

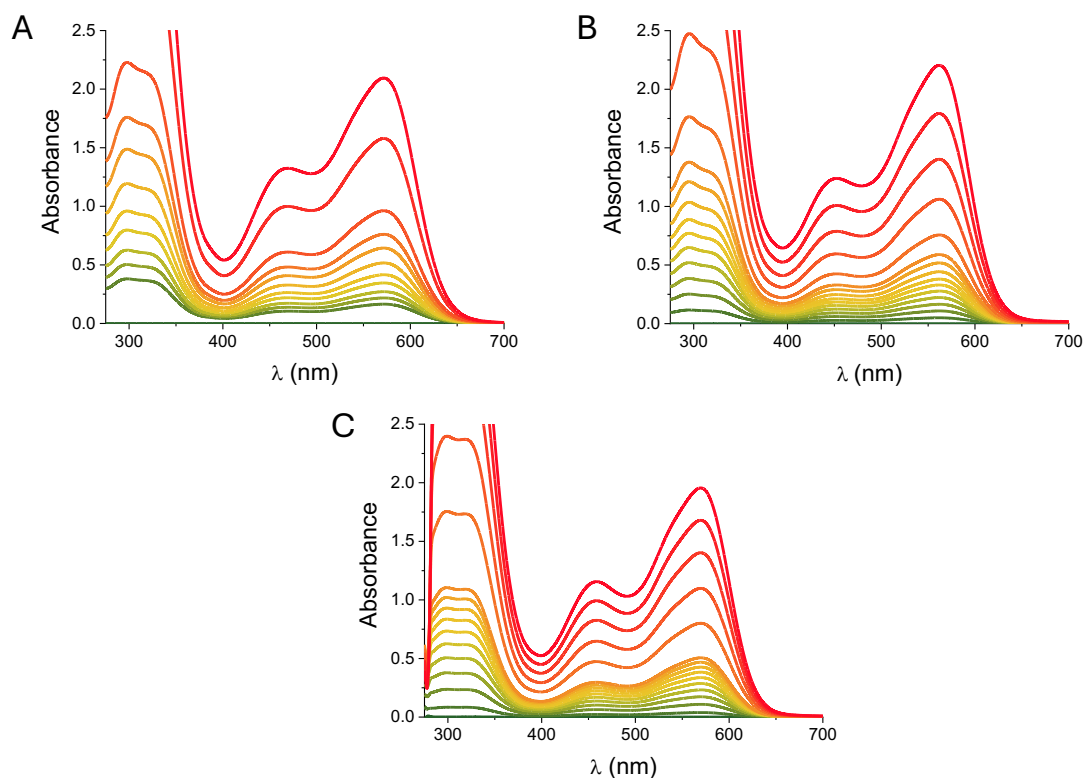
## Article 6 Supplementary Material (Oliveiri, A. *et al.*)

