 wt%) that H_{coupled} matched the experimental data better, while for high-concentration TDBC solutions (4 and 6 wt%) $H_{\text{decoupled}}$ matched the experimental data better.

Hybrid Polaritons

Using the fit results along with the mathematics outlined above (Equations (3) and (4)), we can calculate the light-, TDBC- and BRK-contributions for the obtained polariton modes. Therefore, we can investigate if there are hybrid polaritons present in the investigated system. We found for most cases that there is at least one hybrid polariton with energy in between the TDBC and BRK exciton energies with at least two percent excitonic contribution from TDBC and BRK. The only exceptions were configurations for which no uncoupled cavity mode with energy in between the excitons was present. This happened occasionally at low cavity distances, where only few modes are present in the observed spectral region.

In Figure 3 we plot the resulting polariton energy levels for an effective cavity length of $nL_{\text{cav}} = 10 \mu\text{m}$ and for the coupling

energies $\hbar g_{\text{TDBC}} = 35 \text{ meV}$ and $\hbar g_{\text{BRK}} = 35 \text{ meV}$ as a representative example. As a reference, we plot the exciton energies in the left column and the energies of the uncoupled cavity modes in the center column. In the right column, we show the polariton energies of the coupled system. For each polariton, we indicate the fractions of the three different constituents (TDBC, BRK and light), showing that the two polaritons marked with black arrows are indeed hybrid polaritons.

Conclusions

We have investigated the individual and simultaneous strong optical coupling of the two J-aggregates TDBC and BRK to a tunable multimode FP resonator with several micrometers mirror separation.

By fitting a phenomenological Hamiltonian to the transmission spectra, we are able to determine the coupling energies as a function of the optical path lengths between the mirrors. We find that H_{coupled} describes our experimental data better than $H_{\text{decoupled}}$. For large cavity distances, the coupling energies decrease as $\hbar g \propto (nL_{\text{cav}})^{-1/2}$ with increasing cavity length in excellent agreement with the expected theoretical behaviour.

The values for the coupling energies are consistent with previous studies, which report coupling energies ranging from 20–160 meV.^[2–4,6,51]

Simultaneous strong coupling paves the road for polariton-mediated energy transfer, which has important possible applications *e.g.* in solar energy conversion systems and optoelectronic integration. The large mirror separations in our system shows that tunable microcavities could be integrated into microfluidic systems which could be particularly interesting for combining polaritonic chemistry with microchemistry.

Supporting Information Summary

The authors have cited additional references within the Supporting Information.^[53–57]

Table 1. Results for the fit parameters (“coupling strength” A and optical path length nL_{cav}) from the best fits of H_{coupled} to the transmission spectra. The coupling energy $\hbar g$ is related to A via $\hbar g = A \bullet (nL_{\text{cav}})^{-1/2}$. In the last column, we also indicate the distance between the two J-aggregate-containing layers (by assuming that the layers touched at the start of the measurement).

	Coupling strength A (eV (nm) ^{-1/2}) for $\hbar g_{\text{TDBC}}$	Coupling strength A (eV (nm) ^{-1/2}) for $\hbar g_{\text{BRK}}$	Range of nL_{cav} (μm) during measurement	Distance between J-aggregates (μm)
2M-D	5.5	–	2.456 ... 7.850	–
2M-A	–	4.0	1.138 ... 7.040	–
2M-DA-I	3.5	3.5	1.433 ... 7.210	0 ... 5.8
2M-DA-II	3.5	3.5	7.260 ... 12.800	5.8 ... 11.4

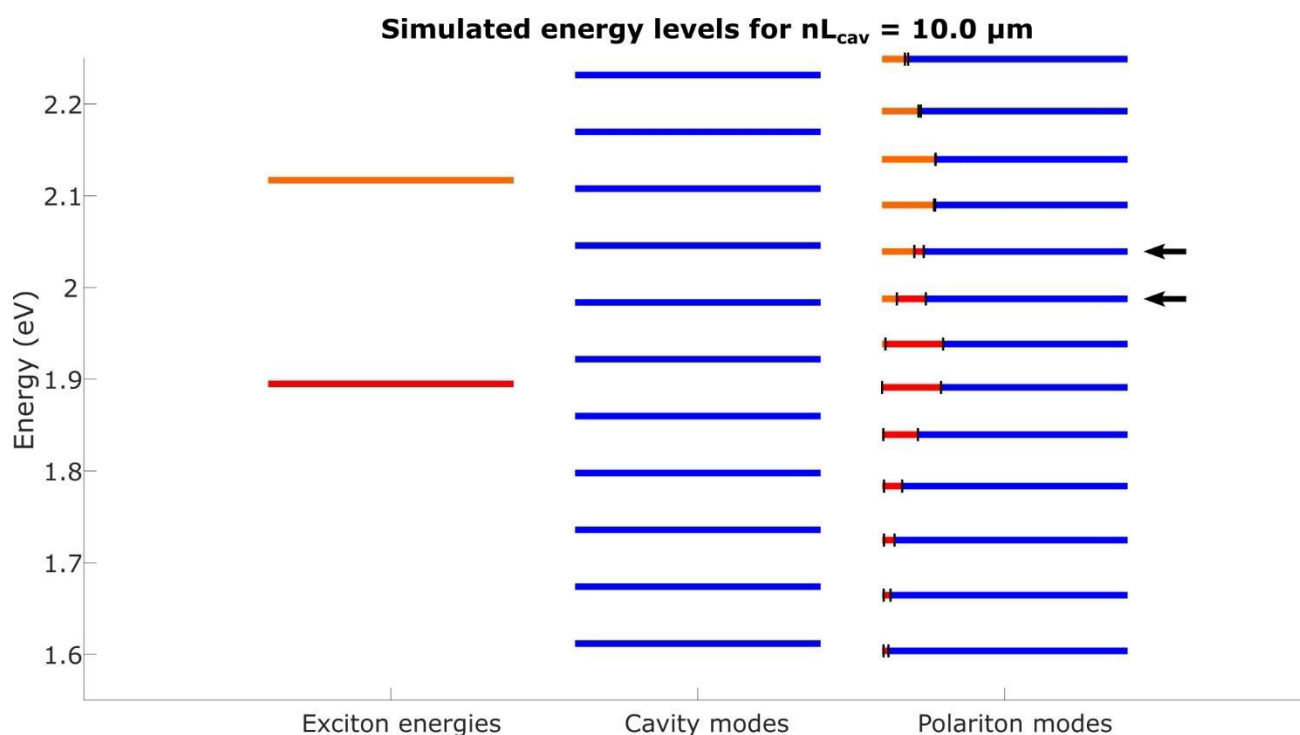


Figure 3. Different energies calculated from H_{coupled} for a cavity with $nL_{\text{cav}} = 10 \mu\text{m}$: Uncoupled exciton energies (left column; TDBC in orange and BRK in red), uncoupled cavity modes (middle column) and polariton modes for $\hbar g_{\text{TDBC}} = 35 \text{ meV}$ and $\hbar g_{\text{BRK}} = 35 \text{ meV}$ (right column). For the polariton modes we indicate the respective light and matter fractions by the length of the differently colored sections of the lines ($|\alpha^{\text{TDBC}}|^2$ in orange, $|\alpha^{\text{BRK}}|^2$ in red and $|\alpha^{\text{light}}|^2$ in blue). Black arrows mark hybrid polaritons, for which significant contributions from both TDBC and BRK are present.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Donor-acceptor systems • Fabry-Pérot resonator • J-aggregate • Photophysics • Polariton

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Supporting Information

Global Spectral Analysis of Polaritonic Coupling of Multiple Organic Dyes to a Tunable Fabry-Pérot Resonator Operating with Mirror Separations up to 10 μm

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Author contributions

JK and CK conceived the experiment. MM performed all measurements. MM and CK analyzed the data, including development of the fitting procedure. CK wrote the manuscript with inputs from all authors. AJM supervised the project, contributed to the discussion of the results, reviewed and edited the manuscript.

Experimental section

Preparation of J-aggregate stock solutions: 1 wt% of the J-aggregate TDBC (5,6-dichloro-2-[[5,6-dichloro-1-ethyl-3-(4-sulphobutyl)benzimidazol-2-ylidene]propenyl]-1-ethyl-3-(4-sulphobutyl)benzimidazolium hydroxide) [FEW Chemicals] or BRK (1-(3-Sulfopropyl)-2-(2-[[1-(3-sulfopropyl)naphtho[1,2-d]thiazol-2(1H)-ylidene]methyl]-1-butenyl)naphtha[1,2-d]thiazoliumhydroxide) [ORGANICA Feinchemie] and 3 wt% of Poly(vinyl alcohol) (PVA) [Mowiol 40-88, Sigma-Aldrich] were dissolved in deionized water at room temperature. These solutions were stored in the dark at 8°C for up to two months and spin coated on the respective resonator mirrors as needed.

Spin coating: 20 µl of the J-aggregate stock solution were spin coated at 5000 rpm. For the measurements presented in this work, the TDBC-solution was spin coated onto the top mirror and the BRK-solution was spin coated onto the bottom mirror of the cavity. The resulting films had a thickness between 500 and 600 nm, as measured with a Bruker Dektak XT-A profilometer.

Cavity preparation: The preparation of optical resonators was performed similar to previous works of our group:^[1-4] For the bottom mirror, a cleaned glass coverslip was coated with 4 nm Cr, 70 nm Ag and 75 nm Al₂O₃ using electron beam evaporation (EDWARDS EB3 for Cr and Ag; Pfeiffer Vacuum PLS 570 for Al₂O₃). For the top mirror, the same procedure was performed, but with a plano-convex lens (LA1433, Thorlabs; Diameter 25.4 mm, Radius of Curvature 77.3 mm) as a substrate instead of the glass coverslip.

After spin coating the J-aggregate solutions onto the mirrors, the two mirrors were fixed in a custom-build cage system containing three µm-screws and piezo-actuators (KC1-PZ/M, Thorlabs) which were used to adjust the position of the top mirror relative to the bottom mirror. Before the cavity was installed into the custom-built confocal microscope, the µm-screws were used to approach the top mirror towards the bottom mirror until Newton's rings became visible (at the spatial position where the top mirror (lens) is approximately parallel to the bottom mirror (coverslip)), signifying that the mirror separation is on the order of visible wavelengths.

White light transmission spectra at different cavity distances were used to characterize the cavity. For each transmission peak, we determined the Q -factor *via* $Q = \frac{\omega}{\Delta\omega}$ with ω being the angular frequency and $\Delta\omega$ the full width at half maximum (FWHM) of the respective peak, obtained from a fit to a Lorentzian. The resulting (wavelength- and distance-dependent) Q -factors were in the range of 150 to 400 (see Figure S3).

Optical measurements: Optical measurements were performed on a custom-built confocal microscope. For recording transmission spectra, the cavity was illuminated by a KL 1500 LCD lab-lamp (Leica), emitting unpolarized white light. The light was focused onto the back side of the top mirror by a lens (NA approx. 0.1). The transmission light was collected by a 0.5 NA objective, which was focused on the bottom mirror of the cavity and guided to a Princeton Instruments Acton SP-2-500i spectrometer with a thermoelectrically cooled ProEM+ 512B eXcelon camera attached.

This setup can also be used for emission measurements by coupling a laser (532 nm; Coherent COMPASS 215M-75 SL) into the objective and blocking the reflected laser light by two RazorEdge Long Pass (LP) E-Grade 532 filters. For a sketch of the two measurement configurations, see Figure S1.

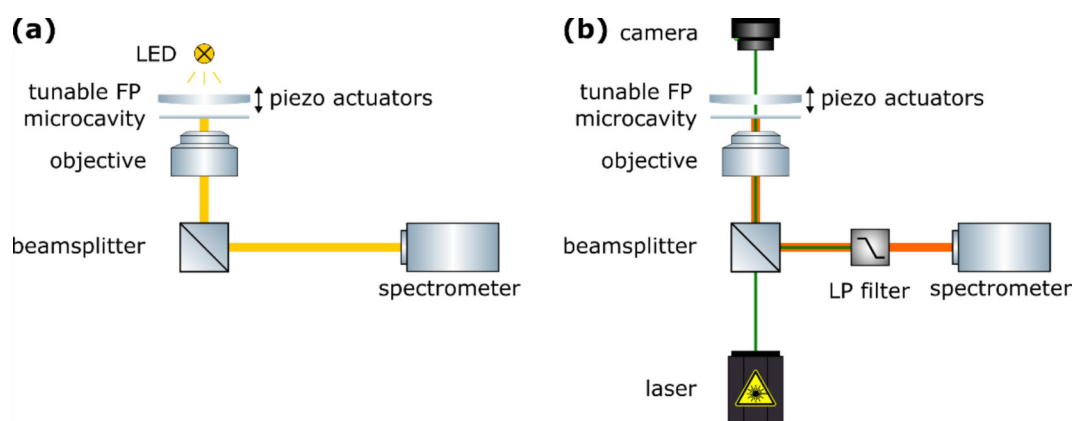


Figure S1. Sketch of the experimental setup configured for transmission measurements shown in (a) and for fluorescence measurements shown in (b).

Free space spectra: Concerning the free space spectra presented in Figure 1: Absorption spectra were measured from PVA thin films using a UV-Vis-NIR spectrophotometer (PerkinElmer Lambda 19). Emission measurements were measured from PVA thin films using the custom-build microscope setup described above.

Software: Data evaluation was performed using MATLAB R2021a.

Transmission measurement of an empty cavity and determining of the Q -factor

In Figure S2 we show the results for a transmission measurement of an empty cavity. The measurement was performed in a way that the two mirrors touched at the start of the measurement. Consequently, for the first seventy spectra, the observed transmission peak changes only slightly. As soon as the mirrors separate, the expected behaviour of linearly red-shifting cavity modes is observed.

The obtained transmission spectra were subsequently used to calculate the Q -factor of the cavity (as described in the experimental section). The obtained values for the Q -factor (for each transmission peak) are displayed in Figure S3. The trend of increasing Q with increasing wavelength for the same mode is explained by the reflectivity of the Ag mirrors, which increases with increasing wavelength for the visible part of the electromagnetic spectrum. The difference between modes is due to the (implicit) relation of the Q -factor to the resonator's lifetime $\tau = \frac{1}{\Delta\omega}$, which is (for constant losses) proportional to the resonator's (round-trip) length. Therefore, the Q -factor increases with increasing cavity distance.

The dips at 555 nm, 655 nm and 760 nm are experimental artifacts due to the "Step and Glue" acquisition mode used to acquire the spectra. The rapid decrease of the Q -factors for wavelengths > 770 nm is probably a consequence of the diminishing detected intensity due to the increasing absorption of Ag at high wavelengths and should be treated as an experimental artifact.

