Cavity-Free Ultrastrong Light-Matter Coupling

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ABSTRACT: Strong coupling between light and matter can occur when the interaction strength between a confined electromagnetic field and a molecular resonance exceeds the losses to the environment, leading to the formation of hybrid light–matter states known as polaritons. Ultrastrong coupling occurs when the coupling strength becomes comparable to the transition energy of the system. It is widely assumed that the confined electromagnetic fields necessary for strong coupling to organic molecules can only be achieved with external structures such as Fabry–Pérot resonators, plasmonic nanostructures, or dielectric resonators. Here, we show experimentally that such structures are unnecessary and that a simple dielectric film of dye molecules supports sufficiently modified vacuum electromagnetic fields to enable room-temperature ultrastrong light-matter coupling. Our results may be of use in the design of experiments to probe polaritonic chemistry and suggest that polaritonic states are perhaps easier to realize than previously thought.

Light–matter interactions can occur when an ensemble of molecular resonators is placed in a confined electromagnetic field. If the molecular resonance and confined electromagnetic field mode occur at similar energies, they can become coupled. When the coupling strength exceeds the losses of the uncoupled modes, the system can enter the so-called strong coupling regime. In this regime, two hybrid states called the upper and lower polariton bands appear, separated by the Rabi splitting energy \( \Omega \), inheriting both molecular and photonic properties. When the coupling strength is comparable to the transition energy of the system \( E_0 \) (typically taken to be when \( \Omega/E_0 > 20\% \)) the system is said to be in the ultrastrong coupling regime. Recent studies have explored the effect of strong and ultrastrong coupling on phenomena such as lasing, Bose–Einstein condensation, and the modification of the emission and absorption of light in organic optoelectronic devices, while the nascent field of polaritonic chemistry explores the possibility of the coupling of molecular energy levels and light in modifying chemical processes.

Understanding the effect of strong coupling on exciton transport in organic systems could also lead to new insights in photosynthesis. Strong coupling of light and organic molecules has been extensively studied, but experiments have typically relied on external structures such as planar microcavities, plasmonic nanostructures, and dielectric resonators (including Mie resonators and dielectric slabs). The use of these structures has provided valuable insights into strong light–matter coupling but they are generally impractical for applications such as polaritonic chemistry, where they restrict access to the molecules involved. Furthermore, the high level of precision required when designing these structures (such as the thickness of a microcavity or the geometric parameters of a plasmonic lattice) implies that polaritonic effects are unlikely to play a significant role in natural processes.

In this work, we show that strong light–matter coupling can occur in extraordinarily simple systems. We experimentally demonstrate ultrastrong coupling between the molecular resonances and confined electromagnetic fields in thin (<1 \( \mu \text{m} \)) soft dielectric films with visible light at room temperature. Our results rely on leaky modes arising from the impedance mismatch between the dielectric thin film and a silicon substrate. Georgiou et al. have previously explored the use of leaky modes in strong coupling with an external dielectric slab microcavity. Similar strong coupling has been observed in transition metal dichalcogenide (TMDC) films (where Fabry–Pérot resonances within the film can couple to the excitonic resonances in the TMDC), but these results are difficult to carry over to polaritonic chemistry. Unlike the recent study of strong coupling in self-assembled organic semiconductors by Rao et al., our sample fabrication only uses spin-coating, and our coupling strengths are an order of magnitude greater. Our results suggest that polaritonic effects...
might be much more prevalent than previously thought, paving the way for simplified strong coupling experiments.

We studied dielectric thin films of organic molecules deposited on silicon substrates by spin-coating (schematic in Figure 1a; see Supplementary Section S1 for fabrication details). We used spiropyran (SPI), a widely used molecule in strong coupling experiments. SPI is a transparent molecule that, when exposed to ultraviolet radiation, undergoes photoisomerisation to merocyanine (MC), which has a strong absorption peak at 2.22 eV (molecular structure and transmission spectrum in Supplementary Section S2). MC can then be reconverted to SPI after exposure to visible radiation. The optical constants for our SPI and MC films are given in Figure 1c; they were determined using spectroscopic ellipsometry (with SPI fitted to a Cauchy dielectric model and MC to a Lorentzian model - see Supplementary Section S1 for fit parameters). The measured optical constants suggest that MC can support bulk polaritons with a Rabi splitting large enough to allow ultrastong coupling (see Supplementary Section S3). The large contrast in permittivity between the SPI/MC films (ε_{SPI} = 2.58 at 2.22 eV) and the Si substrate (ε_{Si} = 16.3 at 2.22 eV), and between the SPI/MC films and the air superstrate leads to the formation of a series of leaky modes in the film for both transverse electric (TE) and transverse magnetic (TM) polarized light. Our “leaky” modes are leaky in the sense that, while tied to the layer of interest, they are radiative in the upper half space. Our nomenclature of “leaky” modes is common in the literature,31 although we note that these modes are also referred to as quasi-normal modes.32