### Supplementary Table

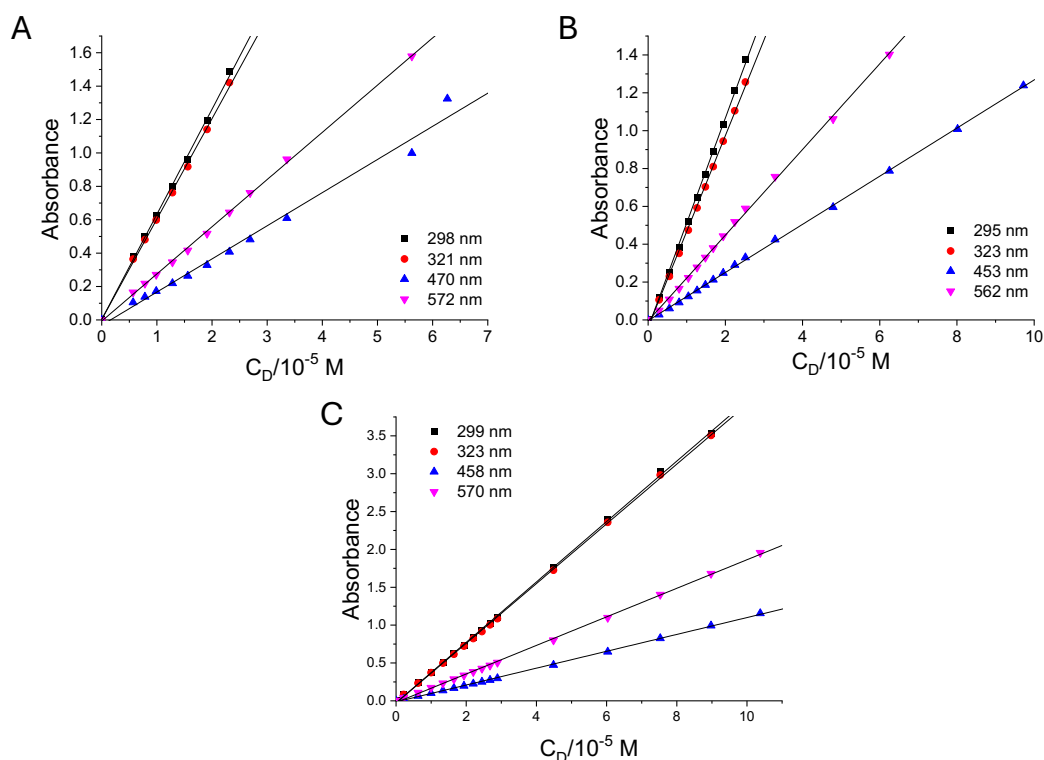
**Table S1** | Estimation of reabsorption losses ( $P_0$ ) for thin-film LSC devices comprising different concentrations of 1,7-DTPEPBI.

