

Supporting Information for

Quantum Yield of Polariton Emission from Hybrid Light-Matter States

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I. Anti-crossing of strongly coupled system

In order to ascertain the nature of the hybrid states, we measured the cavity's dispersion properties by acquiring the angle-dependent transmission. Figure S1 presents two different dispersion diagrams of TDBC layer at the edge ($\hbar\Omega_{\text{VR}} = 310$ meV) and in the center ($\hbar\Omega_{\text{VR}} = 503$ meV) of $\lambda/2$ cavity.

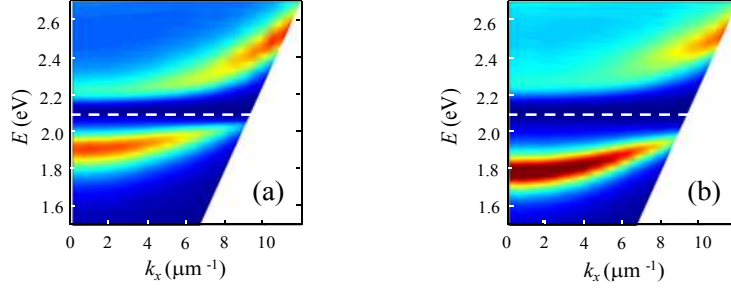


Figure S1. Angle-dependent dispersion of TDBC layer at the edge (a) or in the center (b) of the $\lambda/2$ cavity.

II. Transmission spectra simulated by transfer matrix formalism

In order to model the spectral properties of the microcavities, we used the standard formalism of the transfer matrix method (TMM). It relies on solving Maxwell's equations at each interface of a multilayer stack, each layer being characterized by a complex refractive index. The refractive index of the metallic mirrors and of the PMMA spacer layers were obtained from regular data bases.¹ The complex refractive index of the molecular layer is retrieved from the TDBC bare film absorption spectrum using the Kramers-Krönig relations. The thicknesses of the PMMA spacer layers were measured from the Fabry-Perot transmission peaks of the cavity containing no TDBC. By fitting the transmission spectra predicted by TMM to the experimental ones, we deduce a thickness of 27 nm for the molecular layer. All the parameters of the stack having been determined, the TMM was used to model the transmission spectra of a set of cavities with the TDBC layer in different spatial position inside the cavity (z from edge to the center) as shown in Figure S2.

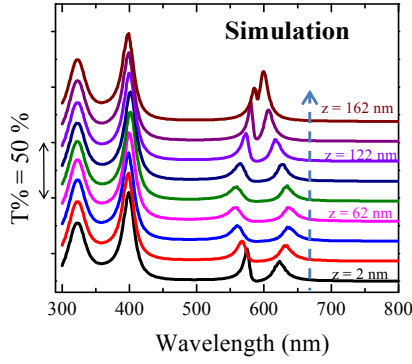


Figure S2. Simulated transmission spectra of a set of λ cavities with TDBC molecular layers in different spatial position inside the cavity (z from edge to the center as indicated by the arrow) offset from each other.

III. Fluorescence quantum yield (QY) measurement

In order to assess the fluorescence quantum yield of strongly coupled TDBC we performed a relative measurement as detailed in reference.² This standard approach is to compare the emission over absorption ratio of the sample to that of a reference of known absolute quantum yield. One writes:

$$\Phi_s = \Phi_r \cdot \frac{I_s}{f_s(\lambda_{ex})} \cdot \frac{f_r(\lambda_{ex})}{I_r} \cdot \frac{n_s^2(\lambda_{em})}{n_r^2(\lambda_{em})} \quad (S1)$$

where Φ_s (Φ_r) is the quantum yield of the sample (reference), I_s (I_r) is the integrated emission intensity of the sample (reference) when pumped at λ_{ex} , $f_s(\lambda_{ex})$ ($f_r(\lambda_{ex})$) is the absorption fraction at this same pumping wavelength and $n_s^2(\lambda_{em})$ ($n_r^2(\lambda_{em})$) is the refractive index of the sample (reference) environment at the average emission wavelength. The protocol proposed here is composed of three steps. First, we measured the absolute quantum yield of a standard dye (Lumogen Red, LR) in a chloroform solution using a commercial integrating sphere setup. This value was then used as a reference for computing the quantum yield of a thin polymer film containing the same standard dye, using Equation (S1). Finally, we obtain the quantum yield of strongly coupled TDBC by comparison to this new reference quantum yield, again using the same equation. Absorption fractions were measured using Shimadzu UV3101 spectrometer at 520 nm (excitation wavelength) (see spectra in Figure 3Sa). In the case of strongly coupled TDBC, this corresponds to non-resonant excitation of the polaritons but the same values were obtained by exciting at 550 nm. The fluorescence spectra were recorded using Fluorolog-3 fluorimeter and the emission intensity was integrated over the emission band (see for instance Fig. 3Sb). For strongly

coupled TDBC, we only integrated the emission spectrum over deconvoluted P- region as the P+ state is not radiative in our conditions. An example of deconvolution is shown below in Figure S3c. It should be noted that since our Fluorolog emission spectrometer has a small numerical aperture of detection, it only collects P- emission over a small range of angles around the bottom of its dispersion branch. By performing angle-resolved photoluminescent measurements on P-, we took into account the anisotropy of the emission.