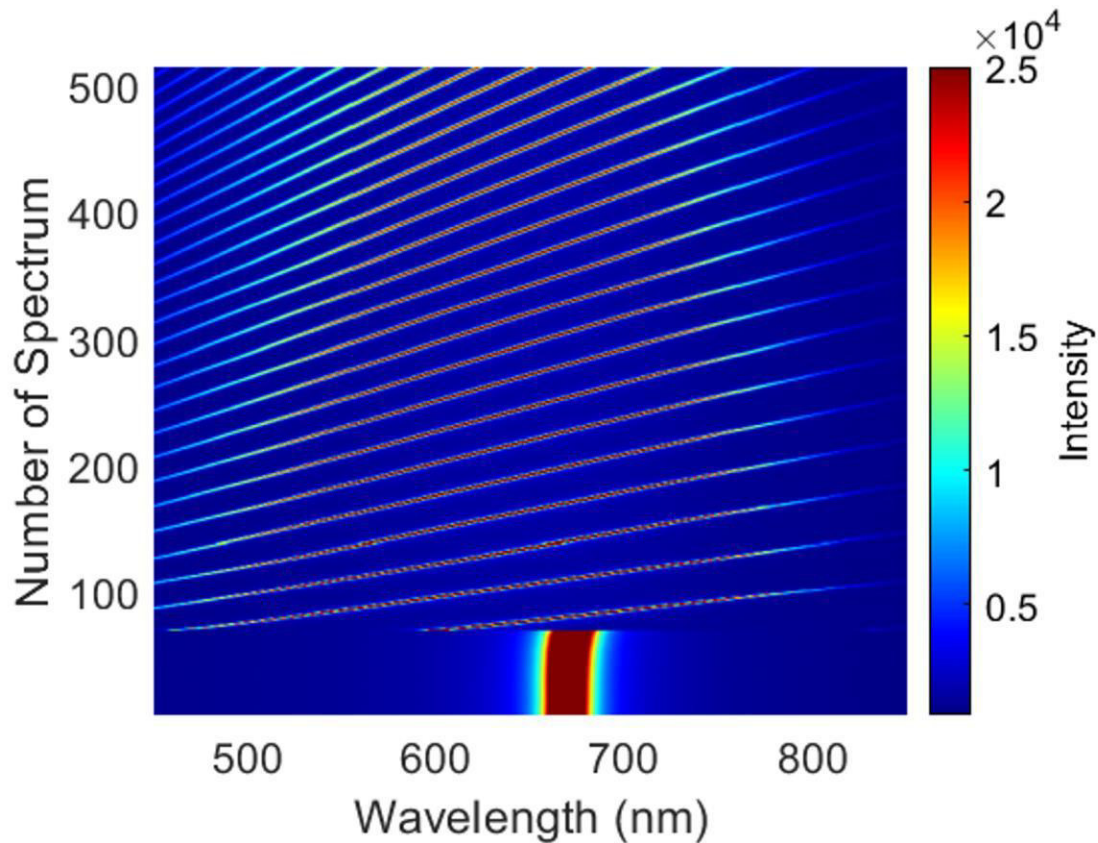


Figure S2. Transmission measurement of an empty cavity. At the start of the measurement, the two mirrors were in contact. We set an upper limit for the color bar to increase contrast.

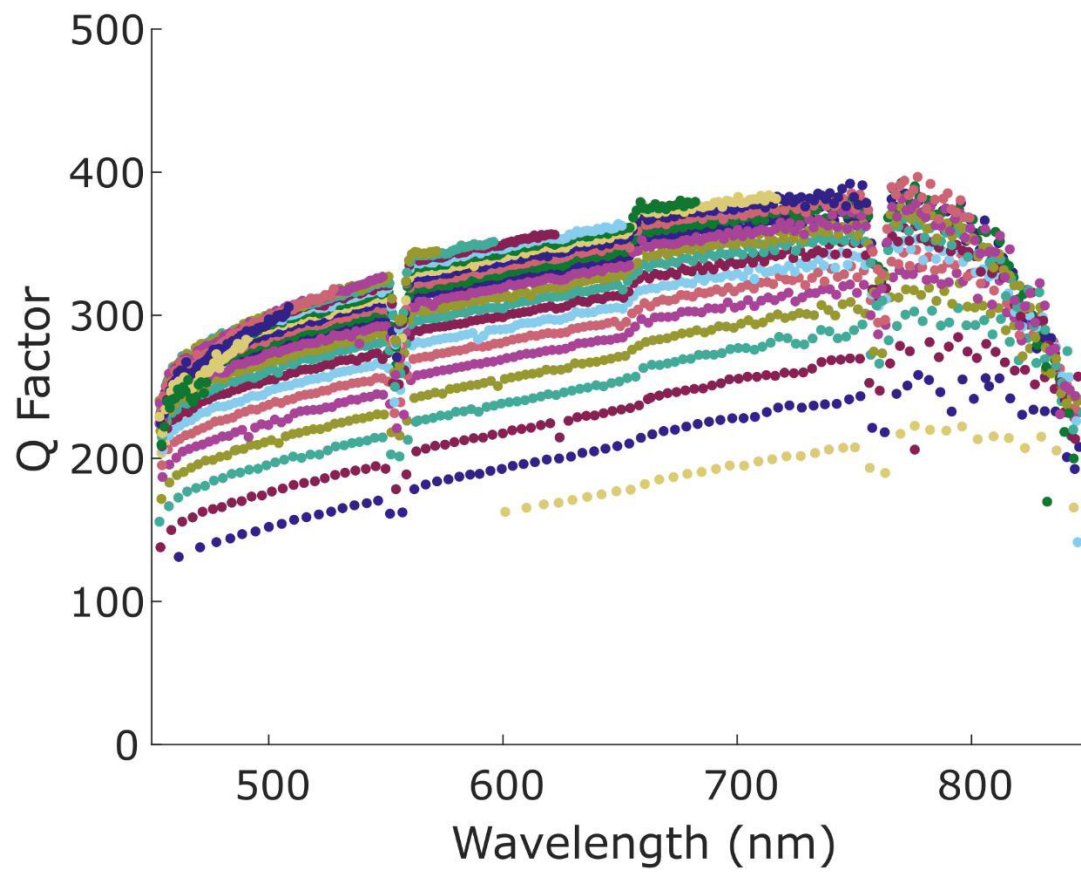


Figure S3. Values for the Q -factor of the cavity, obtained from the transmission peaks shown in Figure S2. Each color represents a specific cavity mode.

Matrix representation for $H_{decoupled}$ and $H_{coupled}$

For $H_{decoupled}$, each cavity mode couples to the excitons independently. For N cavity modes and 2 excitons this results in a matrix of size $3N \times 3N$:

$$H_{decoupled} = \begin{pmatrix} E_{cav,1} & \hbar g_{TDBC} & \hbar g_{BRK} & 0 & 0 & 0 & \cdots & 0 & 0 & 0 \\ \hbar g_{TDBC} & E_{TDBC} & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 \\ \hbar g_{BRK} & 0 & E_{BRK} & 0 & 0 & 0 & \cdots & 0 & 0 & 0 \\ 0 & 0 & 0 & E_{cav,2} & \hbar g_{TDBC} & \hbar g_{BRK} & & & & \\ 0 & 0 & 0 & \hbar g_{TDBC} & E_{TDBC} & 0 & & & & \\ 0 & 0 & 0 & \hbar g_{BRK} & 0 & E_{BRK} & & & & \\ \vdots & \vdots & \vdots & & & & \ddots & & & \\ 0 & 0 & 0 & & & & & E_{cav,N} & \hbar g_{TDBC} & \hbar g_{BRK} \\ 0 & 0 & 0 & & & & & \hbar g_{TDBC} & E_{TDBC} & 0 \\ 0 & 0 & 0 & & & & & \hbar g_{BRK} & 0 & E_{BRK} \end{pmatrix}$$

For comparison, the matrix representation for $H_{coupled}$ is:

$$H_{coupled} = \begin{pmatrix} E_{TDBC} & 0 & \hbar g_{TDBC} & \hbar g_{TDBC} & \cdots & \hbar g_{TDBC} \\ 0 & E_{BRK} & \hbar g_{BRK} & \hbar g_{BRK} & \cdots & \hbar g_{BRK} \\ \hbar g_{TDBC} & \hbar g_{BRK} & E_{cav,1} & 0 & \cdots & 0 \\ \hbar g_{TDBC} & \hbar g_{BRK} & 0 & E_{cav,2} & & 0 \\ \vdots & \vdots & \vdots & & \ddots & 0 \\ \hbar g_{TDBC} & \hbar g_{BRK} & 0 & 0 & 0 & E_{cav,N} \end{pmatrix}$$

Here, the excitons couple with each cavity mode simultaneously.

The main differences between the two Hamiltonians are firstly the different dimensions (for N considered cavity modes and 2 excitons, $size(H_{coupled}) = (N + 2) \times (N + 2)$ and $size(H_{decoupled}) = 3N \times 3N$) and secondly that for $H_{coupled}$, the resulting polariton modes (as a function of cavity distance) cross the exciton energies, while for $H_{decoupled}$, they do not.

Fitting procedure

To fit the series of transmission spectra to the phenomenological Hamiltonians, we developed a fitting routine in MATLAB R2021a.

Fitting of an individual transmission spectrum

To fit the Hamiltonian to an experimental transmission spectrum, we have constructed a model function for the transmission spectra in which the transmission peaks are described by Lorentzian lineshape functions with peak positions related to the energy eigenvalues of the Hamiltonian. In the Hamiltonian, we fix the exciton energies of the J-aggregates and leave the coupling energies and the cavity length as free parameters. The intensities of the measured transmission peaks depend on the spectrum of the white light source and the spectral properties of the mirrors. To account for this, we have first fitted all peaks in the experimental spectra to Lorentzians and then used the obtained values for the peak intensities and FWHMs for the model function as fixed parameters.

Challenging when performing these fits were local minima in the root-mean-square (RMS) deviation as a function of the fitting parameters: Due to the periodic nature of the cavity modes, the deviation between experimental and modelled transmission spectrum can be periodic with respect to the optical path length. Therefore, the choice of good starting parameters is crucial for obtaining correct fit results.

Fitting of a series of transmission spectra

We subsequently performed the fit for every transmission spectrum of the whole series of spectra and obtained values for the optical path length and the coupling energies for every spectrum. Proceeding from one spectrum to the next, we used the results from the spectrum as starting parameters for fitting the next spectrum in the series.

Cavity distances

Figure S4 shows the cavity distances obtained from the fitting procedures (blue lines) along with the smoothed distances (orange lines) used for the plots in the false-color maps. Smoothing was performed with MATLAB's "smoothdata" function with the "rloess" method. We want to point out two findings:

- The obtained distances are almost identical for $H_{coupled}$ and $H_{decoupled}$. This agrees very well with the idea that the cavity distances are mainly determined by the numerous peaks which are off-resonant with the exciton peaks, which makes the fit quite robust.
- For the measurement configurations 2M-D, 2M-A and 2M-DA-I, the two mirrors touched at the start of the measurement. This manifested in the obtained cavity distances, which only increase slightly for the first few voltage decreases (for the most pronounced example, see 2M-DA-I).

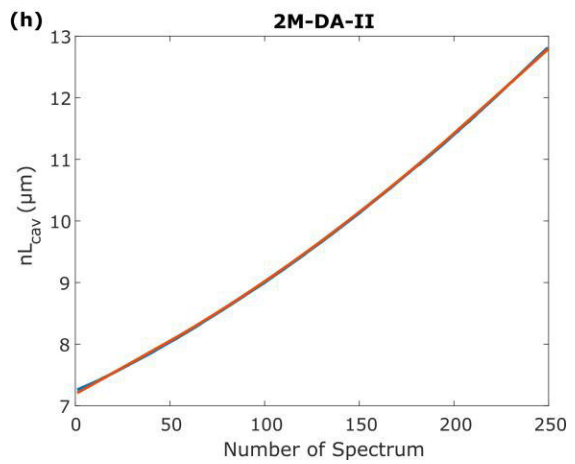
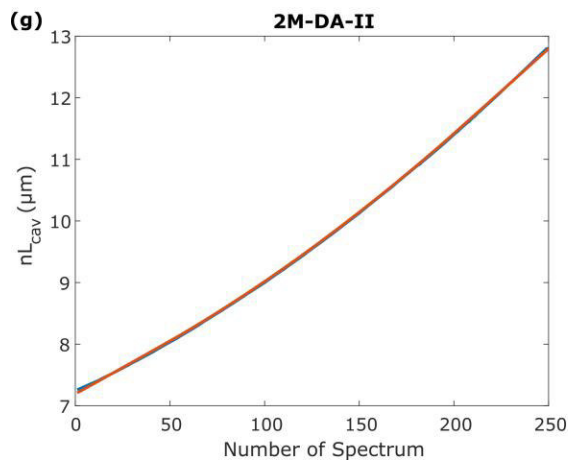
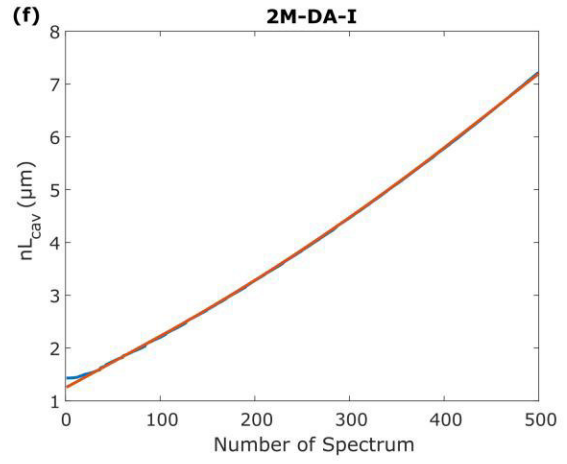
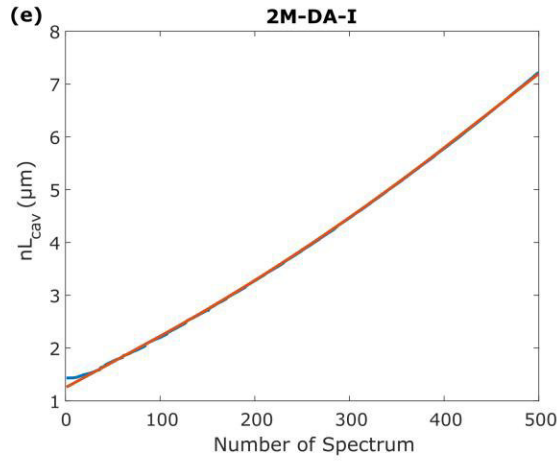
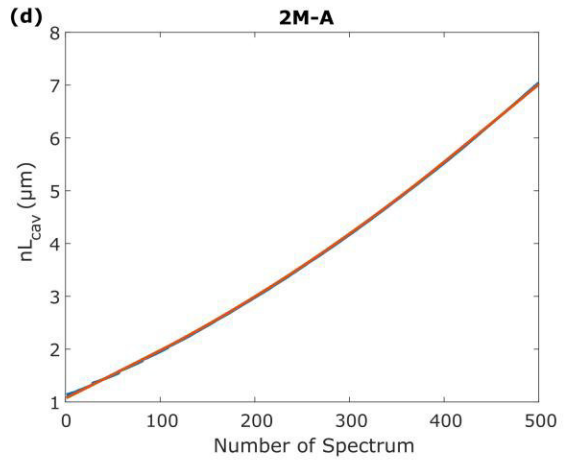
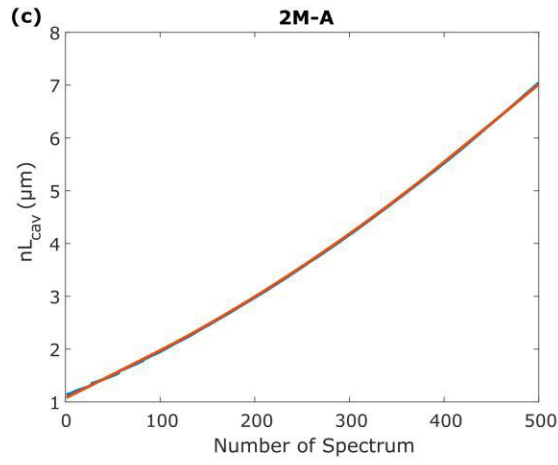
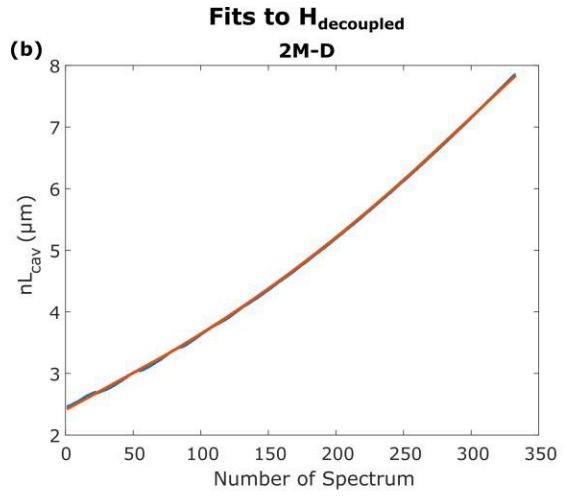
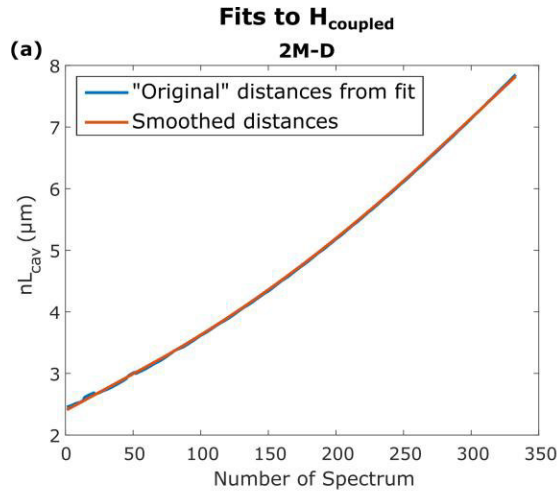


Figure S4. Cavity distances obtained from the fitting procedure. Blue lines show the values obtained from the fits; orange lines show the values after smoothing. In the left column, the results for the fit to H_{coupled} are displayed. In the right column, the results for $H_{\text{decoupled}}$ are displayed.

