

Polariton assisted photoemission from a layered molecular material: Role of vibrational states and molecular absorption

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S1 Experimental setup

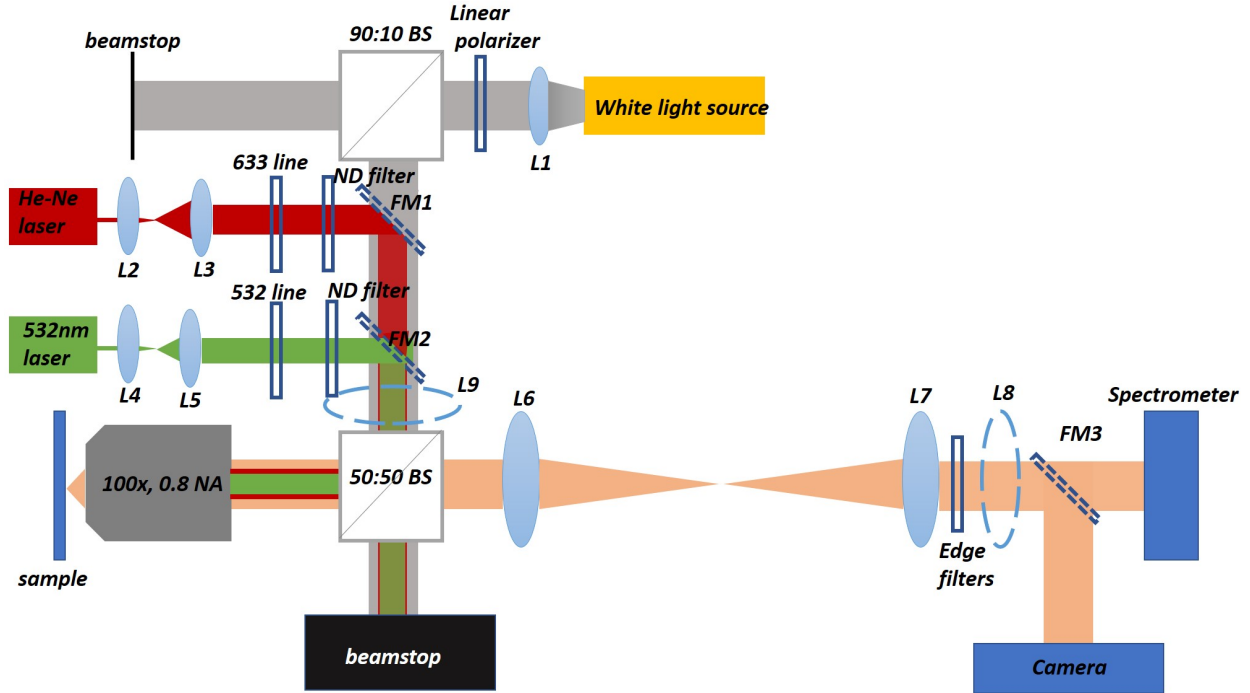


Figure S1: Schematic of the experimental setup used to probe individual microcavity

Figure S1 shows a schematic of the experimental setup. To measure angle resolved reflectivity, a white light source was focused onto the sample using a 0.8 NA 100x objective lens and the reflected signal was collected using the same lens. Lens L6 and L7, together, project the backfocal plane of the objective lens either to the spectrometer or to the camera, depending on the position of flip mirror FM3. Lens L8 was a fliplens used to project the real plane to the spectrometer/camera. For Photoluminescence (PL) measurements, beam expanded 532 nm DPSS or 633 nm HeNe lasers were focused using the objective lens and the PL was collected in the backscattering configuration. The laser line was then rejected using spectral edge filters placed after lens L7. For $k \sim 0$ excitation, we place lens L9 in the input path such that laser will be focused to the back aperture of the objective lens resulting in an approximate parallel beam with $k \sim 0$ at the sample plane.

