Supporting Information for: All-Polymer Microcavities for the Fluorescence Radiative Rate Modification of a Diketopyrrolopyrrole Derivative

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Figure S1 shows the normal-incidence reflectance of the reference thin films deposited on glass substrates. DPP:PS is a thin layer of the DPP dye dispersed in a polystyrene matrix, R1 is a layer of CA capped by one layer of DPP:PS, and R2 is a 5-layer PVK-CA-DPP:PS-CA-PVK stack. For R2, the refractive index contrast between the layers in the stack gives rise to higher reflectance values for certain wavelengths. All samples show a dip in the reflectance spectra around 650 nm due to the absorption of the DPP dye.

**Figure S1.** Reflectance spectra of reference films.

In the microcavities, due to the photonic band structure, the transmittance spectrum is strongly dependent on the angle of incidence or collection, and on light polarization. Panels a and b of Figure S2 show the experimental angle-resolved transmittance spectra collected for S and P polarization, respectively. For the P-polarization the PBG narrows at the Brewster’s angle, while no significant effects on the PBG width are observed for S-polarization. In both cases, the bands shift continuously to shorter wavelengths upon increasing the collection angle.
Figure S2. Contour plots showing experimental angle-resolved transmittance spectra with (a) S-polarization, and (b) P-polarization for MC$_{tuned}$.

Normalized reflectance spectra recorded at normal incidence and at different points on the tuned microcavity MC$_{tuned}$ sample are shown in Figure S3a. All the spectra show the same characteristic features of planar microcavities, including the stop band and the interference fringes, as well as a minimum superimposed to the bandgap and corresponding to the cavity mode. However, the position of the cavity mode slightly changes from point to point, depending on the actual thickness of the defect layers, providing a slight spectral tuning potential. A particular care has been dedicated in recording all measurements with the different set-ups in the same spots on the sample. Panel b shows a digital image of the strong PL from a microcavity cast on a flexible substrate under a violet laser excitation (colors edited to enhance visibility).
Figure S3. (a) Normalized reflectance spectra at different points of the MCtuned microcavity. (b) Digital photograph of planar polymer microcavity cast on a flexible substrate under violet laser excitation.

The analytical simulation of the optical response of the structures requires determining the complex refractive index dispersion of the materials used. While the indices of poly(N-vinylcarbazole)\(^1\) (PVK), polystyrene (PS),\(^2\) cellulose acetate (CA)\(^2\) and Aquivion (AQ)\(^3\) are reported in the literature, that of the DPP/PS blend had to be measured by spectroscopic ellipsometry. The real part of the refractive index \((n)\) in Figure S4a shows the typical dispersion for a polymer in the visible range, as described by the Cauchy–Schott relation, with the superimposed signature of the dye absorption with the anomalous dispersion in the range 640-670 nm. This is quantified by the imaginary part of the refractive index (extinction coefficient \(k)\) as shown in panel b. The broad absorption of the dye from 500 to 750 is comparable with that measured and reported in the manuscript, with a peak at approximately 655 nm wavelength.
Figure S4. Complex refractive index $n + ik$ (n, panel a; k, panel b) dispersion of DPP:PS blends.

SEM imaging allowed the observation of the distinct PVK and AQ layers, where the latter is distinguishable through its aggregates of around 30 nm in diameter (Fig. S5a). While it was possible to observe the individual mirrors in good conditions at some points, the process of freeze-cracking resulted in damage and delamination to MCtuned as seen in Fig. S5b. As such, it was not possible to observe the cavity layers directly for that sample.
Figure S5: SEM images demonstrating (a) layer interfaces and (b) cracking and delamination due to freeze cracking in MC_{tuned} and (c) the full MC structure for MC_{detuned}

However, for MC_{detuned} with thinner layers forming the DBRs, it was possible to observe the whole structure. Figure S5c shows the cross section of the sample, showing the glass substrate, the bottom DBR, the cavity area and the top DBR. Although the different polymers forming the DBRs can be easily discerned, the layers forming the cavity are overexposed and show as a white bar in the middle of the structure. Still, this allows an estimation of the overall thickness of the cavity of approximately 314 nm ±28 nm.