Coupling energies

In Figure S5, we show the coupling energies obtained from the fits for all cavity configurations as a function of cavity distance. The orange and red curves represent the expected theoretical evolution of the coupling energy as a function of the cavity length $\hbar g = A \cdot (nL_{\text{cav}})^{-1/2}$ for an ideal Fabry-Pérot cavity where we adjusted the parameter A to obtain the best agreement with the obtained coupling energies at high cavity lengths. We obtain larger values of A for the spectral series where only one J-aggregate is present in the cavity (2M-D and 2M-A) as compared to those with both J-aggregates (2M-DA-I/II). Under similar irradiation conditions a possible explanation is that the presence of a second absorbing layer leads to higher absorption losses in the cavity and consequently to a lower number of photons in the cavity modes. Since the coupling energy is proportional to the square root of the photon number in the coupling cavity mode,^[5-6] this should lead to a decrease in coupling energy.

In Figure S5 (c) and (d), we observe abrupt steps in the obtained curves at the transition from the measurement 2M-DA-I to 2M-DA-II. Between these two measurements, we used the μm -screws to increase the mirror separation of the cavity by several μm . We cannot be sure that we did not shift the mirrors horizontally to each other with respect to the optical axis. Therefore, these steps might be due to inhomogeneities in the spin coated films, resulting in a slightly lower concentration of TDBC and a slightly higher concentration of BRK for 2M-DA-II as compared to 2M-DA-I for this particular case. Nevertheless, these changes are rather small, and we still obtained good agreement with the theoretical evolution when using the same parameter A for both measurements.

For all cavity configurations displayed in Figure S5, we observe a periodic oscillation of the coupling energies with decreasing amplitude as the cavity length increases. We think that these are due to a subtlety of the setup of the Hamiltonian: We assume that the coupling energy between an exciton and the different cavity modes is the same for all cavity modes (to keep the number of fit parameters reasonable). Hence, we will obtain an average value as the result of the fit as different cavity modes interact with the exciton transition. If now the coupling energies of different cavity modes differ in a systematic way, this can lead to oscillations in the obtained values. We have identified two sources for such differences:

- The spectral width of the excitonic transitions, which was neglected in the Hamiltonian. Here, one would expect different coupling strengths depending on the exact position of the cavity mode in relation to the excitonic maximum. This effect should be averaged out when the free spectral range of the cavity modes is smaller than the width of the excitonic transition.
- The coupling energy also depends on the electric field strength of the cavity mode at the spatial position of the exciton layer. This has been demonstrated experimentally^[7-9] and means that exciton-photon coupling is maximal if the exciton layer is located at an antinode of the electric field and completely suppressed if it is located at a node of the electric field. If the cavity length is changed this also changes the spatial structure of the cavity modes and consequently also the coupling efficiency. Since our exciton layers are on the same order of magnitude as the wavelength of the exciton transitions, we expect only a small modulation.

We conclude that for large cavity lengths $>$ approx. $3.5 \mu\text{m}$, the simple model we proposed works rather well. For small cavity lengths, a more sophisticated model taking into account the effects mentioned above is needed.

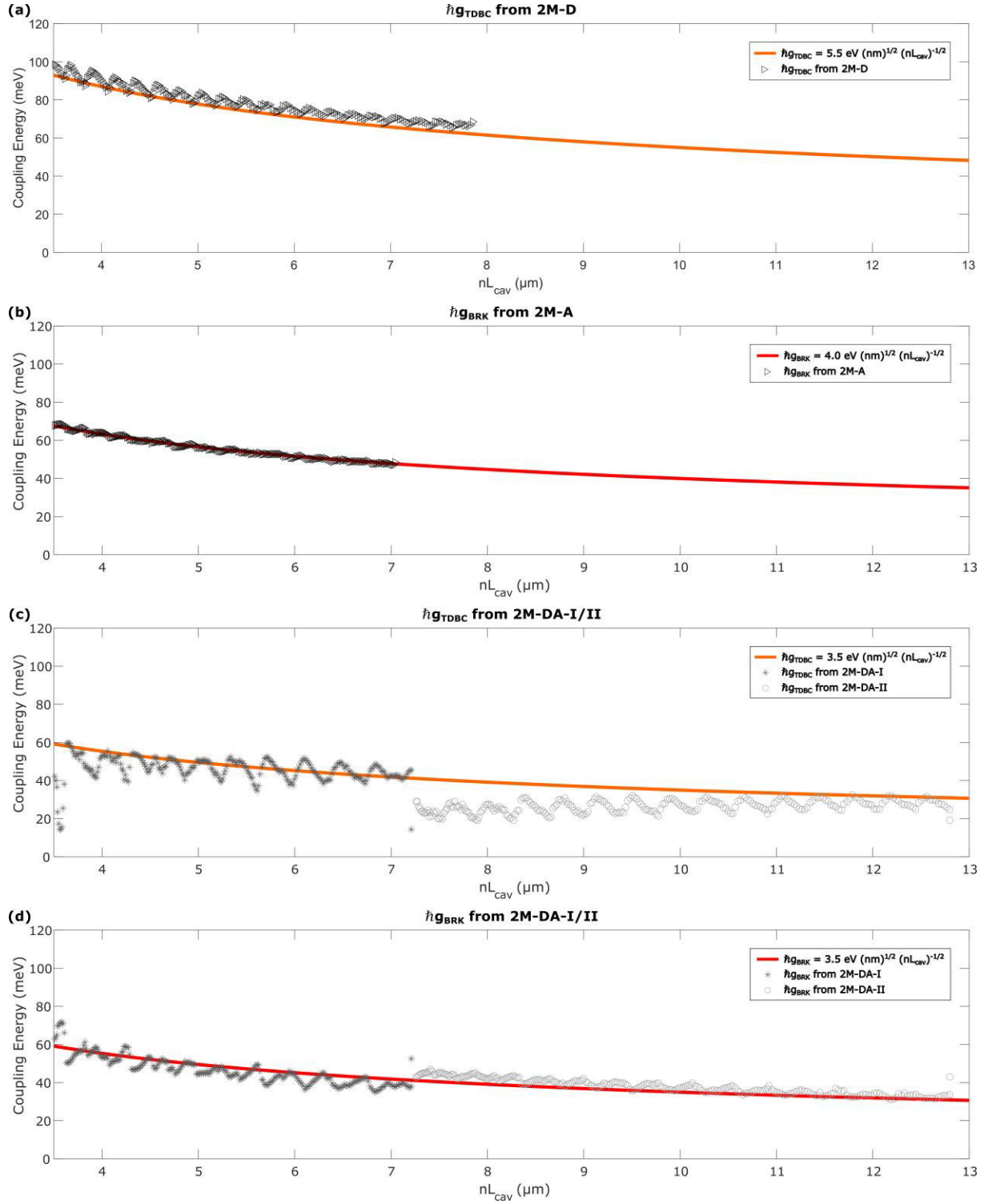


Figure S5: Coupling energies $\hbar g_{TDBC}$ and $\hbar g_{BRK}$ obtained by fitting $H_{coupled}$ to the experimental spectra of 2M-D (a), 2M-A (b) and 2M-DA-I/II (values for $\hbar g_{TDBC}$ in (c) and values for $\hbar g_{BRK}$ in (d)) as a function of the obtained cavity distance. Solid lines show the curves obtained by manually adjusting the function $\hbar g(nL_{cav}) = A \cdot (nL_{cav})^{-1/2}$ for the best agreement with the obtained curves at large distances (TDBC in orange, BRK in red).

Differences between the optical path length and distance between the J-aggregate containing layers

Influence of the refractive index

Concerning the results for the optical path length, we must anticipate a constant offset between optical path length nL_{cav} and “actual” mirror-mirror separation L_{cav} for all measured separations resulting from the refractive index of the Al_2O_3 spacer layer as well as the J-aggregate-containing PVA layers (the space between is filled with air for which $n \approx 1$). If we assume a spacer layer thickness of 75 nm and a PVA layer thickness of around 500 nm for each mirror as well as a refractive index of approximately 1.77 for Al_2O_3 ^[10] and 1.48 for PVA^[11] (neglecting the refractive index of the J-aggregates), we expect a difference of around 600 nm between the optical path length nL_{cav} and the “actual” mirror-mirror separation L_{cav} (if the microcavity is filled with both J-aggregates). The effect of the penetration depth of the electromagnetic field into the Ag mirrors is a few tens of nanometers and therefore small compared to the offsets discussed above.

Calculation of the distance between the J-aggregate containing layers

For the measurements involving both J-aggregates (2M-DA-I and 2M-DA-II), we calculated the distance between the J-aggregate containing layers (Table 1). For this purpose, we assumed that these two layers touched at the start of 2M-DA-I. We then subtracted the corresponding value obtained for the optical path length (1.435 μm). This value corresponds rather well to the estimated values for the film thickness of around 500 – 600 nm and the influence of the refractive index on the optical path length of around 600 nm discussed above, which yields an approximate distance of 1.6 – 1.8 μm .

The assumption of touching mirrors at the start of recording the spectral sequence of 2M-DA-I is further confirmed by the experimental data (Figure S4(e)): The obtained optical path lengths for 2M-DA-I show that the cavity distance changed very little for the first few spectra of this measurement.

Full false-color maps of the transmission measurements with the fit to $H_{coupled}$

In Figures S6-S9, we show the entire series of spectra as false-color maps and the results for the fit to $H_{coupled}$ as black circles for the measurement configuration 2M-D (Figure S6), 2M-A (Figure S7), 2M-DA-I (Figure S8) and 2M-DA-II (Figure S9) for cavity lengths $> 3.5 \mu\text{m}$. Here, we used the coupling energy curves $\hbar g = A \cdot nL_{cav}$ with the values for A displayed in Table 1 of the main text. In the main text (Figure 2), we only show small sections of these false-color maps for better clarity.

A feature in the obtained transmission spectra not discussed in the main text are additional modes of low intensity running parallel to the polariton/cavity modes. These modes are particularly visible at wavelengths greater than 780 nm. We believe that they are caused by the formation of a second cavity between layers that are different from the Ag mirror and therefore have significantly lower reflectivity.

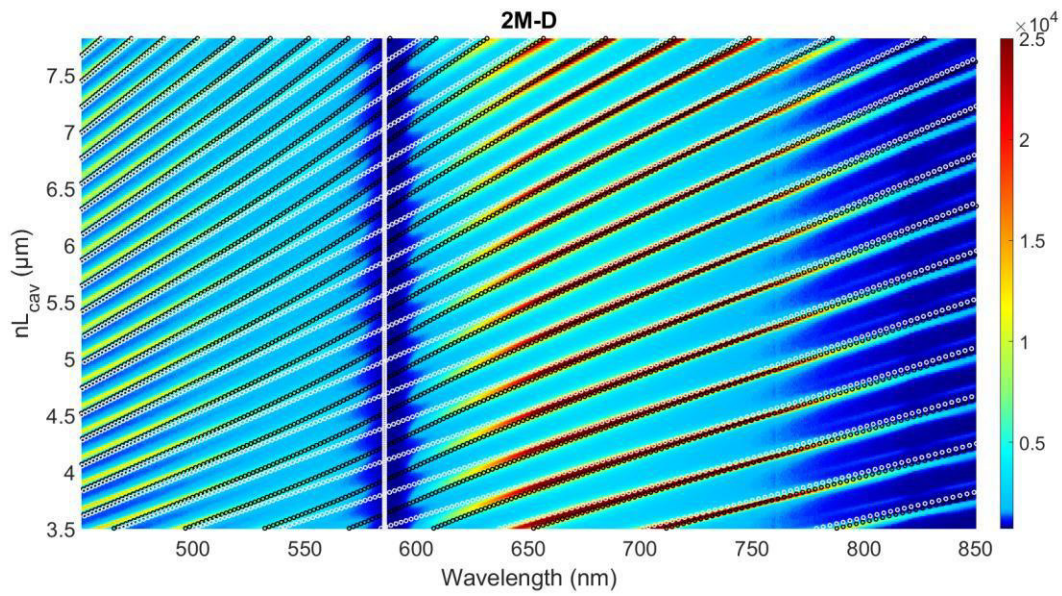


Figure S6. Transmission spectra plotted as false-color maps for 2M-D. Black circles show the fit to $H_{coupled}$. For comparison, white circles show the corresponding uncoupled excitons and cavity modes. The spectra are plotted against the cavity distances from the fit.