S2 Hopfield analysis- Microcavity coupled to 2 layers of PDAC/TDBC

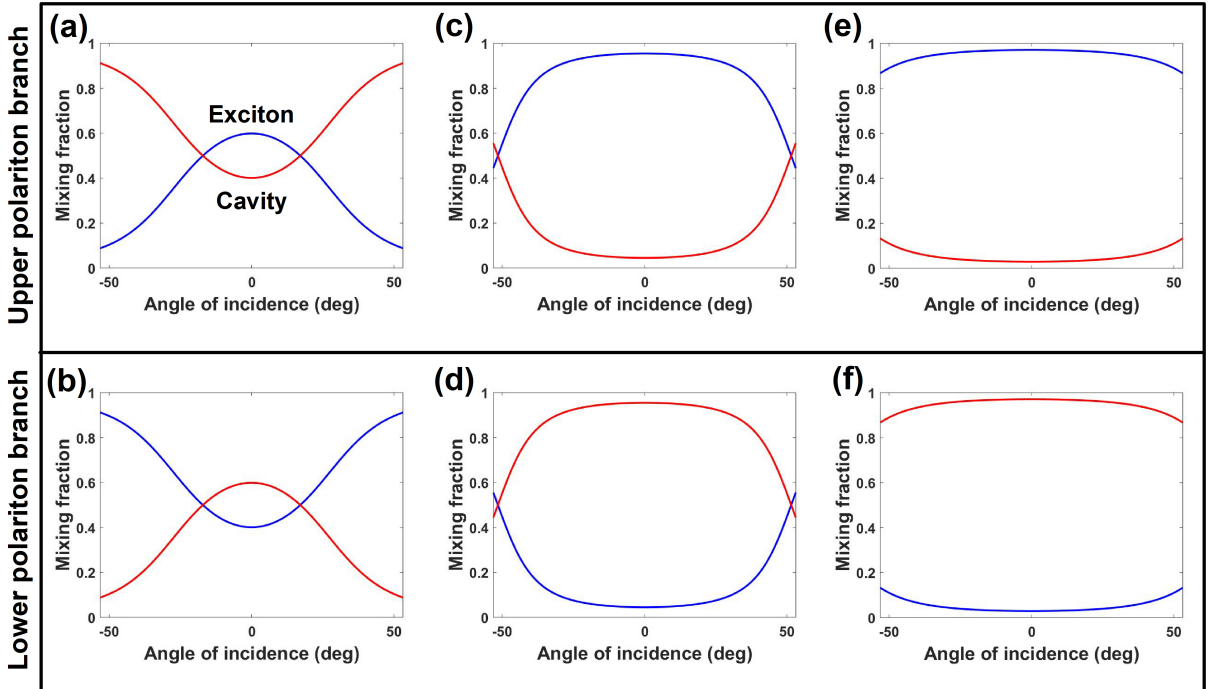


Figure S2: Calculated angle resolved mixing fractions, for a microcavity coupled to 2 layers of PDAC/TDBC with a cavity detuning of 21 meV, of exciton and cavity contribution to (a) Upper polariton branch and (b) Lower polariton branch. Calculated angle resolved mixing fractions, for a microcavity coupled to 2 layers of PDAC/TDBC with a cavity detuning of 175 meV, of exciton and cavity contribution to (c) Upper polariton branch and (d) Lower polariton branch. Calculated angle resolved mixing fractions, for a microcavity coupled to 2 layers of PDAC/TDBC with a cavity detuning of 335 meV, of exciton and cavity contribution to (e) Upper polariton branch and (f) Lower polariton branch.

S3 Evolution of strong coupling as a function of number of molecular layers

Figure S3 shows evolution of strong coupling signatures as a function of number of coupled molecular layers. Figure S3 (a) and (b) show angle resolved white light reflectivity and corresponding PL spectra for 2 layers of PDAC/TDBC coupled to a microcavity with a detuning of 335 meV. The coupling strength, $2g$, was estimated by fitting the experimental white light reflectivity data with a simple coupled oscillator model (see analysis section) and was found to be 100 ± 2 meV. For 4 layers of PDAC/TDBC (figure S3 (c) and (d)) coupling strength, $2g$, was found to be 146 ± 2 meV and the cavity detuning was 209 meV. For 6 layers of PDAC/TDBC (figure S3 (e) and (f)) coupling strength, $2g$, was found to be 180 ± 4 meV and the cavity detuning was 313 meV. For 8 layers of PDAC/TDBC (figure S3 (e) and (f)) coupling strength, $2g$, was found to be 210 ± 5 meV and the cavity detuning was 368 meV. The calculated mixing fractions through Hopfield analysis is shown in figure S4. Angle resolved PL was measured by exciting the cavities with a focused beam of 532 nm laser and spectrally rejecting the laser line using an edge filter.

To understand the evolution of molecular PL we deposited multiple layers of PDAC/TDBC on a silicon substrate and PL was measured by exciting them with a focused beam of 532 nm laser (figure S5). We can clearly see that the intensity of PL increases as a function of number of deposited layers, as expected. Figure S5 (b) shows PL spectra measured by exciting multiple layers of PDAC/TDBC coupled to a microcavity. The cavity was far red detuned to avoid any cavity enhancement factors in PL. As the number of molecular layers