We characterized our samples using spectroscopic ellipsometry (schematic in Figure 1b). Ellipsometry measures the complex reflection ratio ρ in terms of the parameters Ψ and Δ:

\[ \rho = \frac{r_p}{r_s} = \tan(\Psi) e^{i\Delta} \]

where \( r_p \) and \( r_s \) are the Fresnel reflection coefficients for p- and s-polarized light, respectively. tan(Ψ) is the amplitude of ρ and gives the ratio of the moduli of \( r_p \) and \( r_s \). Δ is the difference in the phase shifts undergone by p- and s-polarized light upon reflection. Ellipsometry is an ideal tool for our experiment.28 It allows one to clearly distinguish between TM leaky modes (when \( r_p \to 0 \), tan(Ψ) \to 0 and so Ψ \to 0°) and TE leaky modes (when \( r_s \to 0 \), tan(Ψ) \to ∞ and so Ψ \to 90°) in the same amplitude spectrum. Each ellipsometry spectrum can be used to both characterize any strong coupling and determine the thickness and optical constants of the sample under interrogation. Our choice of ellipsometer (J. A. Woollam Co. M-2000X) allows us to collect spectra over a range of steeper incident angles (45°–75°) at which leaky modes occur; its Xe arc lamp emits a small quantity of ultraviolet radiation which allows us to easily measure the transition from SPI to MC (and so the transition from weak to strong coupling). Additionally, since ellipsometry measures the ratio of two quantities it is a very low-noise measurement technique.

In Figure 2 we plot Ψ spectra for (a) SPI and (b) MC films for film thicknesses in the range 84 nm < L < 680 nm and for a fixed angle of incidence θ = 65°. Both plots are reproduced well by calculations (see Figures 2c,d). These calculations are based on a Fresnel approach, similar to the commonly used transfer-matrix approach. The corresponding plots of ellipsometric phase data are given in Supplementary Section S4. Plotting data for such a large range of thicknesses allows us to observe the coupling of the first-, second-, and third-order TE modes to the MC resonance. Since the reflection of p-polarized light at a SPI/MC-Si interface is considerably weaker than for s-polarized light,34 the TM leaky modes have a lower quality factor than the equivalent-order TE modes. We therefore restrict our analysis to the TE modes, which all show a clear anticrossing, a key signature of strong coupling.3 The lack of evidence for any mid-polariton bands in Figure 2 suggests that the polariton branches in our system are best modeled by a 2N coupling matrix.35 In this case, the coupling between the MC resonance and the jth-order TE leaky mode can be described by the following matrix equation:

\[
\begin{pmatrix}
E_{MC} & g \\
0 & E_{TEj}\end{pmatrix} \begin{pmatrix} a_{(L, U)} \\
0 \end{pmatrix} = E_{(L, U)} \begin{pmatrix} a_{(L, U)} \\
0 \end{pmatrix}
\]

where \( E_{MC} \) is the energy of the MC resonance, \( g \sim \Omega/2 \) is the coupling strength, \( E_{TEj} \) is the jth-order TE leaky mode energy, \( a_{(L, U)} \) are the energies of the lower and upper polariton bands associated with the jth TE leaky mode, and \( |a_{(L, U)}|^2 \) and \( |b_{(L, U)}|^2 \) are the Hopfield coefficients describing the mixing of the MC resonance with the jth TE leaky mode.

The fits are plotted as the black lines in Figure 2b. The best fit to the data was obtained with \( \Omega = 550 \text{ meV} \). This fulfills the strong coupling resolution criterion:

\[ \Omega_{TE1,2,3} > \frac{1}{2}(\gamma_{MC} + \gamma_{TE1,2,3}) \]

where \( \gamma_{MC} \approx 360 \text{ meV} \) is the line width of the MC resonance and \( \gamma_{TE1,2,3} \approx 310 \text{ meV} \). This fulfills the strong coupling resolution criterion:

\[ \frac{\Omega}{E_{MC}} > 20\% \]
where $E_{MC}$ is the MC molecular resonance. Analyzing the data for a fixed, oblique incident angle produces an overestimate of $\Omega$ which must be taken into account in ultrastrong coupling experiments. Supplementary Section S5 shows a dispersion plot (energy versus in-plane wavevector) of the TE$_2$ leaky mode coupling to MC. In this case, the best fit is achieved with $\Omega = 500$ meV, which still fulfills the ultrastrong coupling criterion. In Supplementary Section S6, we plot $\rho$ to study the transition from weak to strong coupling of the MC resonance and TE$_2$ leaky mode and observe a change in ellipsometric topology consistent with our previous observations in strong coupling experiments.28 In Supplementary Section S7, we model the absorption of MC and show that the observed anticrossing is a signature of genuine strong coupling and not just an artifact of ellipsometry.

