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Organic polariton lasing with molecularly isolated perylene diimides

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Abstract

A dye immersed in a polymer matrix represents a promising material class for organic polariton lasers. While polariton condensation has been established for boron-dipyrromethene blends, it has yet to be extended to other small dye blends. Here, we demonstrate polariton lasing in a molecularly isolated perylene diimide immersed in polystyrene. The emission exhibits threshold behavior, strong directionality, and the slight blue-shifting of organic polariton systems. We expect continued exploration of new dyes will allow improved performance in organic polariton lasing.

In the last decade, polariton condensation (BEC) has become an alternative path to achieve lasing in organic materials.[1] BEC requires strong coupling between an exciton and a cavity photon mode, where energy oscillates between the two states at a given Rabi frequency (Ω_f).[2] This quantum superposition results in the formation of two new polariton states, which are separated in energy by the coupling strength, or Rabi splitting ($\Omega = \mathrm{h}\Omega_f$).[3] In organic materials, vibrational scattering and optical pumping from reservoir states facilitate the build-up of polaritons in the lowest $k = 0$ state, forming a polariton condensate. This is allowed because polaritons are bosons, and thus can occupy the same quantum state.[4] When this occurs, all emitted photons will emit coherently, and thus can be essentially termed a laser.[5]

Since the seminal report by Kéna-Cohen and Forrest using anthracene single crystals,[6] other material systems have been shown to demonstrate lasing.[7-11] One example included a boron-dipyrromethene (BODIPY) chromophore immersed within a polymer matrix.[10] This particular study is intriguing, as the system should in theory allow substitution with many different small organic dyes. However, to our knowledge, while BODIPY materials have been used,[12] no other dye classes in matrices have been shown to exhibit polariton lasing. Expanding this library will result in a clearer direction for improved performance.

Recently, we have shown strong exciton-photon coupling with a series of molecularly isolated perylene diimides.[13] These dyes were synthesized initially with the target of minimizing aggregation, while maintaining high photoluminescence quantum yields (PLQYs).[14,15] In terms of polaritons, they also offer narrow absorption linewidths and small Stokes shifts. While three dyes (**bPDI-2, bPDI-3, and bPDI-4**) exhibited strong coupling, both **bPDI-2** and **bPDI-4** showed signs of aggregate emission, which was lower in energy than the polariton emission.[13] Only in **bPDI-3** did polariton emission dominate.

Herein we demonstrate polariton lasing with **bPDI-3**. We place the dye within a polystyrene matrix and sandwich it between two high-reflectivity dielectric stacks. The resulting emission shows threshold behavior, narrow linewidth, and strong directionality, which are key characteristics of BEC[16]. We expect that perylene dyes will become a useful polariton laser class owing to their superior photophysical properties.

To molecularly isolate **bPDI-3**, we immersed it in a matrix of polystyrene (PS) at 120 mM (Figure 1a). The absorption spectrum of a thin film shows the characteristic absorption spectrum of **bPDI-3** (Figure 2a), with the main peak at 2.35 eV. Two peaks within the vibronic progression are visible at higher energies. As the concentration of **bPDI-3**/PS in the spin-coating solution is increased, the **bPDI-3** peak absorbance increases nonlinearly. This is due to the increased viscosity of the solution, which increases the film thickness during spin-coating. Comparing these numbers to the previously obtained calibration,[13] we deduce the film thickness of each sample, which allows determination of the cavity thickness of the corresponding device.