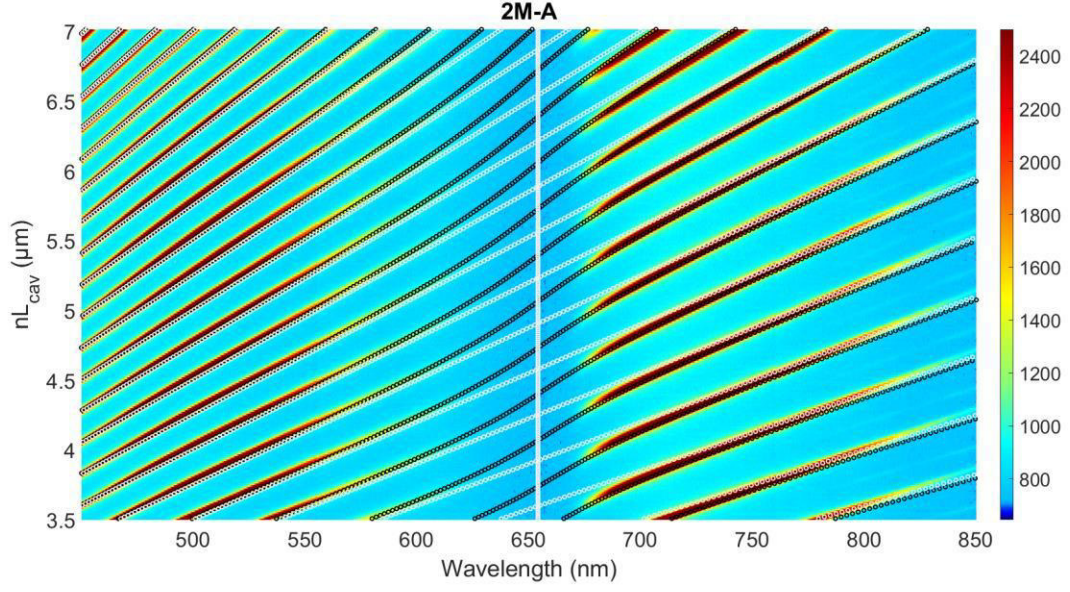


Figure S7. Transmission spectra plotted as false-color maps for 2M-A. Black circles show the fit to H_{coupled} . For comparison, white circles show the corresponding uncoupled excitons and cavity modes. The spectra are plotted against the cavity distances from the fit.

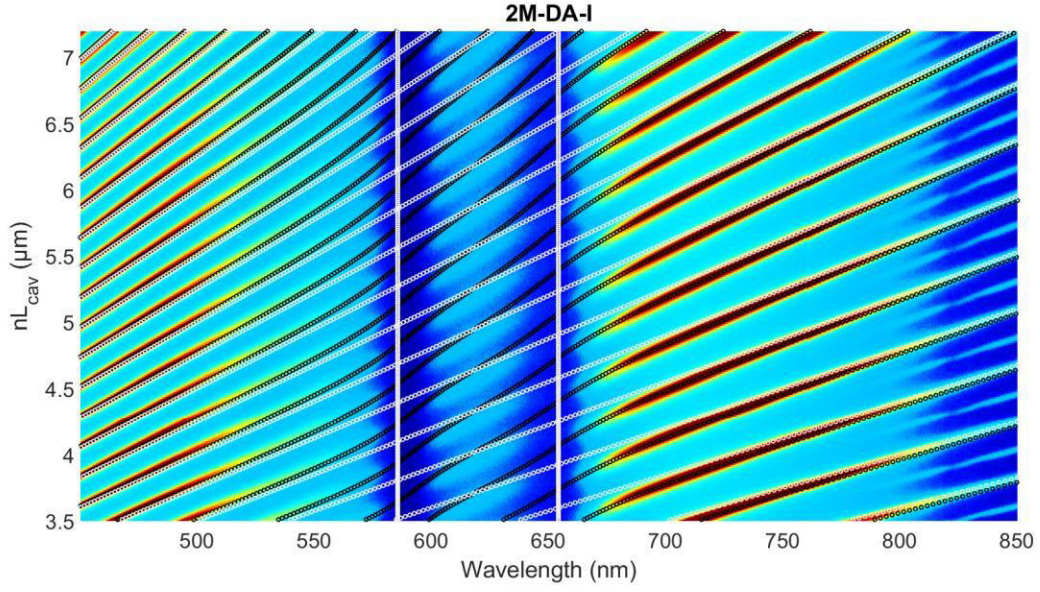


Figure S8. Transmission spectra plotted as false-color maps for 2M-DA-I. Black circles show the fit to H_{coupled} . For comparison, white circles show the corresponding uncoupled excitons and cavity modes. The spectra are plotted against the cavity distances from the fit.

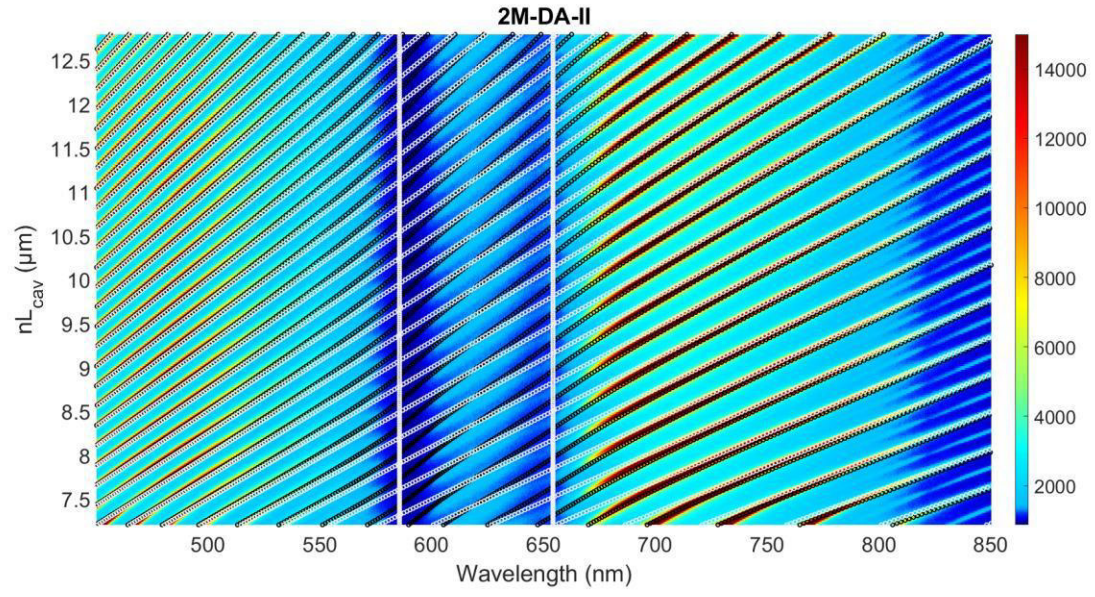


Figure S9. Transmission spectra plotted as false-color maps for 2M-DA-II. Black circles show the fit to H_{coupled} . For comparison, white circles show the corresponding uncoupled excitons and cavity modes. The spectra are plotted against the cavity distances from the fit.

Results for the fits to $H_{decoupled}$

Figures S10-S13 show the same false-color maps as in Figures S6-S9, but with $H_{decoupled}$ used for the fits instead of $H_{coupled}$. For the coupling energies, we obtained slightly different values and chose

- $A = 5.0 \text{ eV (nm)}^{-1/2}$ (TDBC) for 2M-D,
- $A = 4.0 \text{ eV (nm)}^{-1/2}$ (BRK) for 2M-A,
- $A = 4.0 \text{ eV (nm)}^{-1/2}$ (TDBC) and $A = 3.0 \text{ eV (nm)}^{-1/2}$ (BRK) for 2M-DA-I and 2M-DA-II.

The agreement between experimental data and the best fit to the Hamiltonian is significantly worse here. This is most apparent for the spectral region around the TDBC exciton lines, where the resulting polariton modes change far more steeply than the experimental transmission maxima when approaching the exciton line.

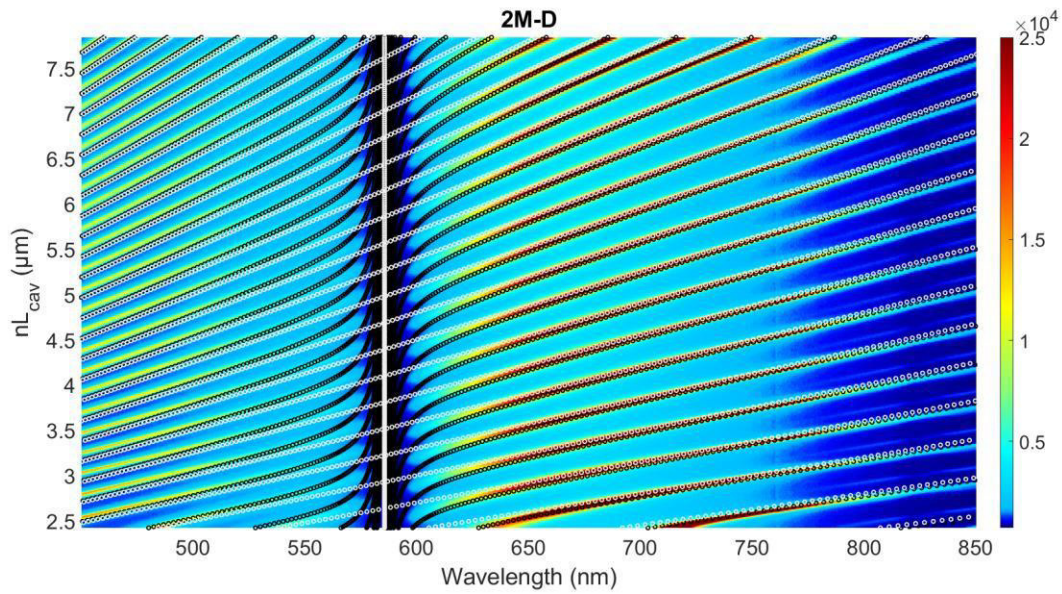


Figure S10. Transmission spectra plotted as false-color maps for 2M-D. Black circles show the fit to $H_{decoupled}$. For comparison, white circles show the corresponding uncoupled excitons and cavity modes. The spectra are plotted against the cavity distances from the fit.

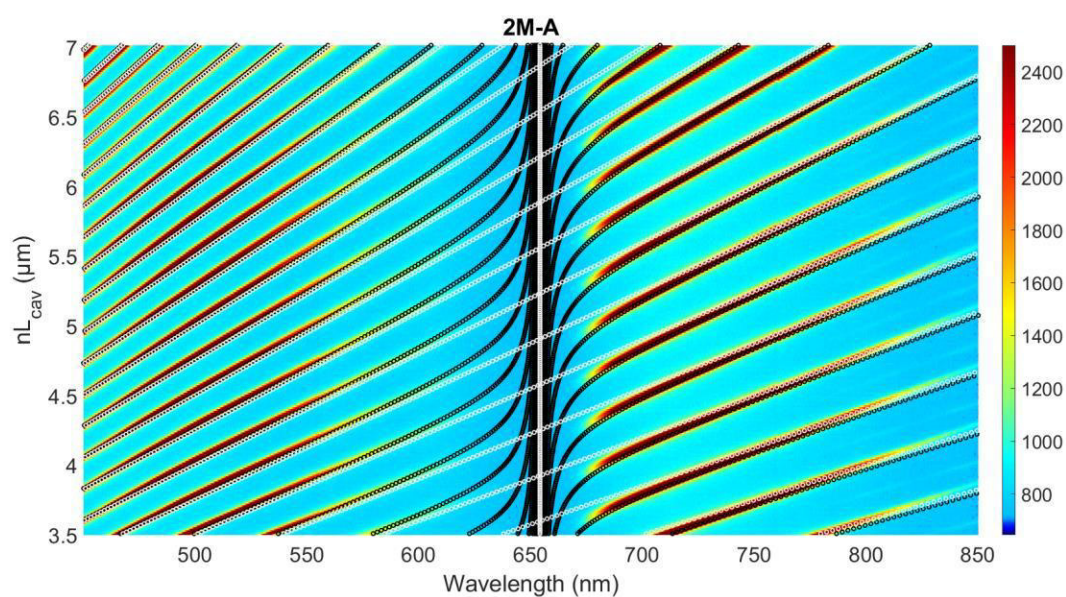


Figure S11. Transmission spectra plotted as false-color maps for 2M-A. Black circles show the fit to $H_{\text{decoupled}}$. For comparison, white circles show the corresponding uncoupled excitons and cavity modes. The spectra are plotted against the cavity distances from the fit.

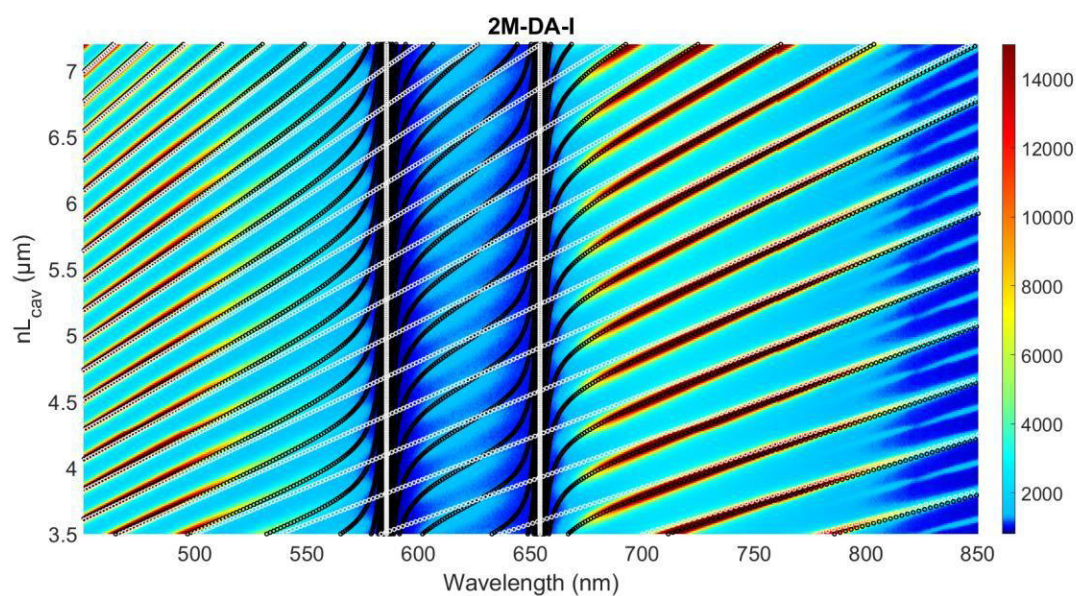


Figure S12. Transmission spectra plotted as false-color maps for 2M-DA-I. Black circles show the fit to $H_{\text{decoupled}}$. For comparison, white circles show the corresponding uncoupled excitons and cavity modes. The spectra are plotted against the cavity distances from the fit.

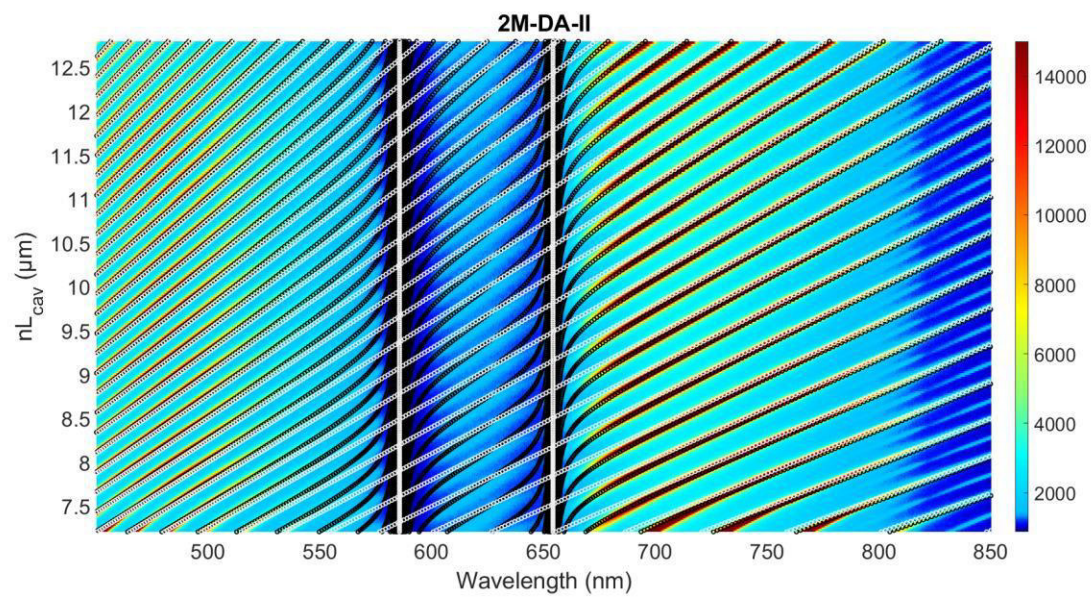


Figure S13. Transmission spectra plotted as false-color maps for 2M-DA-II. Black circles show the fit to $H_{\text{decoupled}}$. For comparison, white circles show the corresponding uncoupled excitons and cavity modes. The spectra are plotted against the cavity distances from the fit.