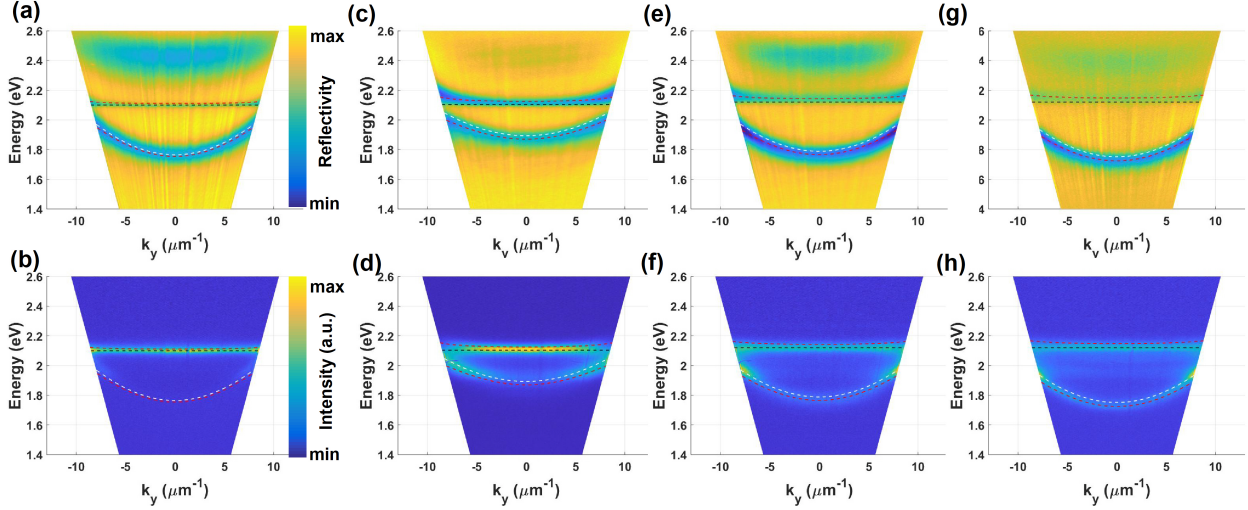


Figure S3: (a) and (b) are angle resolved white light reflectivity and PL spectra for 2 layers of PDAC/TDBC coupled to microcavity. (c) and (d) are angle resolved white light reflectivity and PL spectra for 4 layers of PDAC/TDBC coupled to microcavity. (e) and (f) are angle resolved white light reflectivity and PL spectra for 6 layers of PDAC/TDBC coupled to microcavity. (g) and (h) are angle resolved white light reflectivity and PL spectra for 8 layers of PDAC/TDBC coupled to microcavity. The superimposing dashed lines were calculated using a simple coupled oscillator model to estimate the coupling strength. The dashed white line represents the uncoupled cavity mode, the black line represents the molecular absorption, and the dashed red line represents the polaritons.

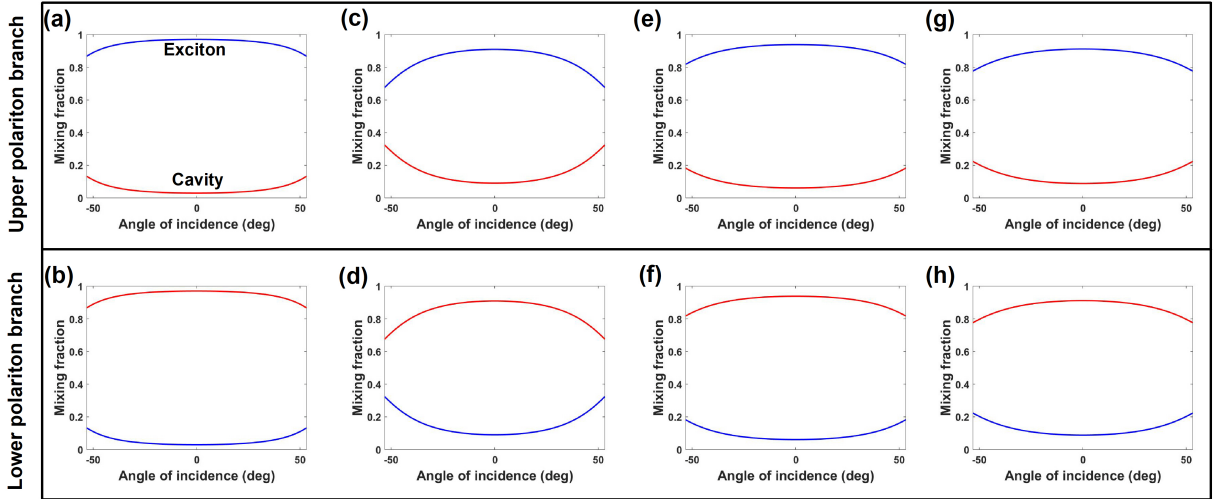


Figure S4: Calculated angle resolved mixing fractions of exciton and cavity contribution for a microcavity coupled to 2 layers of PDAC/TDBC to (a) Upper polariton branch and (b) Lower polariton branch. Calculated angle resolved mixing fractions of exciton and cavity contribution for a microcavity coupled to 4 layers of PDAC/TDBC to (c) Upper polariton branch and (d) Lower polariton branch. Calculated angle resolved mixing fractions of exciton and cavity contribution for a microcavity coupled to 6 layers of PDAC/TDBC to (e) Upper polariton branch and (f) Lower polariton branch. Calculated angle resolved mixing fractions of exciton and cavity contribution for a microcavity coupled to 8 layers of PDAC/TDBC to (g) Upper polariton branch and (h) Lower polariton branch.