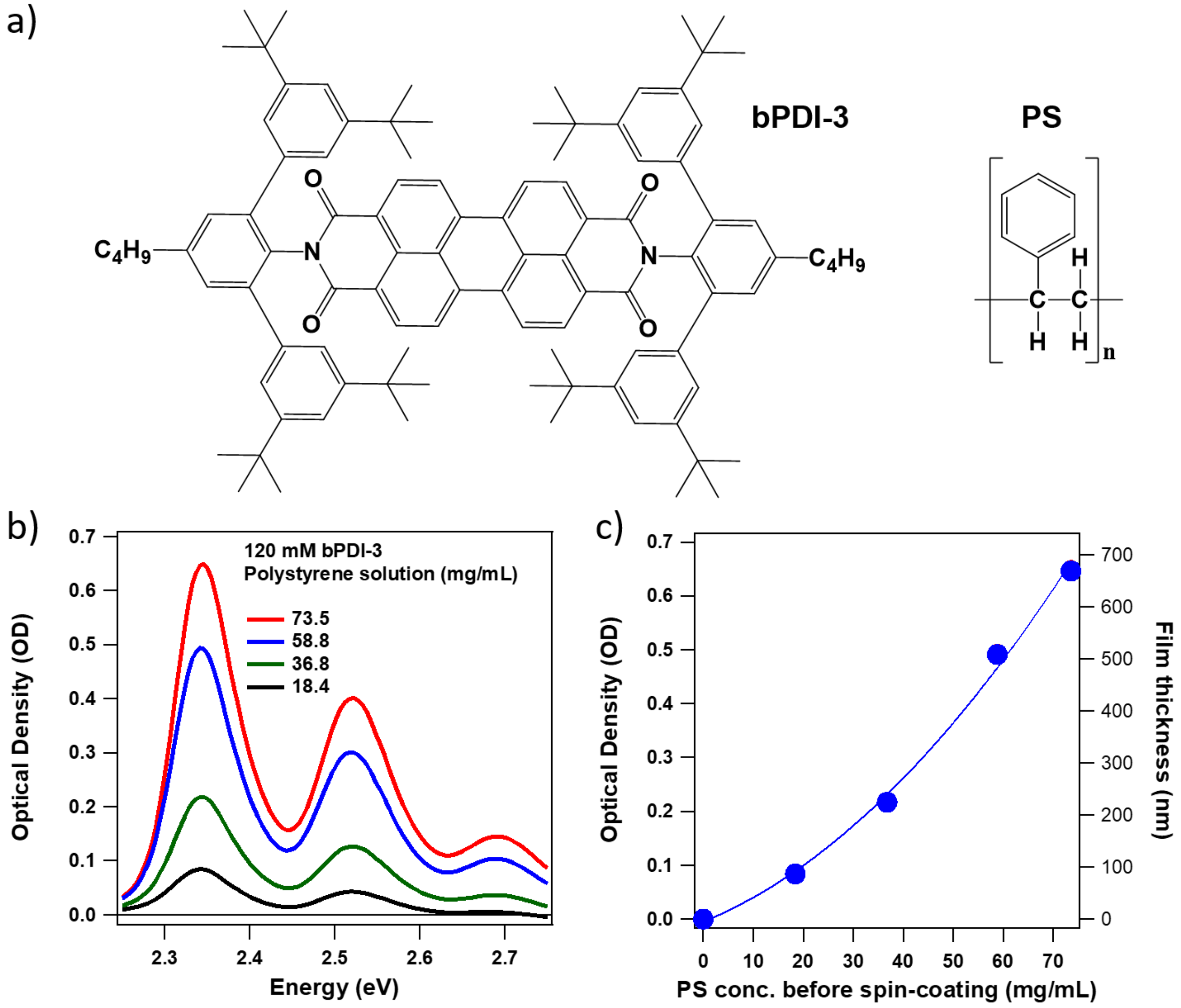

Figure 1: Perylene in matrix. (a) Molecular structures of **bPDI-3** and PS. (b) Absorption spectra of 120 mM **bPDI-3** film in PS for different **bPDI-3**/PS solution concentrations in chlorobenzene. (c) Peak absorbance and film thickness for 120 mM **bPDI-3** in PS for different **bPDI-3**/PS solution concentrations.

We utilize distributed Bragg reflectors (DBRs) to achieve high reflectivity (compared to metal mirrors), and thus high Q-factor of the resulting cavity. The bottom mirror consists of 11.5 pairs of tantalum pentoxide (Ta_2O_5) and silicon dioxide (SiO_2), while the top mirror is composed of either six or nine pairs of Ta_2O_5 and SiO_2 (Figure 2a). During the fabrication process, we discovered that the film quality is sensitive to the polymer matrix chosen. In some cases, the deposition of the top mirror would result in cracking of the polymer film (Figure 2b, left). This occurred when using polymethylmethacrylate (PMMA) at 120k and 350k weight average molecular weights (M_w), as well as with 35k M_w PS. However, with 192k M_w PS, the film remained intact (Figure 2b, right). We expect that some of this is due to differences in tensile strength, which is known to increase with increasing molecular weight.[17] To prevent overheating, the top mirror deposition was carried out in three separate periods (*i.e.* 3 pairs a period), allowing the sample to cool in between. For a nine-pair top mirror, the resulting Q-factor was determined by measuring the linewidth of an empty cavity and was found to be ~760 (Figure 2c). For the organic layer, we spin-coated a ~670 nm thin film of 120mM **bPDI-3** in PS (16.3% dye loading).