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Appendix C

**Second Publication:
Polariton-Mediated Energy
Transfer in a Tunable Optical
Multimode Microcavity
Exceeding 10 μm**

Polariton-Mediated Energy Transfer in a Tunable Optical Multimode Microcavity Exceeding 10 μm

Christoph Kertzsch,*, Michael Mauch, Jakob Keck, and Alfred J. Meixner*

Energy transfer between a donor-acceptor pair of J-aggregated dyes, which are spin-coated onto the mirrors of a tunable Fabry–Pérot microresonator, is studied. It is found that both donor and acceptor are strongly coupled to the optical modes of the resonator and form hybrid light–matter states (polaritons). The shapes of the fluorescence spectra show efficient energy transfer from donor to acceptor, which are separated up to 11 μm . Within the same measurement, the energy transfer efficiency appears to be independent of donor–acceptor separation. The observed fluorescence features are well explained by a phenomenological Hamiltonian, which models the emerging polariton modes and rate equations.

1. Introduction

Strong light–matter coupling between the excitonic transitions of a material and the modes of an optical resonator, first demonstrated for organic molecules by Lidzey et al. in 1998,^[1] has gained considerable attention due to its implications for molecular chemistry, material science, and quantum photonics.^[2–8] Strong coupling occurs if the energy exchange between the excitons and the optical mode is reversible and faster than competing dissipation processes. This leads to the formation of new hybrid light–matter eigenstates, which are called (cavity) polaritons. As a result, certain material properties, for example, transport processes^[9–14] or chemical reactivity,^[15–20] can undergo significant changes, and completely new phenomena might emerge, such as polariton-mediated energy transfer (PMET), which can be observed when two different excitons are coupled to the same microcavity.^[21–25] The resulting hybridization enables efficient energy transfer from the energetically higher exciton called the energy donor to the lower one called the energy acceptor. Different authors stressed that PMET should be independent of donor–acceptor distance^[5,22] and it was demonstrated for donor–acceptor separations of up to 2 μm ,^[25] which is orders

of magnitude larger compared to Förster-type (dipole-dipole interaction)^[26] and Dexter-type (electronic exchange)^[27] energy transfer mechanisms.

In previous works, microcavities were typically sandwich structures consisting of thin films, resulting in rigid Fabry–Pérot (FP) resonators with fixed mirror distances as well as fixed donor–acceptor separations. In this work, we utilize a tunable FP resonator,^[28–38] specifically exactly the same one with which we have systematically investigated transmission spectra as a function of cavity length at much larger donor–

acceptor separations ($>10 \mu\text{m}$) than previously reported.^[39] These large cavity distances also imply that there are many optical modes present interacting with the excitonic transitions, whereas there were usually only one or at maximum a few optical modes in previous works. For the excitons coupled to the resonator, we use thin films containing the well-known J-aggregates TDBC as the energy donor and BRK as the energy acceptor, which were spin-coated onto the mirrors of the cavity. J-aggregates are organic molecules which undergo supramolecular self-organization under certain conditions.^[40] This leads to very favorable optical properties, namely an intense and narrow J-band with a small Stokes shift (see Figure 1c), making the observation of strong coupling at room temperature easily achievable.^[41]

The optical setup can be adjusted to either take white light transmission spectra or fluorescence spectra (532 nm excitation; see Figure 1a). For all cavity-J-aggregate configurations, first a series of transmission spectra was recorded. Subsequently, we adjusted the optical setup and recorded a series of fluorescence spectra over the same voltage range of the piezo actuators.

In previous work,^[39] we analyzed the transmission spectra. Using a phenomenological Hamiltonian, we fitted the transmission peaks and extracted the coupling energies and cavity length. Although the coupling strength decreases with increasing cavity length, we still achieved coupling energies of 35 meV at 10 μm cavity length (see Table S1, Supporting Information for a summary of the fit results). Consequently, we achieved simultaneous strong coupling with both J-aggregates for all investigated distances under the chosen experimental conditions. We also confirmed the presence of “hybrid polaritons”, which contain contributions from both J-aggregates and might play a crucial role in enabling PMET.

Here, we analyze the fluorescence properties of the system experimentally and theoretically based on the results from the investigation of the transmission properties of the system. We will present the measured series of fluorescence spectra and show that PMET occurred for all configurations containing donor

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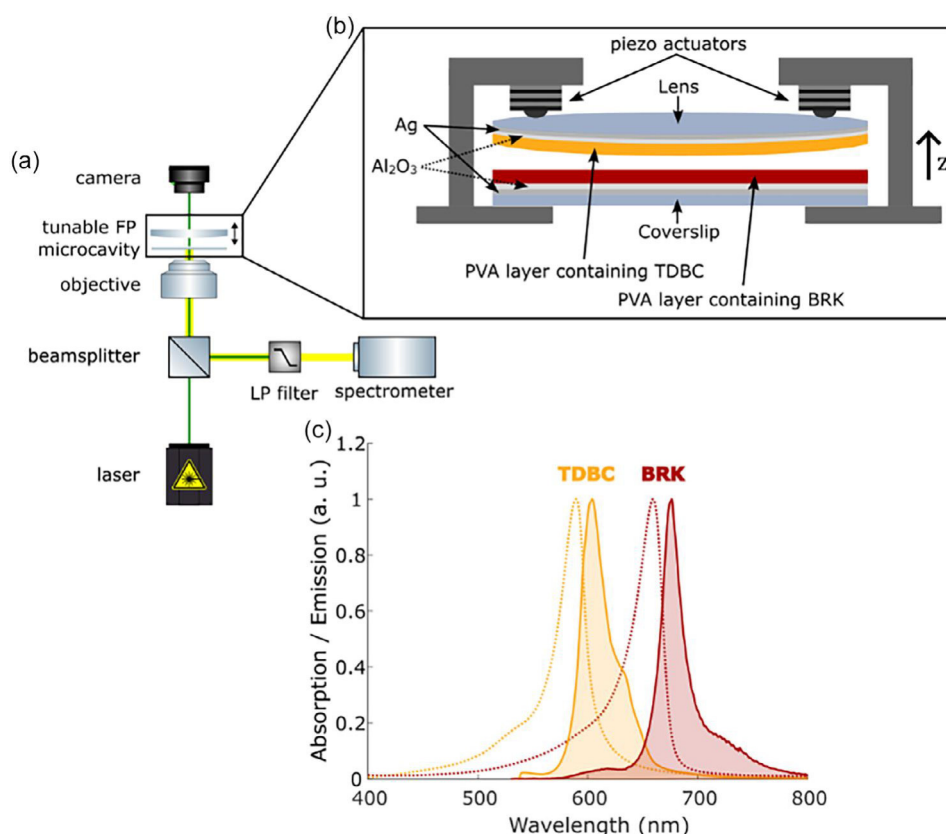


Figure 1. a) Sketch of the experimental setup configured for fluorescence measurements. b) Sketch of the tunable FP resonator. c) Free space absorption (dashed lines) and emission spectra (532 nm excitation; solid lines) of the two J-aggregates TDBC (orange) and BRK (red).

and acceptor with an efficiency seemingly independent of donor–acceptor distance. We explain the behavior of the observed fluorescence features by discussing the influence of the optical mode density of the cavity at the excitation wavelength and fitting a polariton model to the fluorescence maxima. Furthermore, we developed a rate equations (RE) model to describe fluorescence intensities of different polariton modes.

2. Results and Discussion

We performed measurements on three different cavity-J-aggregate configurations: 1) the donor TDBC on the top mirror (2M-D), 2) the acceptor BRK on the bottom mirror (2M-A), and 3) a donor–acceptor configuration with TDBC on the top mirror and at the same time BRK on the bottom mirror (2M-DA-I, see Figure 1b). For 2M-DA-I, we reused the spin-coated mirrors from 2M-D and 2M-A to ensure comparability. After placing the prepared mirrors into the cage system, we can control the mirror separation by μm -screws (for coarse adjustment) and piezo actuators. For systematic measurements as a function of mirror separation, we first brought the top mirror into contact with the bottom mirror by applying a voltage to the piezo actuators, which reflects the smallest mirror separation. We then stepwise decreased the applied voltage, which increased the mirror separation until the minimum voltage was reached. This resulted in

final mirror separations $\approx 5\ \mu\text{m}$ larger than the starting distance. After each voltage step, an optical spectrum was recorded. For the configuration involving both J-aggregates, we performed an additional voltage scan: Using the μm -screws, we increased the mirror separation to the approximate endpoint of the measurement 2M-DA-I and performed a second voltage scan of the piezo actuators at larger distances of $\approx 5\text{--}10\ \mu\text{m}$ (2M-DA-II).

In Figure 2, we show the sequence of fluorescence spectra recorded for the four cavity configurations 2M-D, 2M-A, 2M-DA-I, and 2M-DA-II as false-color maps. We observe fluorescence peaks which shift to the red with increasing cavity length and strongly modulate in intensity, resulting in rather complex intensity patterns.

2.1. General Trends in the Averaged Spectra

Several studies investigated the emission properties of strongly coupled J-aggregates in microcavities with short cavity length.^[42–49] Usually a single excitonic transition was strongly coupled to a single cavity mode, resulting in the formation of an upper and lower polariton, and the emission spectrum was dominated by the lower polariton and the reservoir of uncoupled molecules (exciton reservoir),^[42,46,48] whereas emission from the upper polariton was difficult to observe due to rapid nonradiative decay toward the lower polariton and the exciton reservoir.^[43–45]

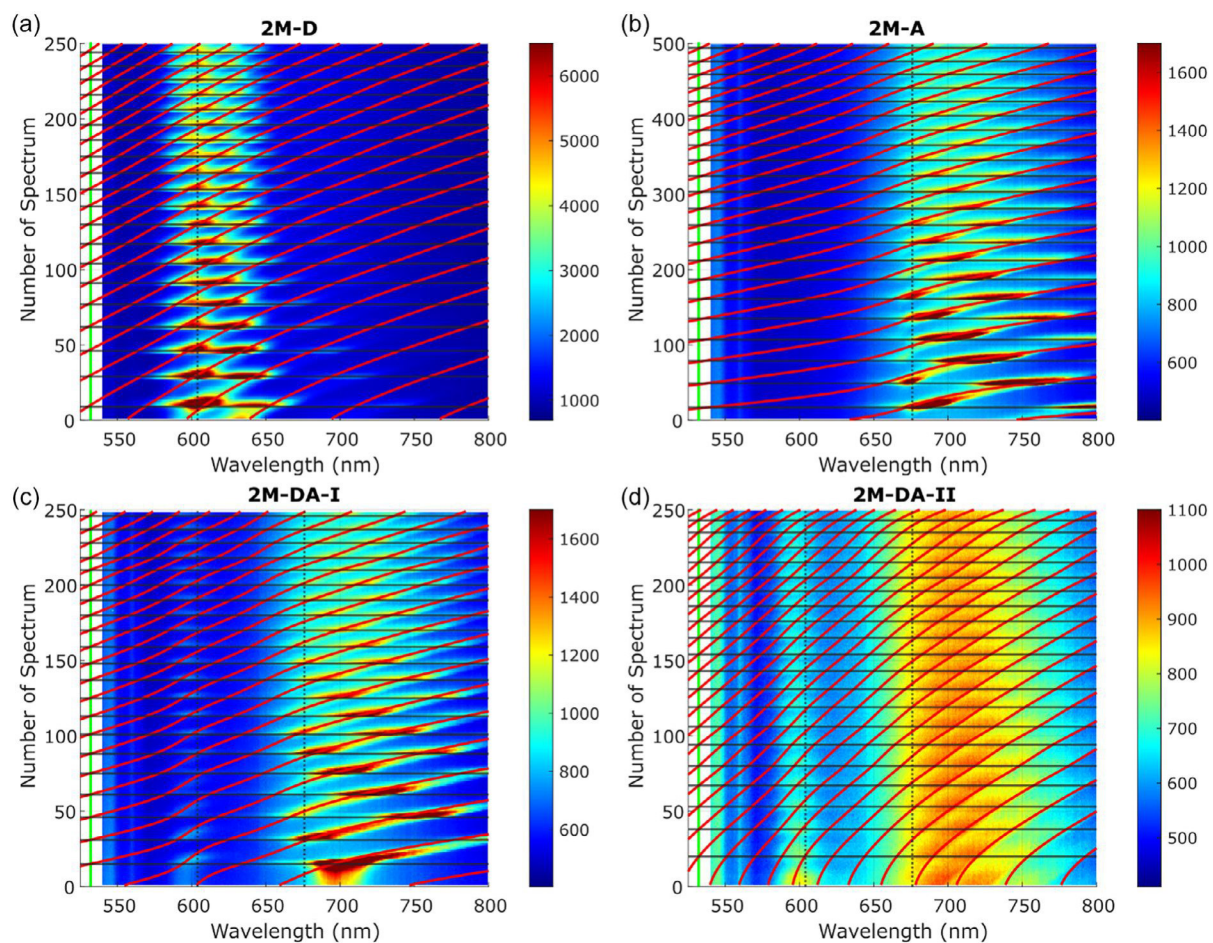


Figure 2. False-color maps displaying fluorescence spectra which were taken consecutively while stepwise increasing the cavity length for the configurations a) with donor 2M-D, b) with acceptor 2M-A, c) with donor and acceptor on opposite mirrors 2M-DA-I, and d) 2M-DA-II. Vertical black dotted lines represent the free space TDBC and BRK fluorescence maxima (604 and 676 nm, respectively). The horizontal black lines mark maxima in the total fluorescence signal. The vertical green line at 532 nm represents the excitation laser wavelength. Red lines represent the polariton modes from our phenomenological Hamiltonian model H_{coupled} , which we fitted to the fluorescence maxima.

For a general impression of the fluorescence behavior, we have summed and normalized the whole series of spectra for each cavity configuration; see the blue curves in **Figure 3**. For the individual dyes, the fluorescence bands are significantly red-shifted and broadened with respect to the fluorescence spectra in free space, represented as orange and red dotted lines in **Figure 3**. The redshift agrees with the expectation that the fluorescence originates from the lower polaritons, and the broadening occurs as a result of the averaging of these polariton modes, which shift to the red with increasing cavity length.

