## Supplementary information for

## Radiative pumping in a strongly coupled microcavity filled with a neat molecular film showing excimer

## emission

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Figure S1. <sup>1</sup>H-NMR spectrum of <sup>tBu</sup>BPEA (400 MHz, CDCl<sub>3</sub>, TMS).



**Figure S2.** Simulated reflectivity of the <sup>tBu</sup>BPEA cavities with thickness of (a) 95 nm, (b) 105 nm, (c) 115 nm, (d) 125 nm.



**Figure S3.** (a) Simulated reflectivity of the cavities with the thickness of 115 nm without contribution of  $^{tBu}$ BPEA transition to the refractive index. (b) The spectrum at 0° fitted with Lorenz function which gave FWHM of 55 meV.



**Figure S4.** Procedure to fabricate microcavities with <sup>tBu</sup>BPEA neat films. Cavities with intended thickness of 90 nm (C90), 100 nm (C100), 110 nm (C110), 120 nm (C120) was encapsulated with Araldite.

Cavity	Detuning	LPB energy at k <sub>//</sub> =0 (eV)	$\hbar \Omega_1 (\mathrm{eV})$	$\hbar\Omega_2$ (eV)
	$\Delta = E_{\rm c} - E_{\rm ex2} \ ({\rm eV})$			
C95	0.15	2.37	0.50	0.50
C105	0.09	2.32	0.52	0.52
C115	-0.02	2.27	0.51	0.51
C125	-0.17	2.17	0.50	0.56

Table S1. Photon-exciton detuning, LPB energy and Rabi splitting energies of the cavities.

Table S2. Transition energies at the singlet ground state optimised structure.

	S <sub>1</sub> (eV)	$T_1 (eV)$
<sup>tBu</sup> BPEA	2.82	1.23
BPEA	2.87	1.26



Figure S5. PXRD of  ${}^{tBu}BPEA$  before and after annealing the crystal.



**Figure S6.** Angle-dependent (a) reflectivity and (b) photoluminescence (PL) of a cavity with a predicted thickness of 95 nm. Hopfield coefficients of (c) UPB, (d) MPB and (e) LPB obtained through the eigenvectors of the coupled-oscillator model.



**Figure S7.** (a) Angle-dependent reflectivity and (b) PL of a cavity with a predicted thickness of 105 nm. Hopfield coefficients of (c) UPB, (d) MPB and (e) LPB obtained through the eigenvectors of the coupled-oscillator model.



**Figure S8.** Hopfield coefficients of (a) UPB, (b) MPB and (c) LPB obtained through the eigenvectors of the coupled-oscillator model for a cavity with a predicted thickness of 115 nm.



**Figure S9**. (a) Angle-dependent reflectivity and (b) PL of a cavity with a predicted thickness of 125 nm. Hopfield coefficients of (c) UPB, (d) MPB and (e) LPB obtained through the eigenvectors of the coupled-oscillator model.



**Figure S10**. Angle-dependent (a) reflectivity and (b) PL of a neat <sup>tBu</sup>BPEA film with a predicted thickness of 100 nm.



**Figure S11**. Time dependent PL spectra of C90 normalized (a) at 680 nm and (b) at maximum intensity. (c) PL decay profiles of C90 integrated from 467 nm to 753 nm (grey), from 496 nm to 516 nm (green) and from 680 nm to 753 nm (red) normalized at 525 ns. (d) PL decay profiles of C90 and B100 integrated from 496 nm to 516nm.



**Figure S12**. Time dependent PL spectra of C100 normalized (a) at 680 nm and (b) at maximum intensity. (c) PL decay profiles of C100 integrated from 467 nm to 753 nm (grey), from 498 nm to 518 nm (green) and from 680 nm to 753 nm (red) normalized at 525 ns. (d) PL decay profiles of C100 and B100 integrated from 498 nm to 518 nm.



**Figure S13**. Time dependent PL spectra of C110 normalized (a) at 680 nm and (b) at maximum intensity. (c) PL decay profiles of C110 integrated from 467 nm to 753 nm (grey), from 518 nm to 538 nm (green) and from 680 nm to 753 nm (red) normalized at 525 ns. (d) PL decay profiles of C110 and B100 integrated from 518 nm to 538 nm.



**Figure S14**. The decay profiles of the integrated PL for C90, C100, C110, and C120. Spectra corresponding to LP emission have been integrated.



**Figure S15**. (a) Time dependent PL spectra of the encapsulated <sup>tBu</sup>BPEA film with bottom mirror and (b) the PL decay profiles integrated from 470 nm to 540 nm (grey), from 480 nm to 650 nm (red) and 680 nm to 753 nm (blue) normalized at 525 ns. (c) PL decay profiles of B100 integrated from 470 nm to 540 nm (grey), from 480 nm to 650 nm (red) and 680 nm to 753 nm (blue) normalized at 525 ns. (d) PL decay profiles of samples with bottom mirror and B100 integrated from 467 nm to 753 nm.



Figure S16. Angle dependent polariton population of (a) C95, (b) C105, (c) C115, (d) C125.



**Figure S17**. (a) 2D plot of the ultrafast TA of the <sup>tBu</sup>BPEA encapsulated film. (b) Time profiles of TA at 445 nm, 480 nm, 525 nm, 610 nm and 645 nm. (c) TA spectra from 0.53 ps to 1000 ps.