Leaky electromagnetic modes are, by definition, not an obvious way of confining electromagnetic fields for strong coupling experiments, yet we have shown that they allow for coupling in the strong and ultrastrong coupling regimes. Supplementary Section S5 shows a dispersion plot (energy versus in-plane wavevector) of the TE$_2$ leaky mode coupling to MC. In this case, the best fit is achieved with $\Omega = 500$ meV, which still fulfills the ultrastrong coupling criterion. In Supplementary Section S6, we plot $\rho$ to study the transition from weak to strong coupling of the MC resonance and TE$_2$ leaky mode and observe a change in ellipsometric topology consistent with our previous observations in strong coupling experiments.28 In Supplementary Section S7, we model the absorption of MC and show that the observed anticrossing is a signature of genuine strong coupling and not just an artifact of ellipsometry.

Leaky electromagnetic modes are, by definition, not an obvious way of confining electromagnetic fields for strong coupling experiments, yet we have shown that they allow for coupling in the strong and ultrastrong coupling regimes. Calculations suggest the impedance mismatch between the SPI/MC film and the Si substrate is high enough to generate a strong electromagnetic field within the film. We have compared the electric field enhancement from a TE$_2$ mode in SPI with the field enhancement arising from a second-order microcavity mode in a metal-clad cavity for $0^\circ \leq \theta \leq 85^\circ$, calculated using finite-element modeling (COMSOL Multiphysics 5.5). In both cases, the substrate was silicon and the SPI thickness was 294 nm (to match the TE$_2$ mode in Supplementary Sections S5–S6). In the microcavity calculations, the SPI layer was placed between two Ag films of thickness 40 nm. At normal incidence, the peak field enhancements of the microcavity and leaky modes differ by less than a factor of 2. As the incident angle is increased, the field enhancement increases for leaky modes and decreases for microcavity modes. For $\theta = 65^\circ$ (the angle of incidence used for all our experiments), the leaky mode field enhancement in our system is as much as 77% of the cavity mode field enhancement in a metal-clad microcavity. This is roughly consistent with the difference between the Rabi splitting measured for coupling between the TE$_2$ and MC resonance in Supplementary Section S5 ($\Omega = 550$ meV) and the Rabi splitting previously measured in a metal-clad microcavity by Schwartz et al.27 ($\Omega = 700$ meV). We note that the impedance mismatch between Si and SPI/MC is not dissimilar to the impedance mismatch between TMDCs and the SiO$_2$ substrate used to achieve self-coupling of light and matter in TMDCs.24 An important difference between the two systems is that while self-coupling in TMDCs relies on their high (15–20) dielectric constants to confine light, SPI/MC films have a relatively low dielectric constant (2.5). Calculations presented in Supplementary Section S8 suggest that, provided the substrate permittivity is greater than the thin film’s permittivity, only a
in strong coupling experiments might be complimented by the simple slab geometry shown here. Furthermore, our results suggest care must be taken when designing control samples used to determine the influence of strong coupling on chemical processes: it is possible, for example, that polaritonic modes will remain even after removing the top mirror from a metal-clad microcavity. In summary, our results suggest a new, simple way of achieving strong and ultrastrong light–matter coupling which will be useful in polaritonic chemistry experiments.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c01695.

Experimental methods; SPI/MC chemical structure and MC transmittance spectrum; calculation of bulk polariton splitting in MC; SPI/MC on Si \( \cos(\Delta) \) plot; SPI/MC on Si ellipsometry spectra plotted as a function of in-planewavevector; SPI/MC on Si change in ellipsometric topology; modeling of absorption of SPI/MC film on Si; effect of substrate permittivity on strong coupling; SPI/MC on SiO\(_2\) \( \Psi \) and \( \Delta \) plots; field profiles of Fabry–Pérot and leaky modes (PDF).

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Notes

The authors declare no competing financial interest.

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