is increased, we see a reduction in the intensity of PL associated with *bare* molecular resonance. It is probably due to the modification of absorption spectrum of the molecule through strong molecule-coupling. As the

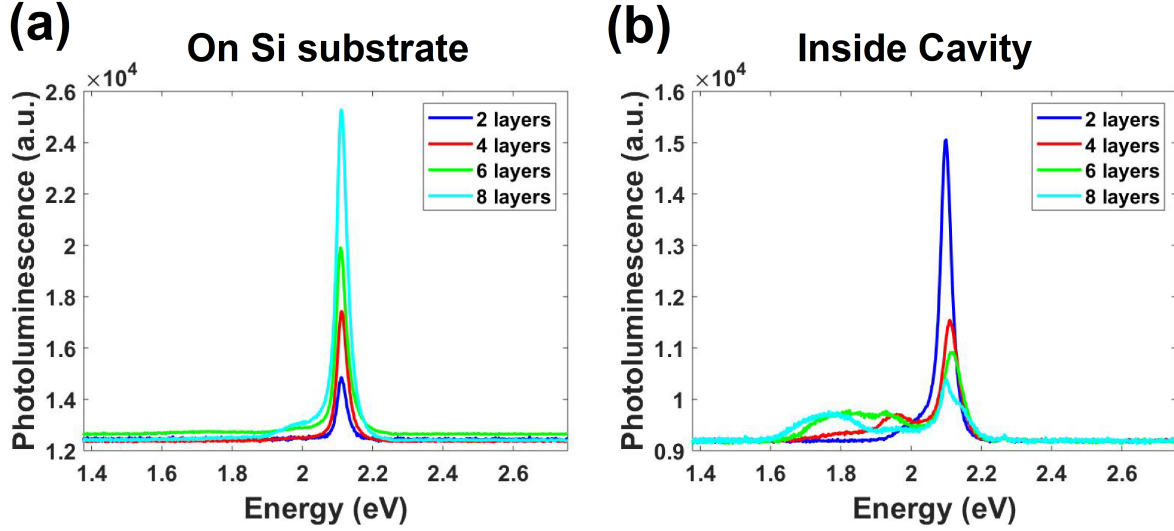


Figure S5: (a) Evolution of PL spectra as a function of number of layers of PDAC/TDBC on a Si substrate. (b) Evolution of PL spectra as a function of number of layers of PDAC/TDBC inside a microcavity.

number of molecular layers are increased, the upper and lower polariton branches become spectrally distinct from the *bare* exciton resonance (see section 2.3). For example: for 2 layers of PDAC/TDBC the absorption spectra of the molecule after coupling has been altered minimally, hence we see majority of emission near the *bare* exciton resonance. This modification becomes significant as one increases the number of molecular layers.

S4 Microcavity coupled to 8 layers of PDAC/TDBC

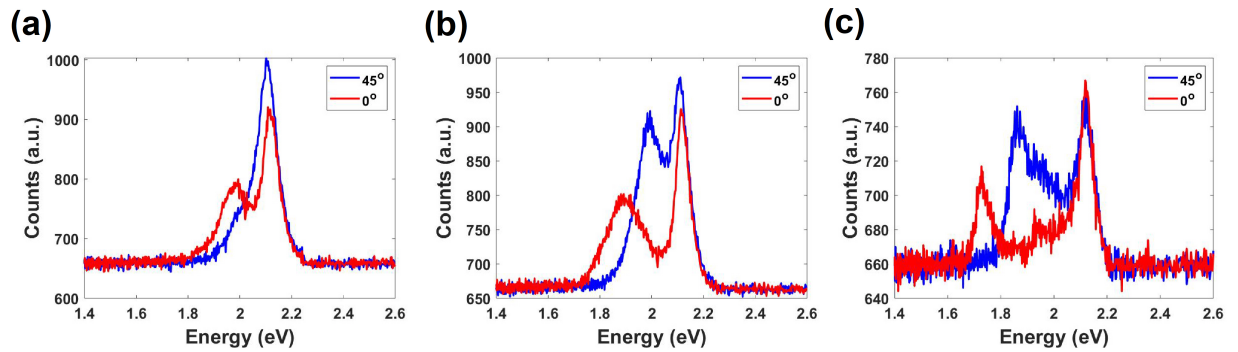


Figure S6: Line profiles of PL spectra plotted for $\theta = 45^\circ$ and $\theta = 0^\circ$ for 8 layers of PDAC/TDBC coupled to a microcavity with detuning of (a) 82 meV, (b) 228 meV, and (c) 368 meV.

Figure S6 shows line profile plotted for 8 layers of PDAC/TDBC coupled to microcavity for different detunings. We can see difference in intensities for higher angles of emission with respect to the lower angles, which is due to non-uniform relaxation of reservoir to the LPB through vibrational assisted scattering.