To extract the layer thicknesses of the DBRs in MC_{tuned}, an image analysis code was built and run with MATLAB to obtain unbiased values from the SEM images. Considering the image as a matrix, the code averages pixel luminosity per row, where the single row average values are represented as a function of the position (in pixel) in Figure S6a. A polynomial background (red line) is fitted by the least squares method to the former curve to represent the fictional illumination gradient.
Figure S6: Thickness analysis workflow from SEM images. (a) pixel luminosity as a function of position (black line) and polynomial background (red). (b) Profile corrected for background (black line) and the squared profile (red). (c) reconstructed layer profiles.

The subtraction of this background results in the black line in panel b. Pixels with positive luminosity (i.e., above x axis) are considered as part of the AQ layers, whereas those below are considered part of the PVK layers, filtering out fictional peaks. A square wave-like pattern can thus be obtained, as shown by the red line in panel b, which is then used to reconstruct the layers in panel c. Then, the number of pixels in each layer is counted and the average thickness in pixel and its standard deviation are obtained. The conversion factor pixel-to nm from the scale bar (which is image dependent, i.e. 200 nm for 35 pixels in Fig.2c) is used to obtain the actual thicknesses, which was repeated for 3 different images allowing the extraction of the average thickness and deviation as reported in the main text.
Figure S7. Extracted height profiles (1) and corresponding AFM scans (2) of (a) a PVK film on glass, (b) CA-PVK bilayer on glass, (c) DPP:PS-CA-PVK on glass.

To estimate the individual layer thickness of the films forming the cavities (i.e., CA and DPP:PS), three different samples were fabricated to better account for the effect of substrates on the thickness. These were: 1) PVK cast on glass, 2) CA on PVK on glass and 3) DPP:PS on CA on PVK on glass. The samples were scratched with a metallic sharp tip, and subsequent AFM measurements allowed an evaluation of their thicknesses. Figure S7.a1 shows the analysis of sample 1, with 10 profiles extracted from Figure S7.1b. The glass is the zero-level; an accumulation of material can be seen at the edge of the scratch, followed by the height profile of the actual PVK film, which is about 107 ± 2 nm thick. The combined thickness of PVK
and CA layers is measured from sample 2 to be 195 ±34 nm, as deduced from Figure S7.b1-2. Finally, sample 3 profiles are represented in Figure S7.c1. The overall thickness of the tri-layer film was evaluated to be 297 nm± 17 nm. The scratching process delaminated the film, making it possible to see also the thickness of the PVK film individually. Subtracting adequately the estimated thicknesses of the films provides values around 88±33 nm for the CA and 113±67 nm for the DPP:PS layer.

Figure S8 shows the ratio between the photoluminescence spectrum from the MC_{tuned} and that of DPP/PS film on glass at normal collection. The PL of DPP below 700 nm is completely suppressed by the photonic band gap effect, while the PL overlapping the defect mode around 717 nm is enhanced by more than 40 times. At longer wavelengths a weaker modulation of PL is evident, due to the effect of the interference fringes.

![Figure S8 Ratio between the MC_{tuned} and the DPP:PS PL spectrum.](image)

The angle-resolved photoluminescence spectra for the DPP:PS reference and the MC_{tuned} are shown in panels a and b of Figure. S9 respectively. The effect of the angular dispersion of the photonic structure is clearly evident in the angle-resolved PL from the MC_{tuned}, reproducing the strong directionality of the PL in the cavity mode. On the other hand, the reference DPP:PS film does not show any angular dispersion of the PL spectrum.
Figure S9. Contour plot of angle-resolved photoluminescence spectra as a function of the collection angle for (a), DPP:PS film and (b) MCtuned.

To further illustrate the effect of the microcavity on the angular fluorescence, Figure S10 shows photoluminescence intensity as a function of the collection angle for the MCtuned (red) compared to the DPP:PS standalone film (black) and the R2 reference (blue). Panel a displays the spectrally integrated photoluminescence signal (over 600-800 nm spectral width), while panel b reports the intensity of the highest signal collected for the microcavity and the references. It is clear that in both cases the intensity of the signal collected for the tuned microcavity is higher than that of the references for all angles in the 0°-50° range. For higher angles, the angular dispersion properties of the photonic structure do not match the PL spectral range, making the comparison meaningless.