Concentration [%]	$P_0$
0.4	0.90
0.8	0.88
1.2	0.88
1.6	0.90
2.0	0.89

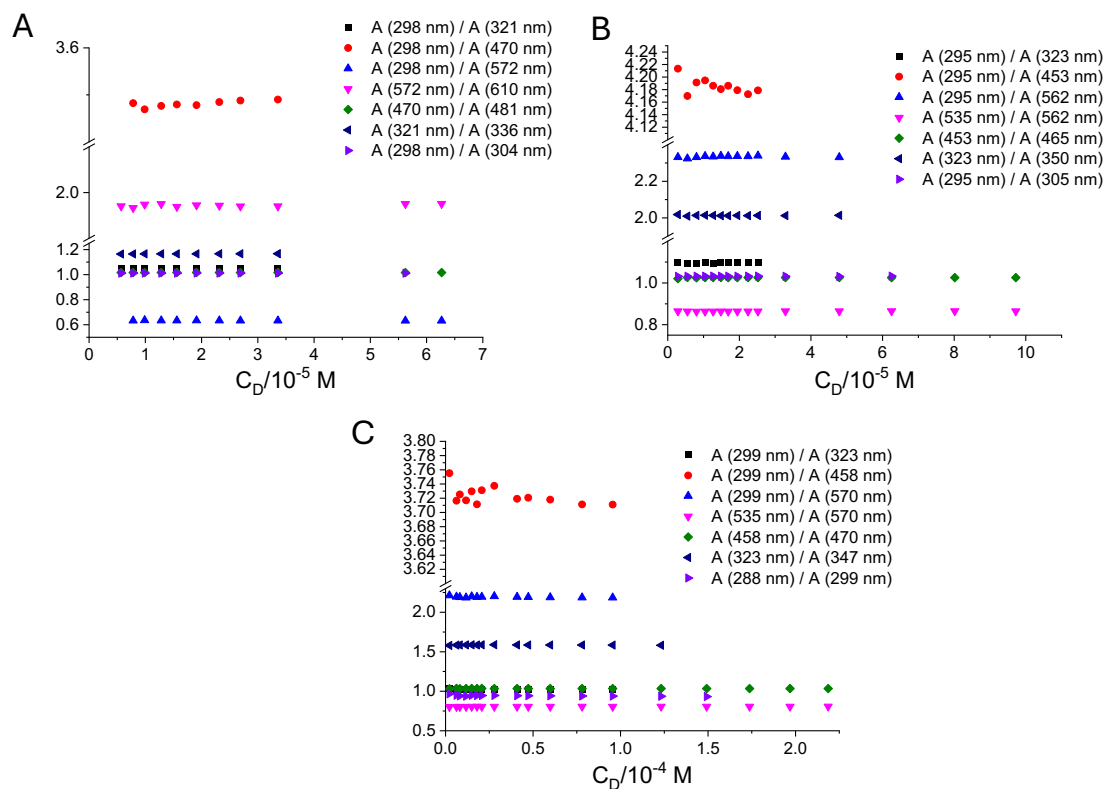
### Supplementary Figures



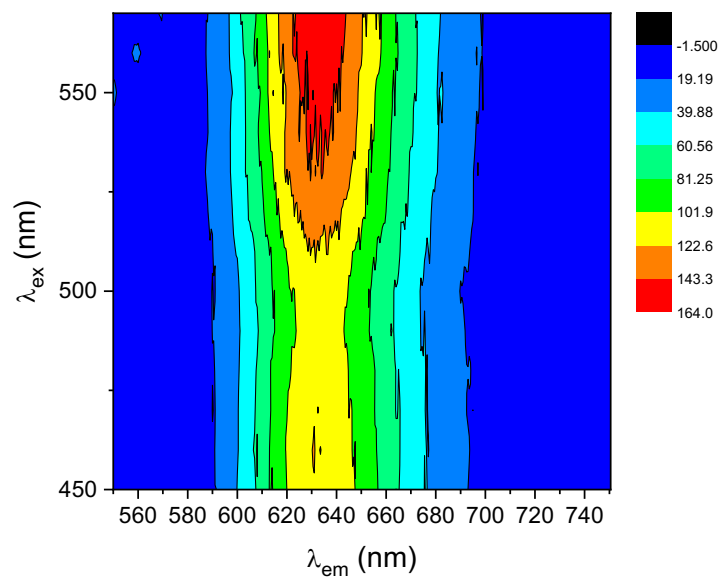
**Figure S1** | (A) Absorption spectra of 1,7-DTPEPBI in: (A)  $\text{CHCl}_3$ ,  $2.83 \times 10^{-6} \leq \text{CD} \leq 9.72 \times 10^{-5} \text{ M}$ ,  $25.0^\circ\text{C}$ ; (B) THF,  $5.70 \times 10^{-6} \leq \text{CD} \leq 6.27 \times 10^{-5} \text{ M}$ ,  $25.0^\circ\text{C}$ ; (C) Toluene,  $2.20 \times 10^{-6} \leq \text{CD} \leq 1.04 \times 10^{-4} \text{ M}$ ,  $25.0^\circ\text{C}$ .