To exclude the possibility of energy transfer between TDBC and BRK in the absence of a cavity, we also recorded a series of fluorescence spectra as a function of increasing donor–acceptor distance where the bottom mirror (the one closer to the detector) was replaced by a pristine cover slide on which BRK was deposited (1M-DA, see **Figure 3d**). Here, we also moved the piezo actuators over the same voltage range as for 2M-DA-I and observed strong fluorescence of TDBC but much weaker fluorescence at the spectral position of BRK. These results confirm that the direct excitation efficiency for TDBC by the incident

laser radiation at 532 nm is significantly higher than for BRK, as expected from the absorption spectra shown in **Figure 1c**, and that no significant energy transfer occurs from TDBC to BRK without the cavity. Therefore, strong BRK emission in the presence of TDBC indicates efficient energy transfer from TDBC to BRK via a process not occurring in free space. It is noteworthy that the TDBC peak is slightly blue-shifted as compared to free space, which is due to absorption by BRK, as the TDBC fluorescence must pass through the BRK layer to be detected.

Upon insertion of the second mirror (2M-DA-I, see **Figure 3c**), we observe a strong fluorescence peak similar to the one for 2M-A and only a small fluorescence peak around the free space TDBC fluorescence. This implies that most of the excitations are transferred toward BRK via a process not occurring in free space.

2.2. Fluorescence as a Function of Cavity Length

In **Figure 4a** and **c** we plot the intensity of excitation radiation at 532 nm transmitted through the cavity and detected by the camera placed behind the top mirror of the cavity (green dotted line), and

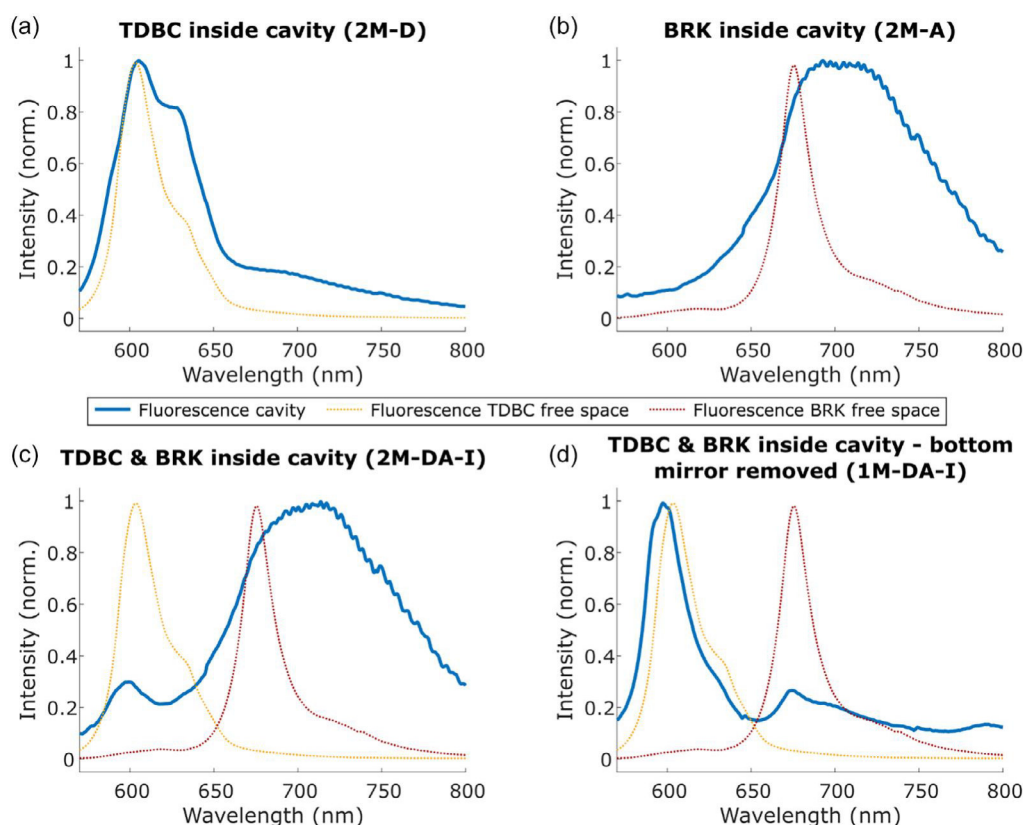


Figure 3. Summed and normalized fluorescence spectra for different experimental configurations shown in Figure 2 and S1, Supporting Information represented as solid blue lines: a) 2M-D, b) 2M-A, c) 2M-DA-I, and d) 1M-DA-I. For comparison, we also show the free space fluorescence spectra of TDBC (orange dotted line) and BRK (red dotted line). The weak modulation of the blue lines from 700 to 800 nm in (b) and (c) are due to fringing effects caused by the coating of the CCD camera in the spectrometer. This effect is more pronounced in the red spectral region and only becomes visible at high intensities.

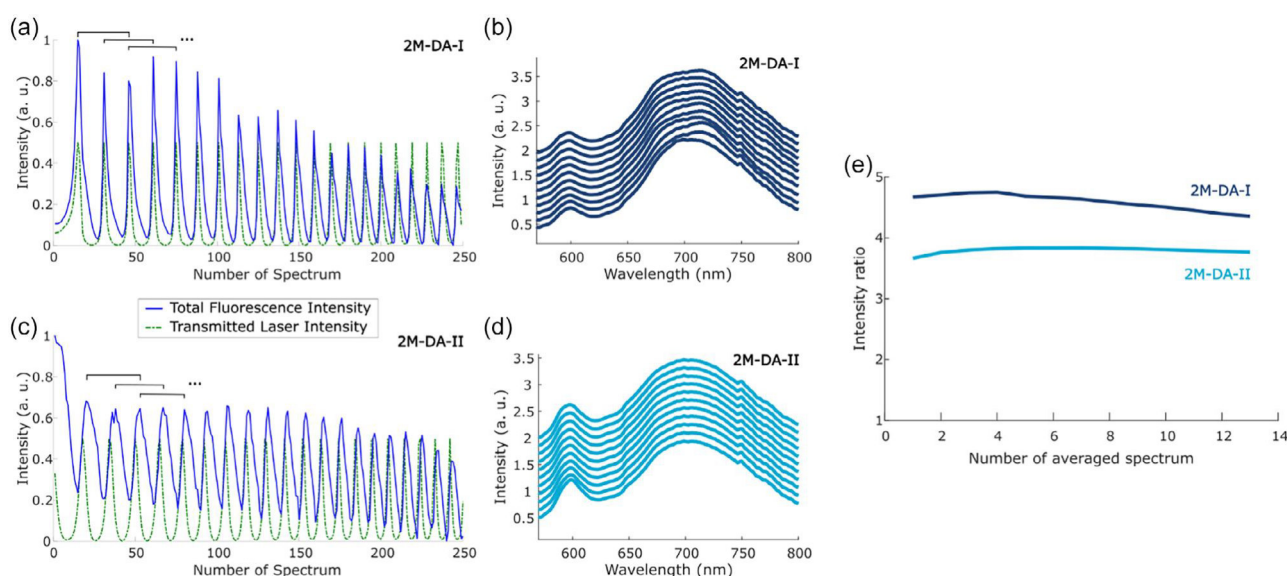


Figure 4. Spectrally integrated fluorescence intensity (blue line) and transmitted laser intensity (green line) as a function of the cavity length represented by the spectrum number for a) 2M-DA-I and c) 2M-DA-II. One can clearly see the correlation between the transmitted laser intensity and the peak fluorescence intensities. For b) and d), we have calculated an average of the fluorescence spectra over a sliding range of two periods as indicated by the black, horizontal brackets in (a) and (c), corresponding to the spectral numbers from a peak in the total intensity curve to the peak after the next one in (a) and (c), respectively. e) For each averaged spectrum, we have calculated the BRK to TDBC intensity ratio (TDBC: 580–630 nm, BRK: 650–800 nm).

the total (spectrally integrated) fluorescence intensity for each spectrum (blue solid line) for 2M-DA-I and 2M-DA-II, respectively.

The transmitted laser intensity is periodically modulated as a function of the mirror separation with maxima when the resonance condition is fulfilled. For an empty FP resonator, we expect a peak every time the cavity distance corresponds to a multiple of $532/2 = 266$ nm. Hence, it can serve as a scale for the mirror separation. The curves show a decrease of the peak-to-peak distances at higher cavity distances, which is due to deviations from perfectly linear displacement behavior of the piezo actuators. (This was already observed in our previous work,^[39] see Figure S4, Supporting Information).

A direct comparison of the transmitted laser intensity with the total intensity of the fluorescence spectra as a function of spectrum number reveals a clear correlation, with the respective peak positions at most two spectrum numbers apart, revealing that the intensity modulation of the fluorescence peaks is due to the periodic modulation of the excitation efficiency, which is determined by the optical mode density of the cavity at 532 nm.

Additionally, we observe a continuous decrease of the fluorescence intensities over the course of the measurements. This might be due to photobleaching of the organic molecules. Additionally, we suspect that the excitation efficiency decreases with increasing cavity length due to a narrowing of the k -vector distribution of resonant cavity modes as the cavity length increases.

2.3. Energy Transfer Efficiency

To investigate general trends in PMET efficiency, we have calculated the BRK to TDBC fluorescence intensity ratio as a function of mirror distance for 2M-DA-I and 2M-DA-II. This was done by averaging the fluorescence spectra over one modulation period as indicated by the horizontal brackets in Figure 4a and c, respectively, thereby performing a kind of moving average of about 50 spectra.

The respective averaged spectra are shown in Figure 4b and d. Within the same measurement, the spectra appear very similar. For each set of averaged spectra, the intensity ratios of BRK to TDBC are plotted in Figure 4e. The intensity ratios remain approximately constant for all investigated distances in a single sequence of spectra, supporting the assumption that PMET is independent of separation of the donor and acceptor layers on opposite mirrors.^[5,22] Between the two measurements, however, we observe significant differences in the obtained ratios. These are most likely due to inhomogeneities in the spin-coated films. When moving the μ m-screws between the measurements 2M-DA-I and 2M-DA-II to adjust the cavity distance, we most likely also changed the cavity position in the xy -plane, resulting in different concentrations of the two J-aggregates. (This also manifested in the transmission measurements, where we have observed small jumps in the obtained coupling energies at the transition point between 2M-DA-I and 2M-DA-II (see Figure S5 in the Supporting Information of our previous work).^[39])

2.4. Theoretical Modelling and Fitting of the Polariton Modes to the False-Color Fluorescence Maps

The emerging polaritonic modes in our system can be modelled by the phenomenological Hamiltonian^[39]

$$H_{\text{coupled}} = \begin{pmatrix} E_{\text{TDBC}} & 0 & \hbar g_{\text{TDBC}} & \hbar g_{\text{TDBC}} & \cdots & \hbar g_{\text{TDBC}} \\ 0 & E_{\text{BRK}} & \hbar g_{\text{BRK}} & \hbar g_{\text{BRK}} & \cdots & \hbar g_{\text{BRK}} \\ \hbar g_{\text{TDBC}} & \hbar g_{\text{BRK}} & E_{\text{cav},1} & 0 & \cdots & 0 \\ \hbar g_{\text{TDBC}} & \hbar g_{\text{BRK}} & 0 & E_{\text{cav},2} & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ \hbar g_{\text{TDBC}} & \hbar g_{\text{BRK}} & 0 & 0 & 0 & E_{\text{cav},N} \end{pmatrix} \quad (1)$$

where

$$E_{\text{cav},m} = m \frac{\pi \hbar c}{n L_{\text{cav}}} \text{ with } m = 1, 2, 3 \dots \quad (2)$$

Here, E_{TDBC} and E_{BRK} are the exciton energies of TDBC and BRK, respectively. As in our previous work,^[39] we chose $E_{\text{TDBC}} = 2.117$ eV and $E_{\text{BRK}} = 1.895$ eV. $\hbar g_{\text{TDBC}}$ and $\hbar g_{\text{BRK}}$ represent the exciton–photon coupling energies. $E_{\text{cav},m}$ is the energy of the m -th cavity mode of an ideal FP resonator, which is determined by the optical path length of the cavity $n L_{\text{cav}}$. $\hbar$ is the reduced Planck's constant, and c is the vacuum speed of light.

The eigenvalue equation of H_{coupled} characterizes the strongly coupled system: The resulting eigenvalues are the energies of the polaritons, and the eigenvectors can be used to calculate coefficients which indicate the fraction or relative contribution of the cavity modes and the excitons (sometimes called “Hopfield coefficients” and labeled $|\alpha^{\text{TDBC}}|^2$, $|\alpha^{\text{BRK}}|^2$, and $|\alpha^{\text{light}}|^2$, respectively) for each polariton mode, quantifying its hybrid light–matter nature.

Using the analysis of the respective transmission spectra performed in our previous work^[39] and the finding that fluorescence maxima correspond to resonance conditions of the laser wavelength (see Figure 4a,c), we fitted the polariton modes of H_{coupled} to the fluorescence maxima, with the coupling energies $\hbar g_{\text{TDBC}}$ and $\hbar g_{\text{BRK}}$ and the cavity length $n L_{\text{cav}}$ as fit parameters. Details are provided in the Supporting Information, including the obtained coupling energies and cavity lengths. The results are plotted as red lines in Figure 2, where we achieve good up to excellent agreement between the fluorescence maxima and the calculated polariton modes.

2.5. Modeling Fluorescence Intensities Using Rate Equations

For the measurements with both J-aggregates (2M-DA-I and 2M-DA-II), we observe the following general features in the fluorescence spectra: There is a small fluorescence peak at around 600 nm (2.07 eV), while most of the fluorescence occurs from the broad fluorescence band between 680 and 780 nm which is superimposed by sharp and narrow peaks. Their spectral positions are well explained by the fit to our polariton model.