Moreover, the integrated fluorescence intensity (Figure. S10a) for the tuned microcavity is far larger than for the references (notice the logarithmic intensity scale). Concerning the peak intensity (Figure S10b), we notice that the spectral position of the microcavity mode shifts to longer wavelengths as collection angle is increased as seen in Figure S9. The intensity of the mode is almost constant until around 7 degrees and then decreases steadily for larger collection angles. As for the references, the maximum PL does not vary as strongly for higher collection angles.
Figure S10. Photoluminescence Intensity Characterization. (a) Angular resolved spectrally integrated photoluminescence intensity for the reference DPP:PS film (black), R2 (blue) and for the MC<sub>tuned</sub> (red). (b) Intensity at cavity mode wavelength for MC<sub>tuned</sub> (red), DPP:PS film (black) and R2 (blue). (c) Enhancement factor ($G_e$) at cavity wavelength. (d) Integrated enhancement intensity as a function of collection angle with respect to references.

The fluorescence enhancement factor ($G_e$) at the cavity mode was calculated as the ratio of the intensity of the PL peak at the cavity mode and those at the corresponding wavelength for the references as shown in Figure. S10c. High enhancement values are observed for all angles below 30° at the cavity mode and no suppression ($G<1$) is observed for all measured angles.

On the other hand, when considering the PL intensity integrated over wavelengths from 600 to 900 nm ($G_{int}$, Figure. S10d), both overall intensity enhancement and suppression were obtained at different collection angles. The latter – observed for high collection angles only – is mostly caused by waveguiding losses within the microcavity, poorly active in the references. The theoretical value for enhancement at the cavity mode for normal collection ($G_{e\ (th)}$) should be estimated by Equation
(S1) where, $R_1$ is the reflectivity of the top mirror and $R_2$ is that of the bottom one at the cavity mode, and $\xi$ is the antinode placement factor (zero for an emitter at the node of the standing wave in the cavity, 2 for an emitter at the antinode and 1 for one smeared across the standing wave, as assumed in this case).

$$G_{e\,(th)} = \frac{\xi}{2} \frac{(1 + \sqrt{R_2})^2 (1 - R_1) \tau_{rad}^{cav}}{(1 - \sqrt{R_1 R_2})^2 \tau_{rad}^{ref}} \quad (S1)$$

Since it is not possible to determine experimentally the absolute reflectivity of the individual mirrors at the cavity/mirror interface, calculated values of $R_1 = R_2 = 0.92$ were used. Using the estimated ratio $\tau_{rad}^{cav} = 42$ and $\tau_{rad}^{ref} = 3$, $G_{e\,(th)}$ is approximately 340. Notably, the experimentally observed enhancement (40) in this geometry is not possible without considering lifetime enhancement. Additionally, the integrated enhancement can be approximated as in Equation (S2).\textsuperscript{54}

$$G_{int} = G_0 \sqrt{\pi \ln 2 \left( \frac{\Delta \lambda_c}{\Delta \lambda_{dye}} \right)} \quad (S2)$$

The full width at half maximum (FWHM) of the cavity mode width at normal collection is $\Delta \lambda_c$ (3.5 nm), and $\Delta \lambda_{dye}$ is the FWHM of the photoluminescence of the emitter (50 nm). As such, the theoretical integrated fluorescence is $\sim 4$, a value in line with the achieved overall enhancement. Even when considering the full widths to be double to account for the second PL peak of the DPP, net enhancement is still theoretically achieved.