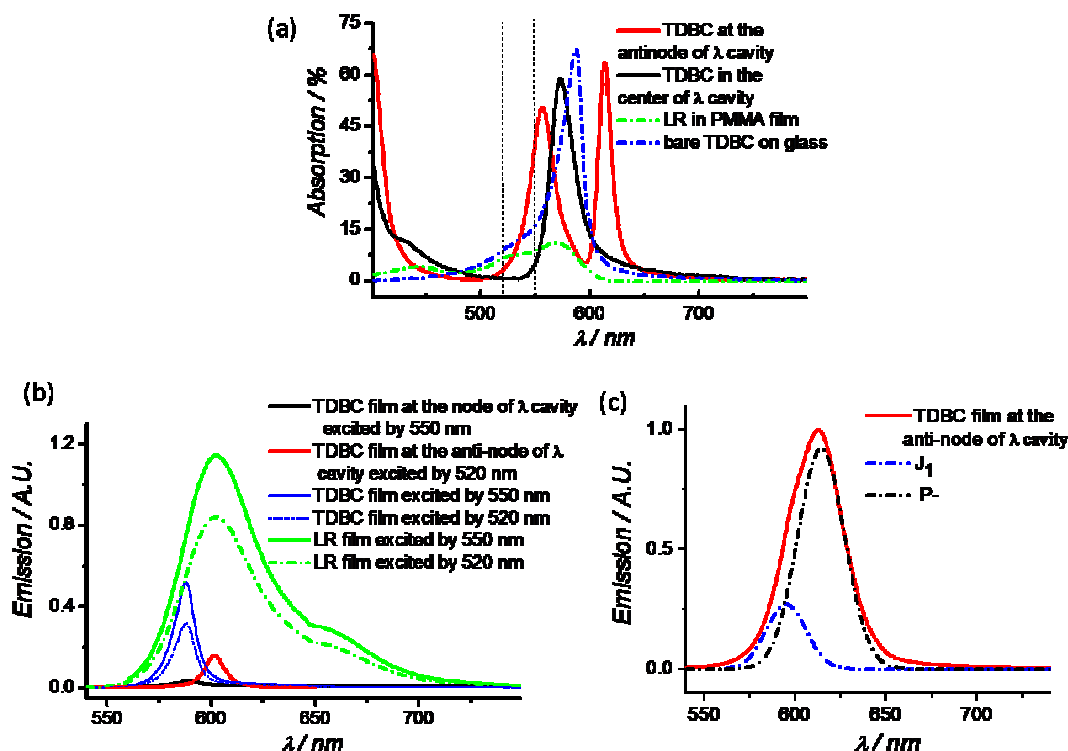


Figure S3. Absorption (a) and emission spectrum (b) of bare LBL TDBC film on quartz substrate, the TDBC film at the anti-node and in the center of the λ cavities, and the reference Lumogen Red in PMMA film (with calibrated QY = 0.3). (c) Example of deconvolution of the emission spectra to determine the contribution of P- and J_1 .

IV. Transient absorption measurements

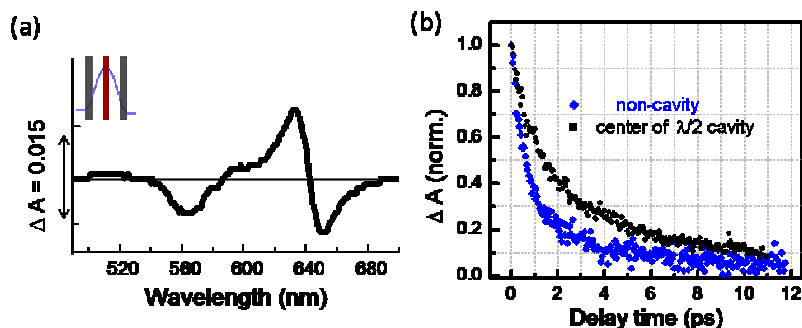


Figure S4. (a) Transient absorption spectrum of TDBC molecular layers in the center of a $\lambda/2$ cavity characteristic of P-. (b) Decay of the coupled state (independent of wavelength) compared to that of TDBC in the absence of a cavity (non-cavity).

References:

- (1) Johnson, P. B.; Christy, R. W. Optical constants of the noble metals. *Phys. Rev. B* **1972**, 6, 4370-4379.
- (2) Würth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U. Relative and absolute determination of fluorescence quantum yields of transparent samples. *Nature protocols* **2013**, 8, 1535-1550.