Figure S7 shows the experimentally measured spectral information collected by exciting 8 layers of PDAC/TDBC coupled to a microcavity with a focused beam of 633 nm laser. The spectrum consists of a broad photoluminescence background with sharp Raman modes of the molecule overriding it. The Raman modes were identified and corroborated with data shown elsewhere¹.

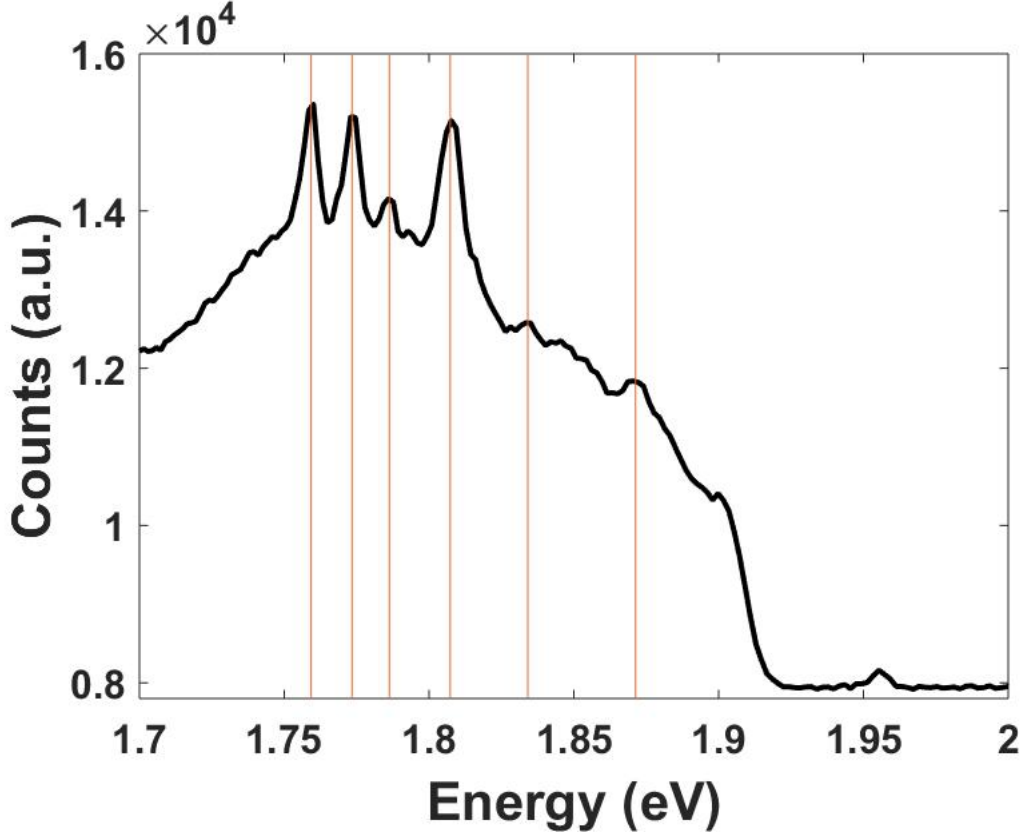


Figure S7: Real plane spectrum of 8 layers of PDAC/TDBC coupled to a microcavity excited with a focused beam of 632.8 nm laser. The orange line show the position of Raman lines in the spectrum. The cavity detuning was 368 meV

Figure S8 (a) and (b) show angle resolved PL spectra captured by exciting 8 layers of PDAC/TDBC coupled to a microcavity with a focused beam of 532 nm and 633 nm laser respectively. We can clearly see a difference in intensities across the lower polariton branch assisted emission (see figure S6). To understand this, we integrate the angular information to plot the integrated spectra as shown in figure S8 (c) and (d).

For 532 nm excitation case, the lower polariton branch is populated by the relaxation of reservoir states. This relaxation is aided by the vibrational quanta provided by the molecule. If we superimpose the vibrational quanta supported by bare TDBC molecule (Raman modes spectrally shifted with respect to the bare molecular absorption¹) on the PL spectra (figure S8 (a) and (c)) we can see that the intensity maxima coincides with the energy of the vibrational modes supported by the molecule (typically around 1.95 eV). Hence LPB is specifically populated at those wavevectors and will eventually relax through polariton scattering.

For 632.8 nm excitation case, the situation is different as there are no reservoir states to consider. Figure S8 (d) shows sharp peaks overlying on a broad intensity background. Here the Raman scattered photons of PDAC/TDBC molecule populate the LPB directly along with excitation of the LPB aided by the laser due to the modified absorption of the molecule. Hence we see broad intensity background due to the relaxation of LPB with overriding Raman peaks.