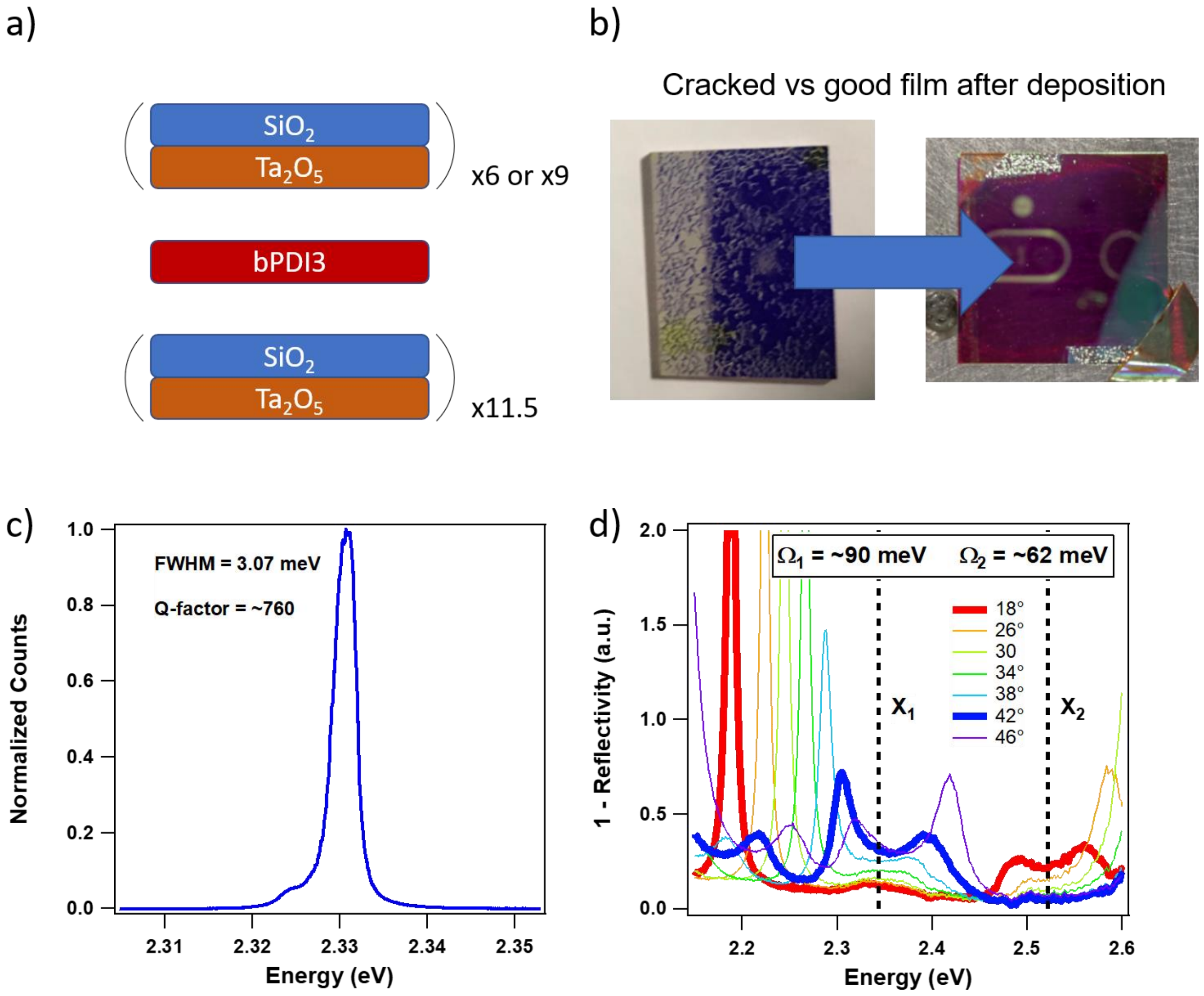

Figure 2: DBR mirrors. (a) Representation of DBR stacks surrounding **bPDI-3** film, forming the laser cavity. (b) Pictures of device after top mirror deposition, based on choice of polymer matrix. (c) Resonance peak of empty laser cavity. (d) Reflectivity of **bPDI-3** device, showing Rabi splitting around both exciton peaks. Reflectivity measurements were performed with a top mirror containing six dielectric pairs. X_1 and X_2 represent exciton energies.