The PL lifetime measurements for all samples were fitted by a monoexponential decay function with a background ($I(t) = I_0 e^{-t/\tau_{bg}} + I_{bg}$) to obtain the PL lifetime ($\tau_{pl}$), as reported in Table S1 along with their effective refractive index ($n_{eff}$), quantum yield ($\eta$), and radiative lifetime ($\tau_{rad}$). All references have comparable $\eta$, while both microcavities have a lower value. On the other hand, $\tau_{pl}$ and $\tau_{rad}$ are much longer for the MC\textsubscript{tuned} sample. The different $\eta$ can be due to enhanced self-absorption due to the small Stokes shift and longer photon dwell time in the cavity. Indeed, multiple reflections within the cavity layer of PL photons increase the probability of their self-absorption by the long wavelength tail of dye absorption (see Figure 1b and Figure S4). This effect is limited only to the bandgap and microcavity spectral ranges as can be seen in Figure S11a, reporting the PL decay measurement for the microcavity at the cavity mode (red) and at shorter wavelengths than the bandgap (violet). Panel b reports the corresponding decay measurements for the DPP:PS film (black), R1 (red) and R2 (green) samples.
**Figure S11.** Time-resolved PL decay kinetics (a) in the MC\text{tuned} sample for different wavelength ranges and (b) for the different thin-film references at $\lambda_c$.

Small differences among the reference kinetics might be assigned to waveguiding effects, as well as outcoupling and light extraction differences or the slight difference in the effective refractive index of the whole structure hosting the emitter. However, the large difference between MC\text{tuned} and MC\text{detuned} cannot be accounted for by such effects, only by the nature of light-matter interaction in the tuned microcavity.

**Table S1.** Effective refractive index ($n_{\text{eff}}$), external quantum yield ($\eta$), lifetimes obtained from fitting ($\tau_{\text{PL}}$) and calculated radiative and nonradiative lifetimes ($\tau_{\text{rad}}$, $\tau_{\text{NR}}$).

| Sample   | $n_{\text{eff}}$ | $\eta$ (%) | $\tau_{\text{PL}}$ (ps) | $I_{\text{bg}}$ | $\tau_{\text{rad}}$ (10$^3$ ps) | $\tau_{\text{NR}}$ (ps) |
|----------|------------------|------------|--------------------------|-----------------|----------------------------------|-------------------------|
| DPP:PS   | 1.59             | 6 ± 2      | 190 ± 20                 | 0.02            | 3.2 ± 1.4                        | 202 ± 89                |
| R1       | 1.53             | 6 ± 3      | 233 ± 20                 | 0.05            | 5.8 ± 2.9                        | 248 ± 126               |
| R2       | 1.55             | 8 ± 3      | 280 ± 20                 | 0.02            | 3.5 ± 1.3                        | 304 ± 116               |
| MC\text{detuned} | 1.49       | 3 ± 1      | 185 ± 20                 | 0.02            | 6.2 ± 2.7                        | 191 ± 84                |
| MC\text{tuned} | 1.47       | 1 ± 0.5    | 416 ± 20                 | 0.09            | 41.6 ± 22.8                      | 420 ± 230               |

Finally, we report a comparison between the structure fabricated with respect to similar microcavities reported in the literature where the Purcell effect was not observed. In Table S2, we report the polymers used for the dielectric mirrors, their refractive indices at the cavity wavelength, the number of bilayers used per mirror, their actual overall thickness versus the effective cavity length $L_{\text{eff}}$ as calculated using approximations found in literature. These data indicate the paramount
importance of the polymer dielectric contrast in order to engineer light-matter interaction, paving the way for broader development in polymer photonics.

**Table S2.** Characteristics of 1D all-polymer microcavities reported in literature.

| Polymer pairs | Bilayers/mirror | n<sub>low</sub> | n<sub>high</sub> | Δn | L<sub>eff</sub> (mm) | L<sub>geometrical</sub> (mm) |
|---------------|-----------------|----------------|----------------|----|-------------------|-----------------------------|
| PVK/PAA<sup>7</sup> | 25              | 1.51           | 1.68           | 0.17 | 7.5               | 10.0                        |
| PVK/PAA<sup>2b</sup> | 20              | 1.51           | 1.68           | 0.17 | 8.8               | 9.3                         |
| PVK/CA<sup>8</sup> | 25              | 1.48           | 1.66           | 0.18 | 7.0               | 10.0                        |
| PS/CA<sup>9</sup> | 30              | 1.46           | 1.58           | 0.12 | 9.3               | 10.0                        |
| PVK/CA<sup>10</sup> | bottom: 20 top: 10 | 1.48           | 1.68           | 0.20 | 6.2               | 6.0                         |
| PVK/AQ        | 20              | 1.35           | 1.69           | 0.34 | 4.6               | 10.0                        |