Figure S9 shows the angle resolved PL from 8 layers of PDAC/TDBC coupled to a microcavity excited with laser in $k \sim 0$ configuration. For 532 nm case the PL spectra is virtually same as that for focused beam due to the presence of reservoir. However for 633 nm, the LPB was populated by the Raman scattered photons, predominantly. The excitation wavevectors are limited (around $k=0$). However, the secondary Raman scattered photons have a wide range of wavevectors that can populate the LPB which eventually relaxes. Thus we see emission at large wavevectors even though the excitation has $k \sim 0$. The integrated spectra shown in figure S9(d) shows the Raman peaks on the broad background similar to the focused laser

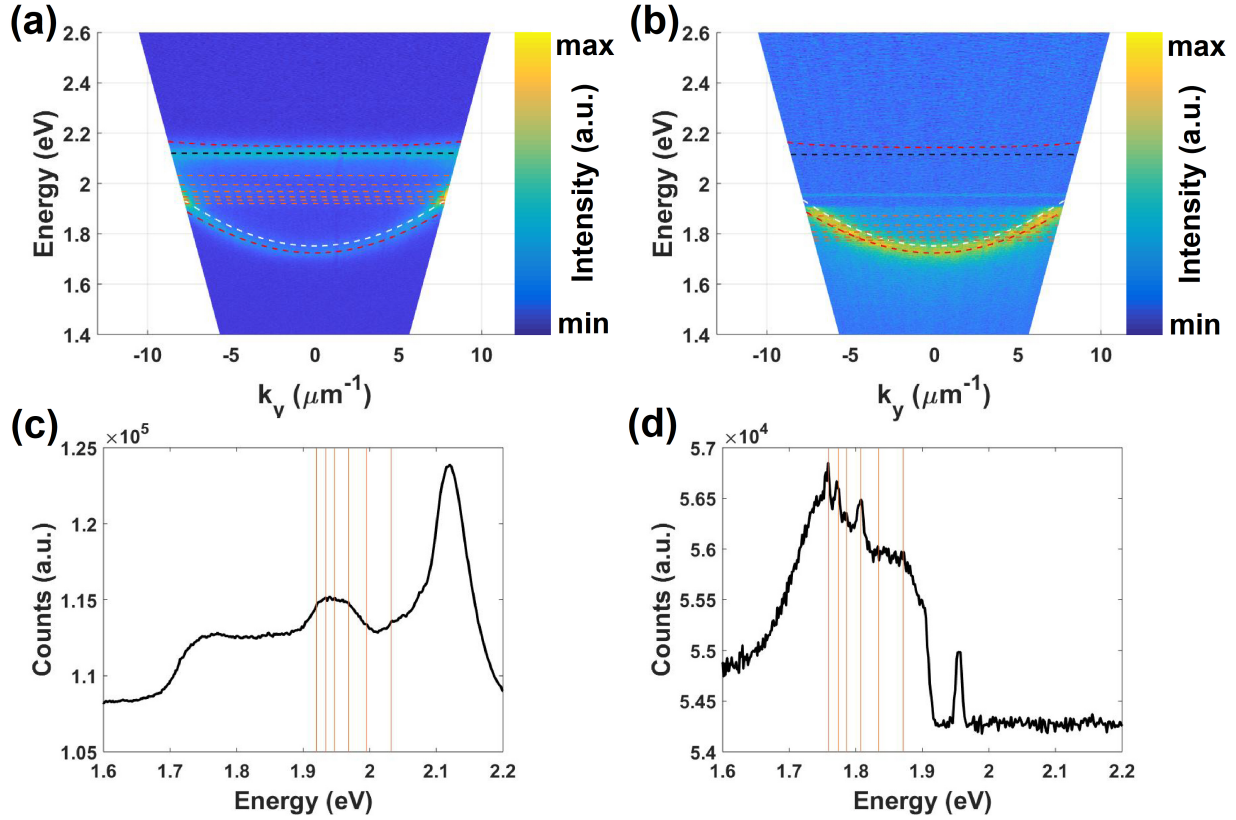


Figure S8: (a) and (b) are angle resolved PL spectra for 8 layers of PDAC/TDBC coupled to a microcavity excited with a focused beam of 532 nm and 633 nm laser respectively. The superimposing dashed lines were calculated using a simple coupled oscillator model to estimate the Rabi splitting. The dashed white line represents the uncoupled cavity mode, the black line represents the molecular absorption, and the dashed red line represents the polaritons. The dashed orange lines represent Raman modes of the TDBC molecule. (c) and (d) are corresponding spectra calculated by integrating the angular information (from $\theta=-53.13^\circ$ to $\theta=53.13^\circ$). The spectral positions of vibrational quanta supported by the molecule are represented using orange lines.

case (see figure S8).