We can interpret the cavity-dependent fluorescence spectra along the energy level diagram in Figure 5a: In a first step, most of the excitations of the system populate the TDBC exciton reservoir. Since most of the organic molecules are uncoupled^[45,47,48,50] and TDBC has a much stronger absorption than BRK at the laser excitation wavelength, direct excitation of the TDBC exciton reservoir should be prevalent. Additionally, fast nonradiative decay should occur from directly excited polaritons toward the TDBC exciton reservoir as reported previously.^[43–45] Radiative relaxation from the TDBC exciton reservoir leads to the small peak around

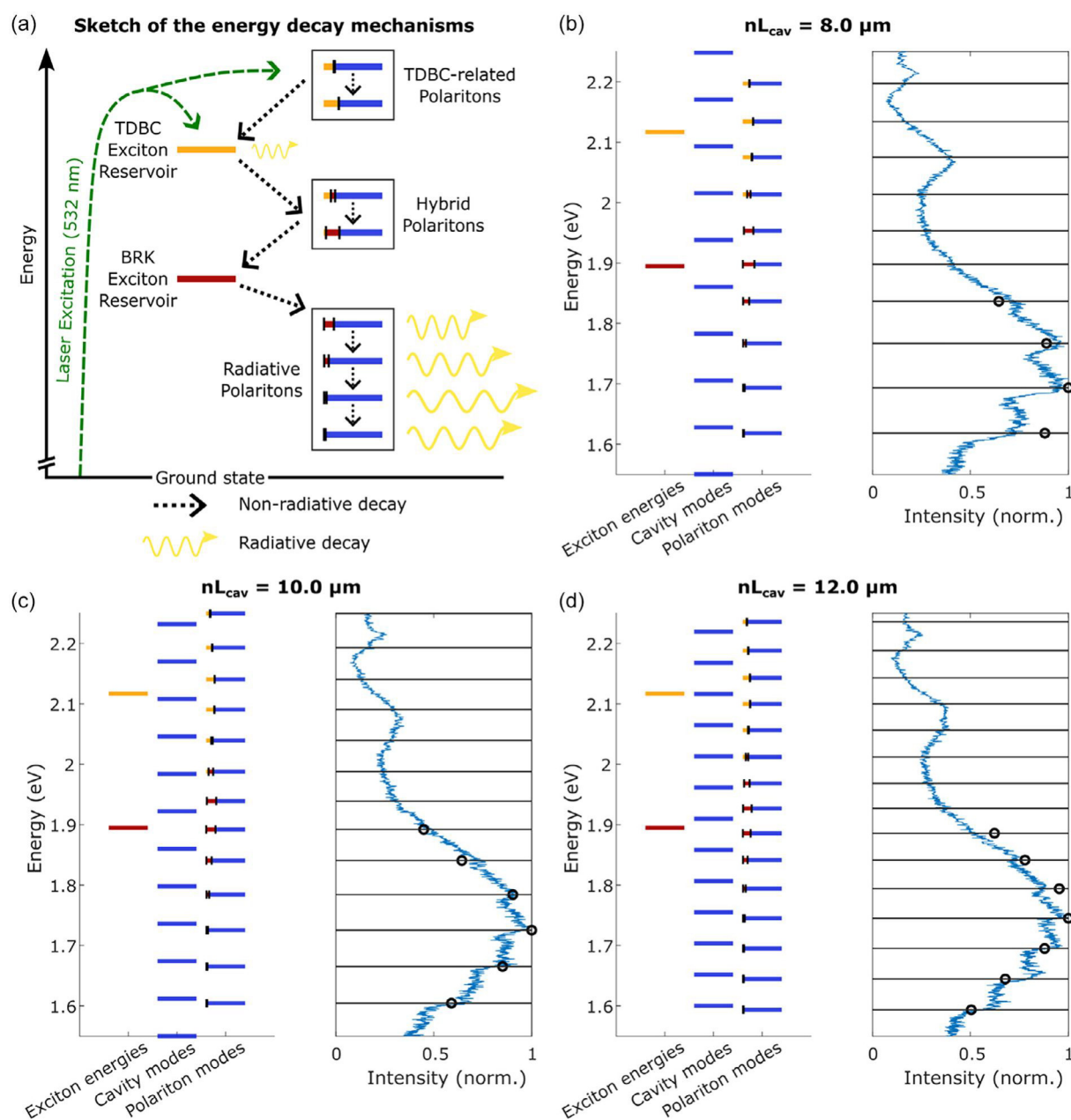


Figure 5. a) Sketch of the energy decay mechanisms for the strongly coupled cavity containing donor and acceptor (2M-DA-I/II). b–d) Three individual fluorescence spectra and corresponding best fits to H_{coupled} from 2M-DA-II with increasing mirror separation (8 μm in (b), 10 μm in (c), and 12 μm in (d)). In the left panels, we show the energies resulting from the fit of our model to the fluorescence false-color map in Figure 2d. For reference, the left and middle columns show the uncoupled energies of TDBC (orange) and BRK (red) together with the uncoupled cavity modes (blue). In the right column the resulting polariton modes are displayed. Here, we indicate the respective light and matter fractions by the length of the differently colored sections of the lines for each polariton mode ($|\alpha^{\text{TDBC}}|^2$ in orange, $|\alpha^{\text{BRK}}|^2$ in red, and $|\alpha^{\text{light}}|^2$ in blue). In the right panels, the corresponding fluorescence spectrum is shown (with the same y-axis as the left panels, which corresponds to the wavelength range of 550–800 nm). Horizontal black lines correspond to the energies of the polariton modes. Black circles show the results for the polariton emission intensities from our rate equation model. The small peak at 2.2 eV is an artifact from the laser system.

600 nm, which does not redshift with increasing cavity distance, in contrast to the polaritonic fluorescence peaks. Note the respective band in the spectra recorded without the bottom mirror (1M-DA-I, Figure 3d).

Aside from the radiative decays from the TDBC exciton reservoir, most of the energy, however, decays nonradiatively, leading to a local minimum of the fluorescence signal between the exciton reservoirs. Radiative decay dominantly occurs from polaritonic

states with slower energy than the BRK exciton reservoir, resulting in a broad fluorescence band at 680–780 nm superimposed by sharp and narrow peaks which results from the radiative decay of individual polaritonic states, with the most intense ones occurring around 720 nm. Their spectral positions are well described by the modeled polariton energies (see Figure 2 and 5b–d).

For the nonradiative decay processes from the TDBC exciton reservoir to the polaritonic states around 720 nm, the role of hybrid polaritonic states, which contain significant contributions from both TDBC and BRK, might be crucial in linking TDBC- and BRK-related polaritonic states. Notice that our model suggests that the formation of hybrid polaritons occurred for all investigated cavity distances during 2M-DA-I and 2M-DA-II (see Figure 5 and our previous work).^[39] Additionally, scattering to and from the BRK exciton reservoir might also play an important role in offering a fast decay path toward polaritonic states with lower energy than the BRK reservoir, which consequently suppresses radiative emission of polaritons with higher energy than the BRK exciton reservoir.

For the polaritonic states lower in energy than the BRK exciton reservoir, we observe radiative emission with an emission maximum around 720 nm. We propose that the resulting intensities of the individual polariton modes are the result of an increasing radiative rate due to the higher photonic character and a decrease in occupancy with lower energy. To further investigate this point, we use REs to describe the populations of the radiative polariton modes and the respective fluorescence intensities.

From the fit to H_{coupled} , we can, in addition to the energies, also calculate the different fractions ($|\alpha_i^{\text{TDBC}}|^2$, $|\alpha_i^{\text{BRK}}|^2$, $|\alpha_i^{\text{light}}|^2$) of the resulting polariton modes, as shown in Figure 5. For the RE model, we consider the polariton modes whose energies overlap with the broad fluorescence band between 1.55 and 1.895 eV. For the highest polariton mode ($i = 1$), we assume a constant pumping rate ϕ . Additionally, we assume two decay channels for each polariton mode, nonradiative decay toward the next lower polariton mode due to exciton–exciton scattering, which is proportional to the exciton fraction of the polariton $|\alpha_i^{\text{BRK}}|^2$ (the TDBC fractions are negligible for the polariton modes between 1.55 and 1.895 eV, as can be seen in Figure 5), and radiative decay, which is proportional to the light fraction of the polariton $|\alpha_i^{\text{light}}|^2$. We assume that the nonradiative decay rates k_{nrad} as well as the radiative rates k_{rad} are the same for all polariton modes, respectively, giving the following set of RE

$$\begin{aligned}\frac{dN_1}{dt} &= \phi - k_{\text{nrad}}|\alpha_1^{\text{BRK}}|^2 N_1 - k_{\text{rad}}|\alpha_1^{\text{light}}|^2 N_1 \\ \frac{dN_2}{dt} &= k_{\text{nrad}}|\alpha_1^{\text{BRK}}|^2 N_1 - k_{\text{nrad}}|\alpha_2^{\text{BRK}}|^2 N_2 - k_{\text{rad}}|\alpha_2^{\text{light}}|^2 N_2 \\ \frac{dN_3}{dt} &= k_{\text{nrad}}|\alpha_2^{\text{BRK}}|^2 N_2 - k_{\text{nrad}}|\alpha_3^{\text{BRK}}|^2 N_3 - k_{\text{rad}}|\alpha_3^{\text{light}}|^2 N_3 \\ &\vdots\end{aligned}\quad (3)$$

Under steady-state conditions, $dN_i/dt = 0$, the relative radiative intensities of the different polariton modes are then proportional to the steady-state population of the respective mode times the radiative decay rate times the light fraction, $I_i \propto N_i k_{\text{rad}} |\alpha_i^{\text{light}}|^2$.

Consequently, the only free parameter of the model is the ratio between the nonradiative scattering rate and the radiative decay rate, which determines the spectral position of the fluorescence maxima. We tested different ratios and obtained the best agreement with the experimental fluorescence spectra for $k_{\text{nrad}}/k_{\text{rad}} = 40$. This agrees with published ratios, which are between 2^[42] and 100.^[46]

In Figure 5b–d we plot the results of our RE model as black circles on top of three fluorescence spectra from 2M-DA-II. All three spectra show very good agreement between the fluorescence intensity maxima and the energies of the polariton modes. The arguably simple RE model describes the shape of the observed fluorescence band with the superimposed fluorescence peaks quite well.

3. Conclusion

In summary, we have investigated the fluorescence properties of different strongly coupled cavity configurations with J-aggregates of TDBC as the energy donor and BRK as the acceptor coupled to a tunable multimode FP resonator with several micrometers of mirror separation. The fluorescence behavior in the measurements with both J-aggregates strongly coupled to the microcavity is dominated by the radiative decay of acceptor-related polaritons, indicating efficient energy transfer from donor to acceptor. Fast nonradiative decay processes toward the exciton reservoirs in the presence of hybrid polaritons offer an efficient pathway from donor-related to acceptor-related states. The spectral shape of the radiative decay from acceptor-related polaritons results from the interplay of an increasing photonic character, which increases the radiative rate, and a diminishing steady-state population with decreasing polariton energy.

We observed efficient energy transfer to the energy acceptor, manifested in a high BRK fluorescence intensity, for all investigated distances (0 ... 11 μm layer-to-layer distance). This result is quite striking (notice that PMET at 2 μm ^[25] was already given the prefix “ultralong-range” by the respective authors). As a general trend, the energy transfer efficiency (manifested in the BRK to TDBC fluorescence intensity ratio) was largely independent of donor–acceptor distance within the same measurement. The large donor–acceptor separations in our system leave much space for further system integration, for example, optoelectronic or microfluidic systems. Hence, PMET could be of interest for, for example, (solar) energy conversion.

Limiting factors for achieving efficient PMET are most likely the presence of hybrid polaritons and the ratio of the nonradiative scattering rate to the radiative decay rate, $k_{\text{nrad}}/k_{\text{rad}}$, which must be large. Since we did not observe a breakdown of the acceptor fluorescence, it remains unclear where the (practically realizable) upper limit of donor–acceptor separations for PMET lies.

Finally, one may ask how the proposed mechanism for PMET relates to other energy transfer mechanisms. The most important intermolecular energy transfer mechanism for organic molecules is Förster resonance energy transfer (FRET),^[26] which originates from the near-field dipole–dipole interaction of an excited energy donor with an energy acceptor. We indeed found an analogy between PMET and FRET: By coupling the excitonic transitions with the cavity modes, the resulting polaritons spectrally

spread out and lead to an overlap between donor and acceptor, which is manifested in the hybrid polaritons. Similarly, an (energetic) overlap between the donor emission spectrum and the acceptor absorption spectrum is a crucial requirement for efficient FRET. The main difference between PMET and FRET is the distance dependence: In FRET the dipole–dipole coupling is dominated by the near field and hence scales as the inverse of the sixth power of the distance between the dipoles, whereas in PMET the donor and acceptor couple to a common cavity mode that can transport energy over very large distances with very low losses.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

donor–acceptor systems, Fabry–Pérot resonator, J-aggregates, photophysics, polaritons

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Supporting Information

Polariton-Mediated Energy Transfer in a Tunable Optical Multimode Microcavity Exceeding 10 μm

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Author contributions

JK and CK conceived the experiment. MM performed all measurements. MM and CK analysed the data. CK developed and implemented the fitting procedure and rate equations model. CK wrote the manuscript with inputs from all authors. AJM supervised the project, contributed to the discussion of the results, reviewed and edited the manuscript.

Experimental Section

Experimental procedures were similar to our previous work:^[1]

Preparation of J-aggregate stock solutions: 1 wt% of the J-aggregate TDBC (5,6-dichloro-2-[[5,6-dichloro-1-ethyl-3-(4-sulphobutyl)benzimidazol-2-ylidene]propenyl]-1-ethyl-3-(4-sulphobutyl)benzimidazolium hydroxide) [FEW Chemicals] or BRK (1-(3-Sulfopropyl)-2-(2-[[1-(3-sulfopropyl)naphtho[1,2-d]thiazol-2(1H)-ylidene]methyl]-1-butenyl)naphtho[1,2-d]thiazoliumhydroxide) [ORGANICA Feinchemie] and 3 wt% of Poly(vinyl alcohol) (PVA) [Mowiol 40-88, Sigma-Aldrich] were dissolved in deionized water at room temperature. These solutions were stored in the dark at 8°C for up to two months and spin coated on the respective resonator mirrors as needed.

Spin coating: 20 µl of the J-aggregate stock solution were spin coated at 5000 rpm. For the measurements presented in this work, the TDBC-solution was spin coated onto the top mirror and the BRK-solution was spin coated onto the bottom mirror of the cavity. The resulting films had a thickness between 500 and 600 nm, as measured with a Bruker Dektak XT-A profilometer.

Cavity preparation: The preparation of optical resonators was performed similar to previous works of our group:^[2-5] For the bottom mirror, a cleaned glass coverslip was coated with 4 nm Cr, 70 nm Ag and 75 nm Al₂O₃ using electron beam evaporation (EDWARDS EB3 for Cr and Ag; Pfeiffer Vacuum PLS 570 for Al₂O₃). For the top mirror, the same procedure was performed, but with a plano-convex lens (LA1433, Thorlabs; Diameter 25.4 mm, Radius of Curvature 77.3 mm) as a substrate instead of the glass coverslip.

After spin coating the J-aggregate solutions onto the mirrors, the two mirrors were fixed in a custom-build cage system containing three µm-screws and piezo-actuators (KC1-PZ/M, Thorlabs) which were used to adjust the position of the top mirror relative to the bottom mirror. Before the cavity was installed into the custom-built confocal microscope, the µm-screws were used to approach the top mirror towards the bottom mirror until Newton's rings became visible (at the spatial position where the top mirror (lens) is approximately parallel to the bottom mirror (coverslip)), signifying that the mirror separation is on the order of visible wavelengths.

Optical measurements: Optical measurements were performed on a custom-built confocal microscope. Transmission spectra were performed and analysed in our previous work. Fluorescence measurements were performed by coupling a laser (532 nm; Coherent COMPASS 215M-75 SL) into the objective and blocking the reflected laser light by two RazorEdge Long Pass (LP) E-Grade 532 filters. Additionally, we placed a camera (motiCam 2000) behind the top mirror to record the transmitted laser intensity.

Free space spectra: Concerning the free space spectra presented in Figure 1(c): Absorption spectra were measured from PVA thin films using a UV-Vis-NIR spectrophotometer (PerkinElmer Lambda 19). Emission measurements were measured from PVA thin films using the custom-build microscope setup described above.

Software: Data evaluation was performed using MATLAB R2021a.

False-Color Fluorescence Map for the Measurement with One Mirror Removed (1M-DA-I)

In Figure S1 we show the series of fluorescence spectra for the measurement configuration 1M-DA-I (bottom mirror exchanged for a pristine coverslip, same voltage range as 2M-DA-I). The average spectrum of this series is shown in Figure 3(d) of the manuscript.

At around 600 nm, we observe the TDBC fluorescence peak, which is modulated as a function of spectrum number. This modulation is most likely due to the formation of an optical cavity between the Ag mirror and the pristine coverslip which modulates the optical mode density at the excitation wavelength similar to 2M-DA-I/II (but less pronounced).