We then performed angle-dependent reflectivity measurements to assess strong coupling within the system. This was measured on the device with a six-pair top mirror (lower Q-factor of ~140) to maximize visibility of the upper polariton band.[8] The reflectivity spectra reveal anticrossing behavior around both the first and second exciton peak (Figure 2d). Note that the peaks in the reflectivity spectra actually denote dips in reflection, and we have inverted them (*i.e.* 1 – reflectivity) for clarity. The peaks in the reflection data were fit with the coupled oscillator model to obtain the dispersion for the lower, middle, and upper polariton (LP, MP, and UP) bands (Figure 3). The observed Rabi splitting for the main peak is ~90 meV. Considering the film thickness and penetration depth of the DBRs (~200 nm for each mirror at 528 nm), this number matches well with the ~140 meV observed previously for the metal mirrors.[13] Angle-resolved emission is overlaid on Figure 3. The shape of its dispersion is consistent with that of the reflectivity; however, its absolute value is slightly off due to a different position on the sample.

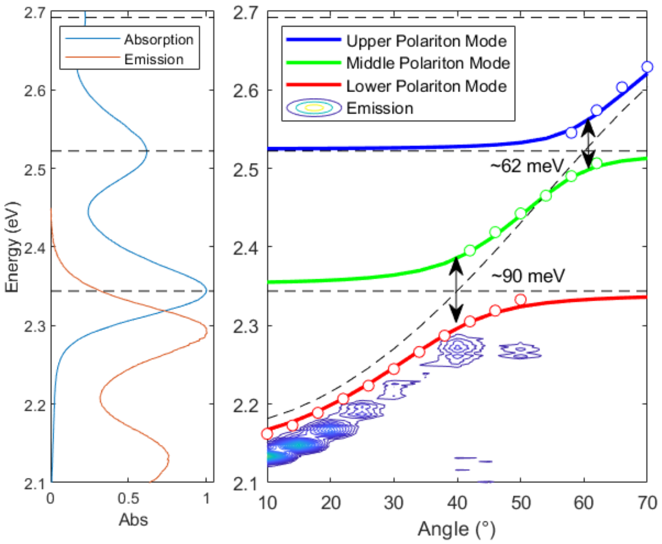

Figure 3: Rabi splitting. Polariton band energies of a **bPDI-3** device based on angle-dependent reflection measurements. Fits were made with the coupled oscillator model. Angle-dependent emission is overlaid on the graph. The energies for reflectivity and emission are slightly off as they were measured on different parts of the sample. Left inset: Absorption and emission spectra of a **bPDI-3** thin film.

To test for polariton lasing, the device was excited with a 150 fs laser pulse at 390 nm. The pulse repetition rate was 1 kHz, and the spot size on the sample was ~2.5 x 10^{-4} cm^2. To prevent photo-induced damage to the sample, the pump was blocked after a spectrum was collected for a given power. This was repeated for each measured power. At fluences below threshold, the emission increases linearly and maintains the same shape (Figure 4a). Above threshold, the peak blue-shifts slightly (Figure S1a-b), consistent with organic polariton systems[18], and experiences a sharp rise in intensity. Plotting the intensity as a function of absorbed fluence (Figure 4b), we observe a threshold of ~265 $\mu J/cm^2$ in terms of light absorbed; without taking reflection and transmission into account, the threshold in terms of incident light was 560 $\mu J/cm^2$. However, we expect this is an upper limit; the experiments were carried out in ambient conditions, and the dye photo-oxidized readily, potentially increasing the measured threshold (see Note 1 in the Supporting Information for details).

The strong directionality of the laser emission was detected by placing a card in front of the emission spot (Figure 4b inset). When lasing occurs, an orange spot is apparent, showcasing the directionality of the emission. Compared to the linewidth of the cavity resonance (*i.e.* emission under threshold), which is 1.48 nm (5.4 meV), the polariton laser linewidth is narrower at ~0.55 nm (~2.3 meV) (Figure 4c), which is limited by the resolution of the detection setup. For comparison, amplified spontaneous emission from a film is much broader than both the resonance and laser emission. Owing to heterogeneity in the cavity thickness (spin-coating leaves thicker films toward the edges), we detect the narrow lasing peaks at k = 0 at different wavelengths depending on the sample positions (Figure 4d).