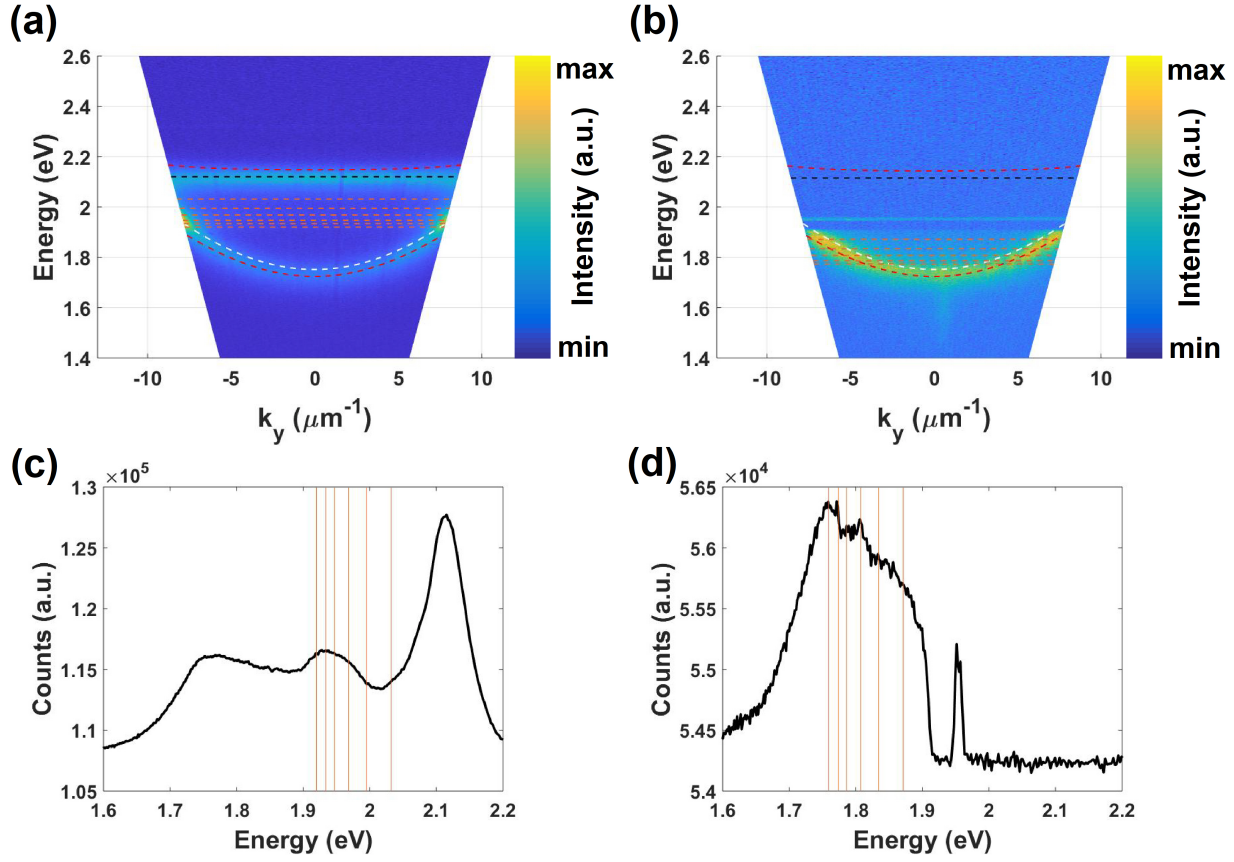


Figure S9: (a) and (b) are angle resolved PL spectra for 8 layers of PDAC/TDBC coupled to a microcavity excited with a laser beam of 532 nm and 633 nm laser at $k \sim 0$ respectively. The superimposing dashed lines were calculated using a simple coupled oscillator model to estimate the Rabi splitting. The dashed white line represents the uncoupled cavity mode, the black line represents the molecular absorption, and the dashed red line represents the polaritons. The dashed orange lines represent Raman modes of the TDBC molecule. (c) and (d) are corresponding spectra calculated by integrating the angular information (from $\theta = -53.13^\circ$ to $\theta = 53.13^\circ$). The spectral positions of vibrational quanta supported by the molecule are represented using orange lines.