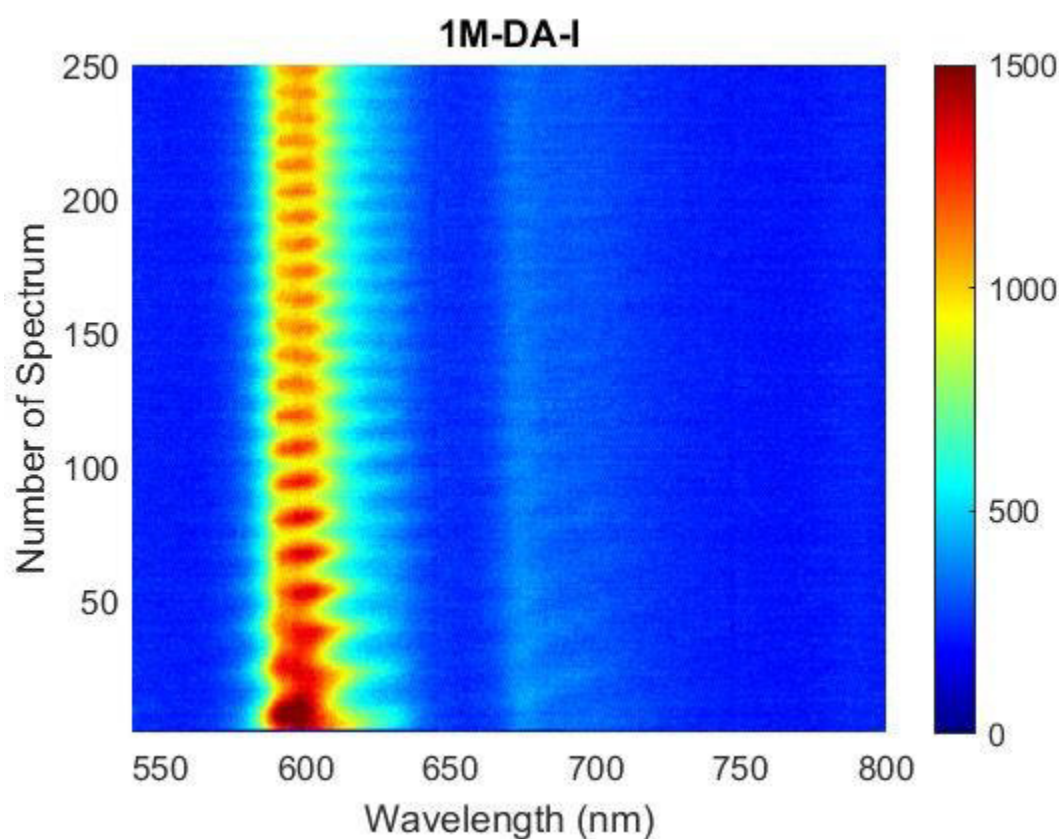


Figure S1. Series of fluorescence spectra for 1M-DA-I plotted as false-color map.

Total Intensity vs. Laser Transmission

In Figures S2 and S3 we show the spectrally integrated fluorescence intensity along with the transmitted laser intensity for 2M-D and 2M-A, respectively, complementing Figure 4(a,c), where we show the same for 2M-DA-I and 2M-DA-II.

Generally, we observe the same features as described in the manuscript for 2M-DA-I/II: A strong correlation between the total fluorescence intensity and the transmitted laser intensity along with a continuous decrease of the fluorescence signal.

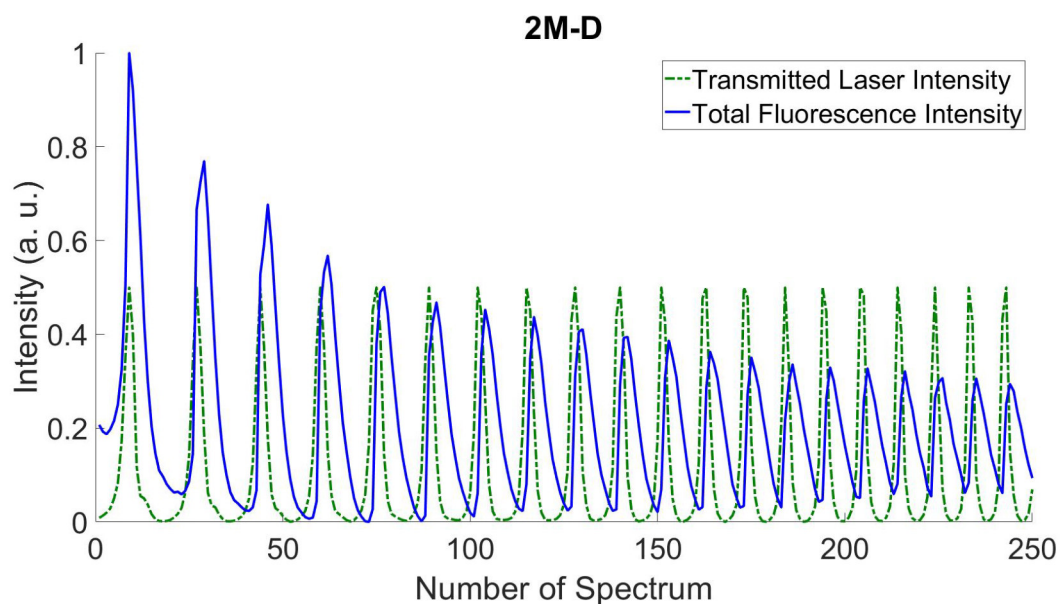


Figure S2. Spectrally integrated intensity (blue line) and transmitted laser intensity (green line) as a function of the cavity length represented by the spectrum number for 2M-D.

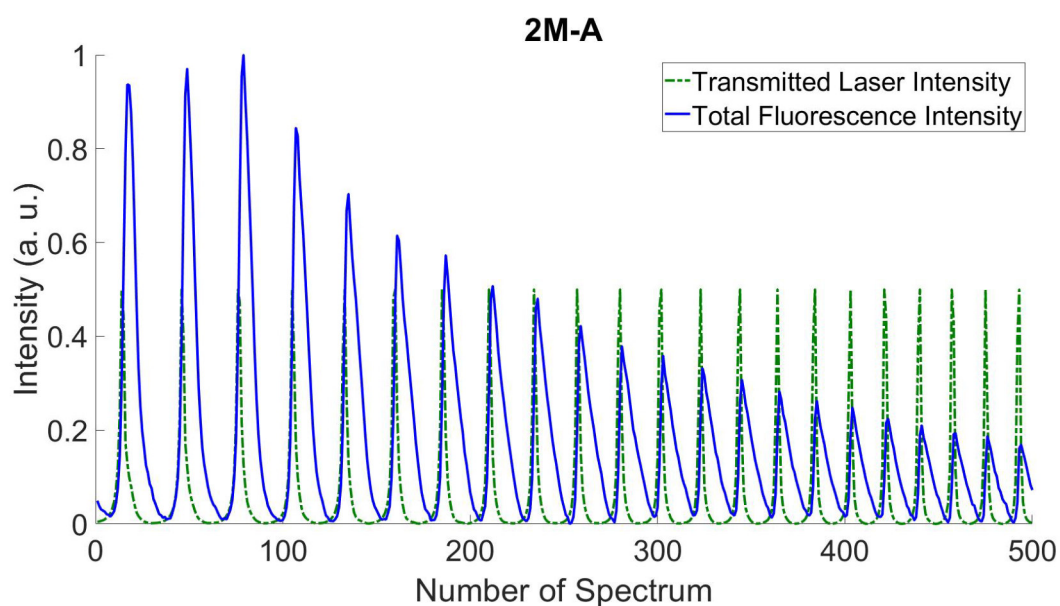


Figure S3. Spectrally integrated intensity (blue line) and transmitted laser intensity (green line) as a function of the cavity length represented by the spectrum number for 2M-A.

Fitting Procedure to fit Polariton Modes to the False-Color Fluorescence Maps

In our previous work,^[1] we treated the coupling energies $\hbar g_{TDBC}$ and $\hbar g_{BRK}$ as well as the cavity length nL_{cav} as parameters and fitted them to the acquired transmission data. For the coupling energies we observed a decrease as $\hbar g = A \cdot (nL_{cav})^{-1/2}$. The results of these fits are summarized in Table S1. We had also determined that the difference between the optical path length nL_{cav} and the donor-acceptor separation for 2M-DA-I/II is about 1.5 μm . Therefore, the investigated donor-acceptor separations range from 0 to 11.3 μm .

Table S1. Results for the fits to $H_{coupled}$ for the four cavity configurations. From the transmission measurements, we obtained the “coupling strength” A , which is related to the coupling energy $\hbar g$ via $\hbar g = A \cdot (nL_{cav})^{-1/2}$ (second and third column), and the optical path length nL_{cav} (fourth column). For the fluorescence measurements, we recalculated the optical path lengths (fifth column).

	Coupling strength A ($\text{eV (nm)}^{1/2}$) for $\hbar g_{TDBC}$	Coupling strength A (eV ($\text{nm)}^{1/2}$) for $\hbar g_{BRK}$	Range of nL_{cav} (μm):	
			Transmission measurements	Fluorescence measurements
2M-D	5.5	-	2.456 ... 7.850	3.403 ... 8.704
2M-A	-	4.0	1.138 ... 7.040	0.690 ... 6.495
2M-DA-I	3.5	3.5	1.433 ... 7.210	1.426 ... 7.026
2M-DA-II	3.5	3.5	7.260 ... 12.800	7.322 ... 12.860

With these results as a starting point, we developed a procedure to fit polariton modes to the fluorescence peaks in Figure 2: During measurements, we observed certain offsets between the achieved distances of transmission and fluorescence measurements due to heating of the cavity by the white light source and hysteresis of the piezo actuators. Consequently, we cannot assume that the distances obtained from the transmission measurements also hold for the fluorescence measurements, although they should be rather close. For the coupling energies, on the other hand, we used the energy-distance relationships we derived in our previous work.

To calculate the cavity distances during the fluorescence measurements, we use the finding that the fluorescence intensity maxima correspond to situations where a polariton mode is on resonance with the excitation laser wavelength (532 nm). We assign subsequent fluorescence maxima to subsequent resonance conditions and interpolate for the remaining spectra. Then, the only free parameter is the assignment of the first maximum.

The procedure consists of the following steps:

- Using $H_{coupled}$ and the coupling energies from the transmission measurements, we calculate the cavity distances for which there is a cavity mode resonant with 532 nm.
- We identify the peaks in the spectrally integrated fluorescence signal using MATLAB’s “findpeaks”-function.
- We assume that subsequent fluorescence peaks correspond to subsequent resonance conditions. Therefore, the only free parameter is the assignment of the first resonance / fluorescence maximum.
- After the assignment, we use MATLAB’s “interp1”-function to interpolate the distances for the spectra without fluorescence maximum.

- To choose the correct assignment, we compare the resulting distances with the distances from the transmission measurements. Additionally, we plot the resulting polariton modes (using $H_{coupled}$ with the previously derived energy-distance relationships) and manually check if the resulting polariton modes match with the fluorescence maxima.

The newly chosen distances are shown in Figure S4 as blue lines. Blue dots mark the spectra with fluorescence maxima. For comparison, we show the cavity distances calculated from the transmission measurements as red dotted lines.

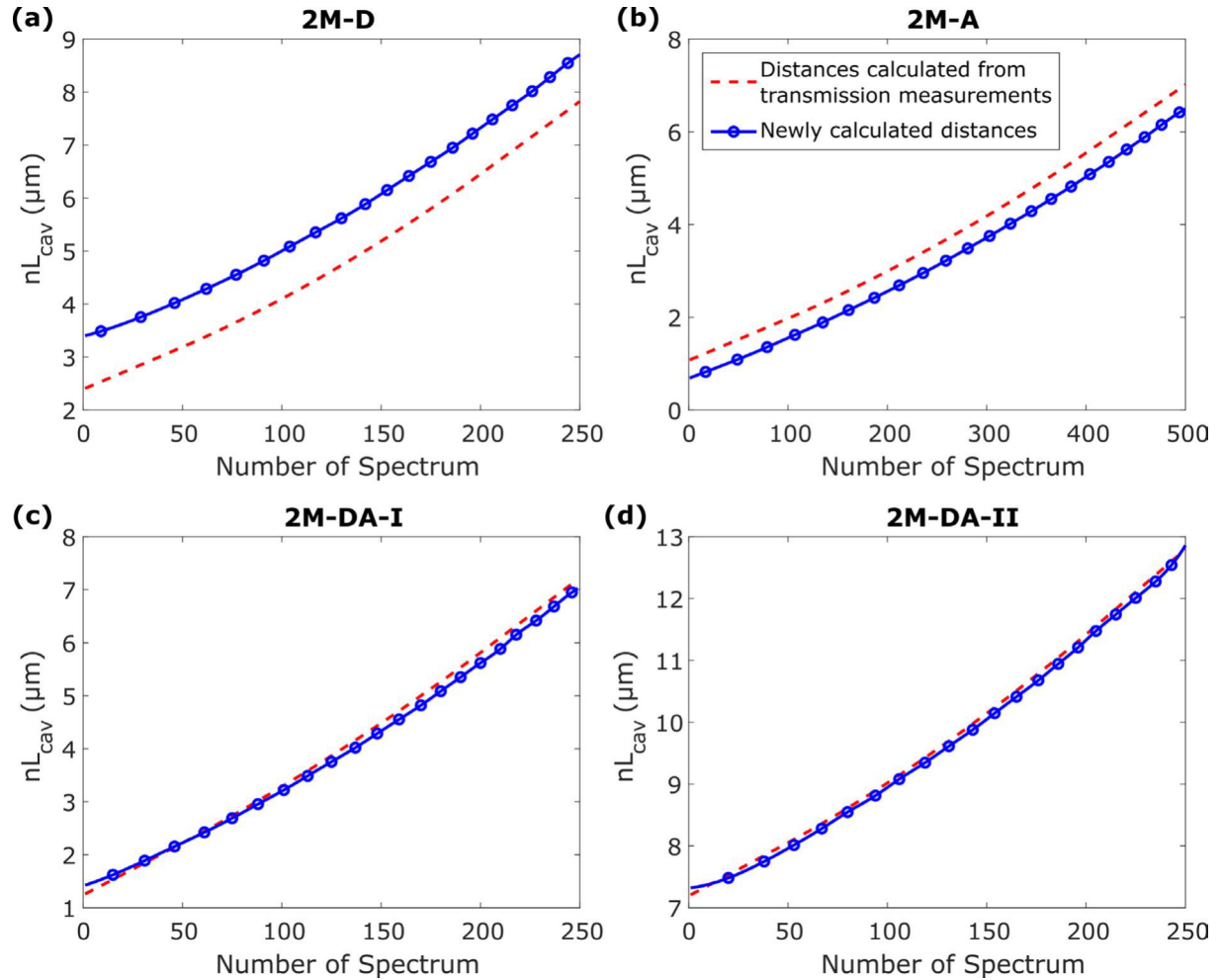


Figure S4. Comparison of the calculated cavity distances nL_{cav} for all four cavity configurations (2M-D in (a), 2M-A in (b), 2M-DA-I in (c) and 2M-DA-II in (d)). Calculated distances from our previous work based on transmission measurements are displayed as red dotted lines. The newly calculated distances from fluorescence measurements are displayed as blue solid lines. Blue circles mark spectra with a maximum in the total fluorescence signal.

Using the newly calculated distances (see Figure S4 and Table S1), which deviate from the distances calculated from the transmission measurements by only a few up to a few hundred nm, we achieve good up to excellent agreement between the fluorescence maxima and the calculated polariton modes, which are plotted as red lines in Figure 2. Note that the polariton modes (red lines) cross the laser excitation wavelength (532 nm, vertical green line) at the total fluorescence maxima (horizontal black lines), which is how the fitting procedure was set up.

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