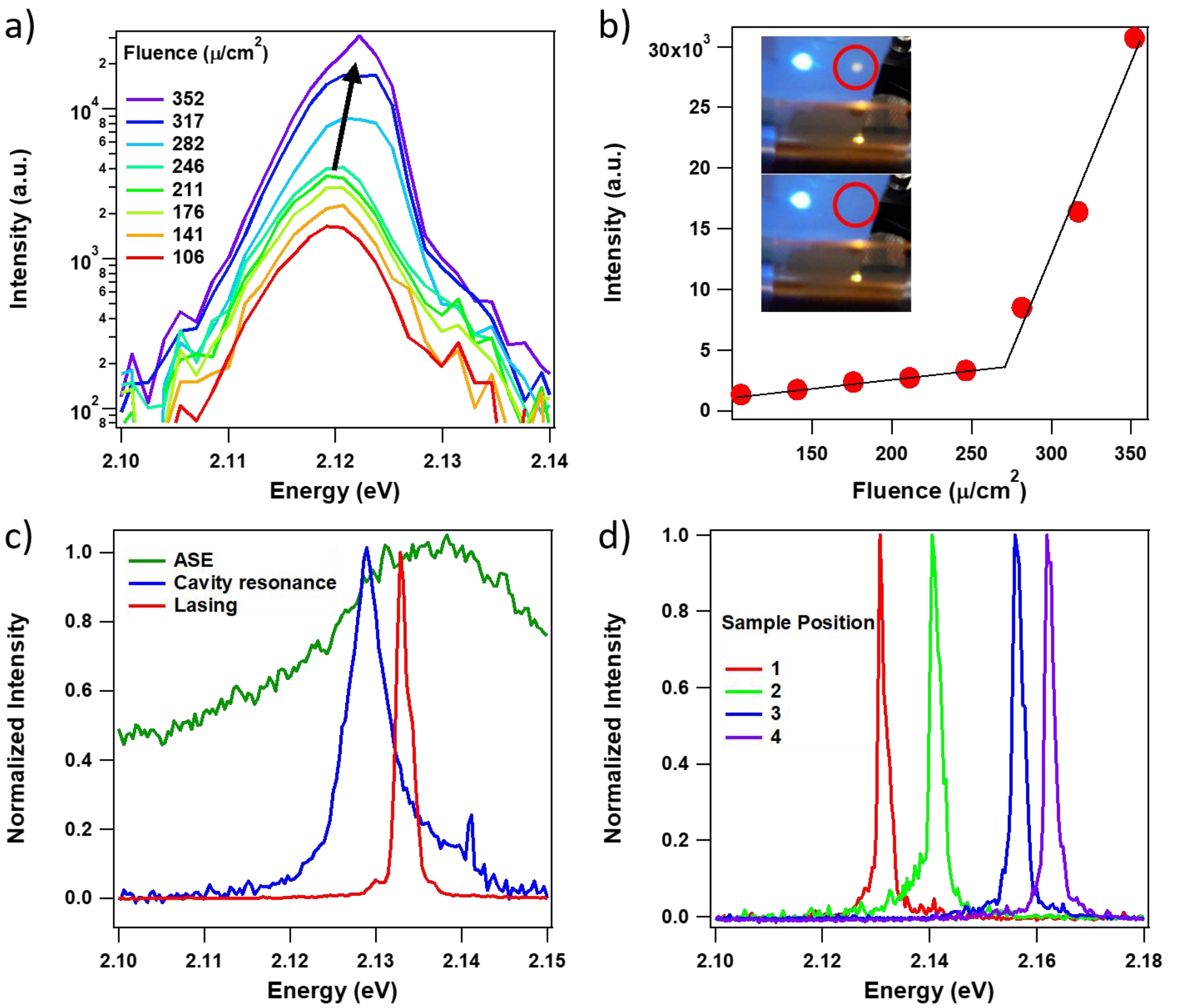

Figure 4: Polariton condensation. (a) Fluence dependent emission spectra of **bPDI-3** device. A small blue shift is observed above threshold. (b) Intensity at lasing wavelength as a function of absorbed intensity. Threshold behavior is observed. (inset) Strong directionality of laser output, with images above threshold (top) and below threshold (bottom). (c) Emission linewidths of film ASE, the device cavity resonance, and device lasing peak. (d) Lasing peaks at different spots on the sample, where the cavity thickness is slightly different.

In conclusion, we have demonstrated polariton lasing in a molecularly isolated perylene diimide immersed within a polymer matrix. The perylene derivative **bPDI-3** exhibits a large extinction coefficient and narrow absorption linewidth, which enable strong coupling to be maintained within a DBR cavity. The observed threshold behavior, slight blue-shifting, and strong directionality reveal Polariton condensation. We believe that perylene derivatives will provide another path to achieve high-efficiency organic polariton devices.

SUPPLEMENTARY MATERIAL

See supplementary material for description of methods.

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AIP PUBLISHING DATA SHARING POLICY

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

ADDITIONAL INFORMATION

Competing financial interests: the authors declare no competing financial interests.

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Notes

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