S5 Hopfield analysis- Microcavity coupled to 8 layers of PDAC/TDBC

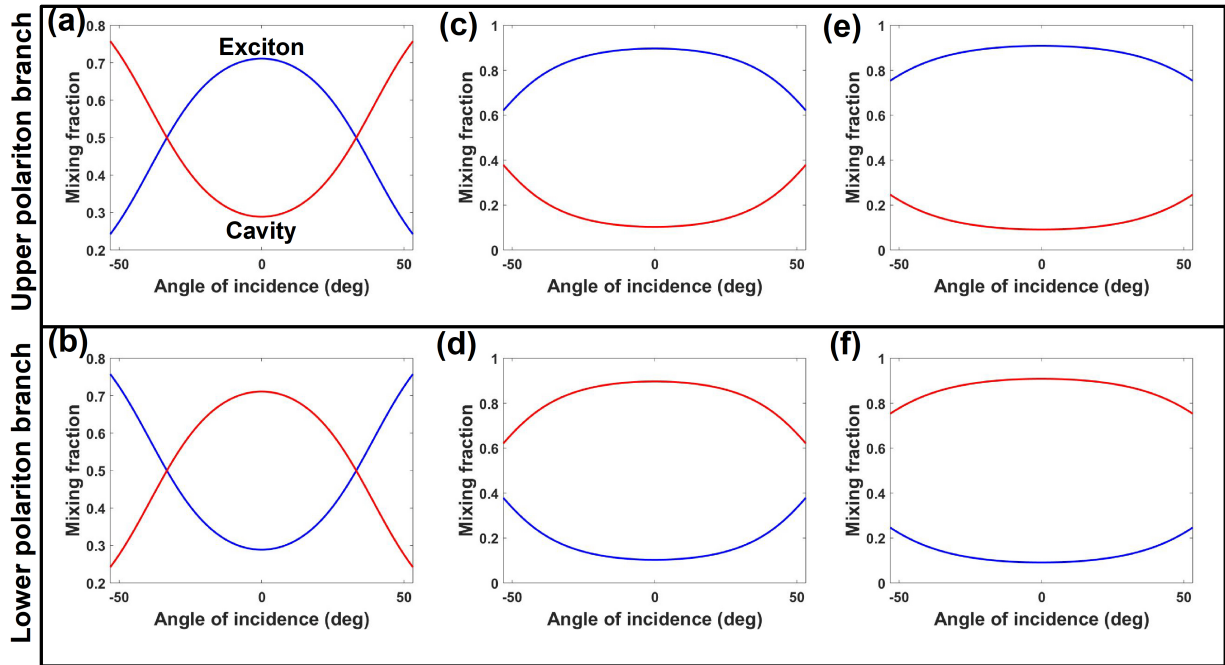


Figure S10: Calculated angle resolved mixing fractions of exciton and cavity contribution for a microcavity coupled to 8 layers of PDAC/TDBC with a cavity detuning of 82 meV to (a) Upper polariton branch and (b) Lower polariton branch. Calculated angle resolved mixing fractions of exciton and cavity contribution for a microcavity coupled to 8 layers of PDAC/TDBC with a cavity detuning of 228 meV to (c) Upper polariton branch and (d) Lower polariton branch. Calculated angle resolved mixing fractions of exciton and cavity contribution for a microcavity coupled to 8 layers of PDAC/TDBC with a cavity detuning of 368 meV to (e) Upper polariton branch and (f) Lower polariton branch.

S6 Molecular PL from 8 layers of PDAC/TDBC coupled to a microcavity

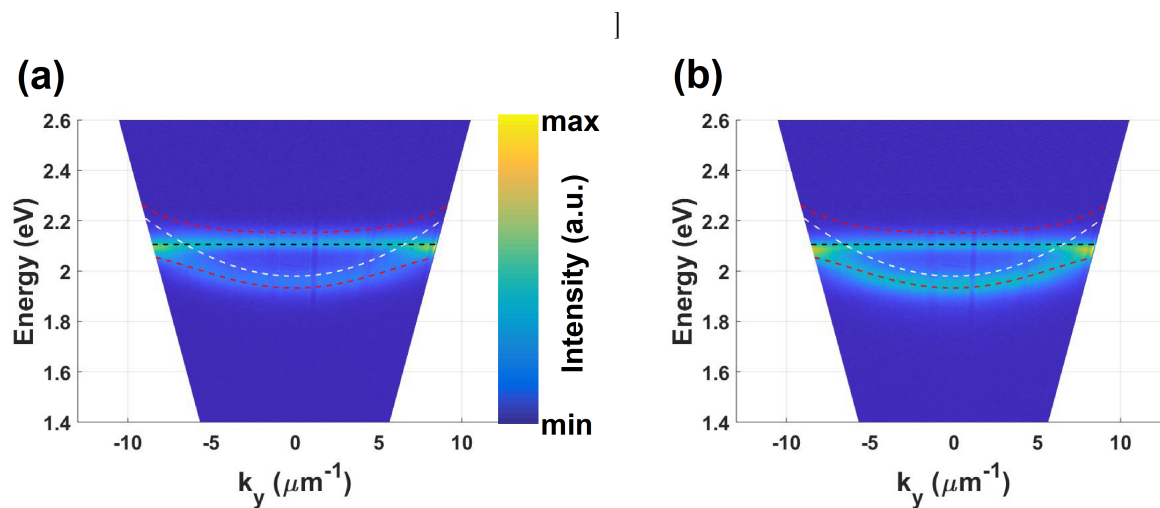


Figure S11: Angle resolved PL for 8 layers of PDAC/TDBC molecules coupled to a microcavity with a detuning of 32 meV excited with (a) focused beam and with (b) $k \sim 0$ configuration of 532 nm laser.

References

- [1] Coles, D. M.; Meijer, A. J. H. M.; Tsoi, W. C.; Charlton, M. D. B.; Kim, J.-S.; Lidzey, D. G. A Characterization of the Raman Modes in a J-Aggregate-Forming Dye: A Comparison between Theory and Experiment. *J. Phys. Chem. A* **2010**, *114*, 11920–11927.