PVK = poly(N-vinylcarbazole), PAA = poly(acrylic acid), PS = polystyrene, CA = cellulose acetate.
To further clarify the effect of the cavity structure on the propagation of the electric field at the DPP/PS layer in MCtuned, the square modulus of the electric field at the cavity mode wavelength along the structure was calculated using the transfer matrix method.\textsuperscript{11, 12} The modulation of the square modulus of the absolute electric field amplitude ($|E|^2$) is shown in Figure S12a, against the depth position in the samples (highlighted in red is the DPP:PS layer position), showing a strong enhancement in the electric field of more than 40-fold at the defect layers at the center of the cavity. Closer observation of the cavity electric field at the cavity modes is reported in Fig.12b.

![Figure S12](image)

**Figure S12.** Calculated square modulus of electric field at $\lambda_c$ as a function of depth (a). The red bar indicates the position of DPP:PS layer. (b), Magnification of calculated normalized electric field for $\lambda_c$ inside MCtuned at the boundaries of the defect layer (red: DPP:PS film, green: CA capping layers, blue: PVK, white: AQ).

**REFERENCES**

1. (a) Lova, P., et al., Advances in functional solution processed planar one-dimensional photonic crystals. *Adv. Opt. Mater.* **2018**, *6* (24), 1800730-26; (b) Lova, P., et al., All-polymer photonic microcavities doped with perylene bisimide j-aggregates. *Adv. Opt. Mater.* **2017**, *5* (21), 1700523.
2. Sultanova, N., et al., Dispersion Properties of Optical Polymers. *Acta Phys. Pol. A* **2009**, *116*, 585.
3. Megahd, H., et al., Aquivion–Poly(N-vinylcarbazole) Holistic Flory–Huggins Photonic Vapor Sensors. *Adv. Opt. Mater.* **2021**, *9* (5), 2170017.
4. Barth, M., et al., Spectral and angular redistribution of photoluminescence near a photonic stop band. *Phys. Rev. B* **2005**, *72* (8), 085129.
5. (a) Schubert, E. F., et al., Highly Efficient Light-Emitting Diodes with Microcavities. *Science* **1994**, *265* (5174), 943-945; (b) Hunt, N. E. J., et al., Increased fiber communications bandwidth from a resonant cavity light emitting diode emitting at $\lambda=940$ nm. *Appl. Phys. Lett.* **1993**, *63* (19), 2600-2602.
6. Lova, P., et al., Strategies for dielectric contrast enhancement in 1D planar polymeric photonic crystals. *Appl. Sci.* **2020**, *10* (12), 4122.
7. Lova, P., et al., Polymeric Planar Microcavities Doped with a Europium Complex. *Crystals* **2020**, *10* (4), 287.
8. Manfredi, G., et al., Directional Fluorescence Spectral Narrowing in All-Polymer Microcavities Doped with CdSe/CdS Dot-in-rod Nanocrystals. *ACS Photonics* **2017**, *4* (7), 1761–1769.
9. Frezza, L., et al., Directional enhancement of spontaneous emission in polymer flexible microcavities. *J. Phys. Chem. C* **2011**, *115* (40), 19939 - 19946.
10. Menon, V. M., et al., Lasing from InGaP quantum dots in a spin-coated flexible microcavity. *Opt. Express* **2008**, *16* (24), 19535-19540.
11. Sukhoivanov, I. A.; Guryev, I. V., *Photonic crystals: Physics and Practical Modeling*. Springer: Verlag Berlin Heidelberg, 2009; Vol. 152.
12. Nevou, L. https://github.com/LaurentNevou/Light_WaveTransmission1D_dispersion (accessed January 22, 2021).