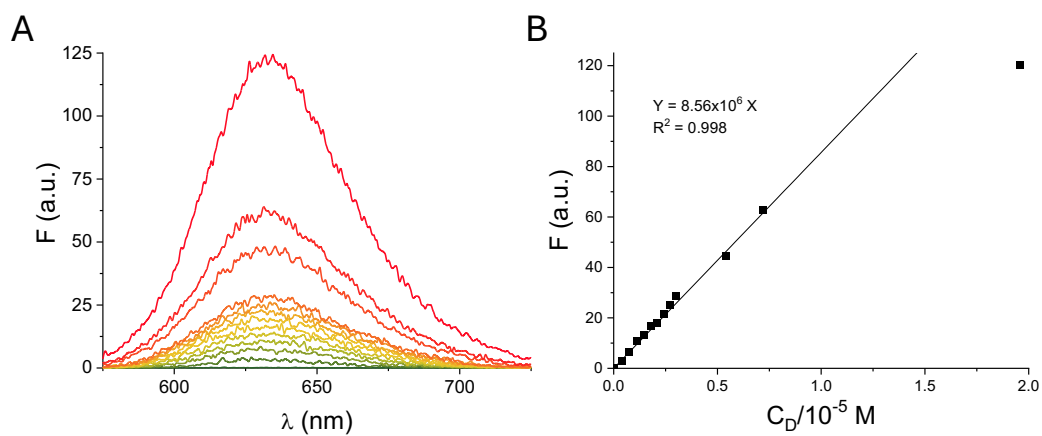
**Figure S2** | (A) Absorption spectra of 1,7- DTPEPBI in: (A) CHCl<sub>3</sub>,  $2.83 \times 10^{-6} \leq C_D \leq 9.72 \times 10^{-5} \text{ M}$ , 25.0 °C; (B) THF,  $5.70 \times 10^{-6} \leq C_D \leq 6.27 \times 10^{-5} \text{ M}$ , 25.0 °C; (C) Toluene,  $2.20 \times 10^{-6} \leq C_D \leq 1.04 \times 10^{-4} \text{ M}$ , 25.0 °C.



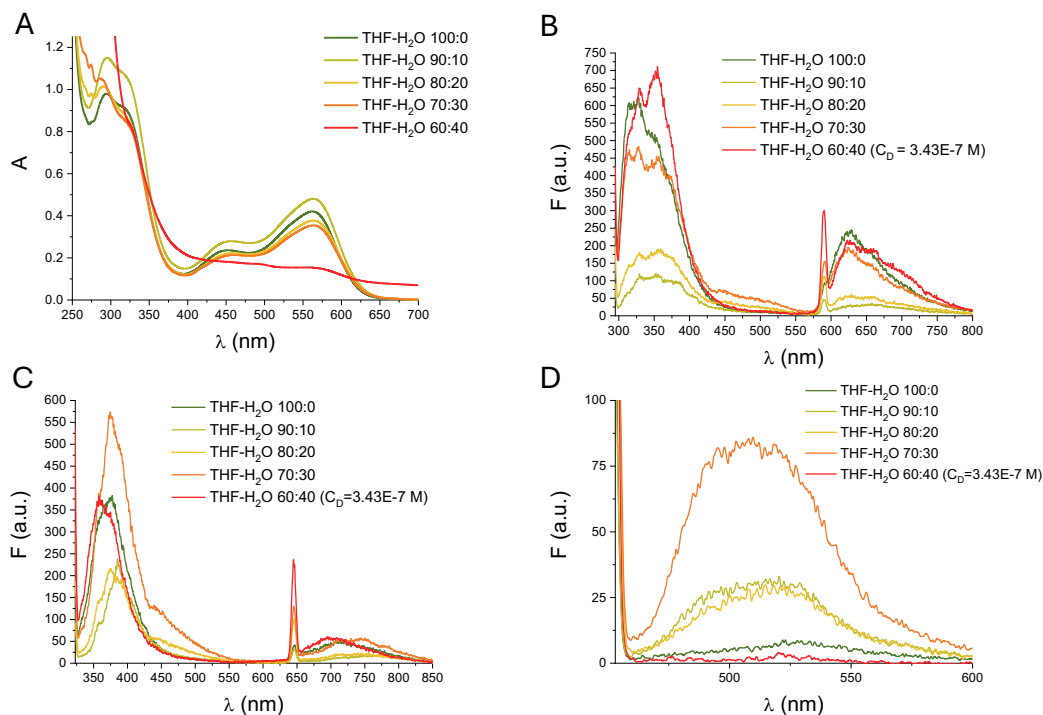
**Figure S3** | Ratio of absorbances (25.0 °C) measured at two wavelengths at varying concentrations of 1,7-DTPEPBI (CD) in (a) THF; (b) CHCl<sub>3</sub>; (c) Toluene.



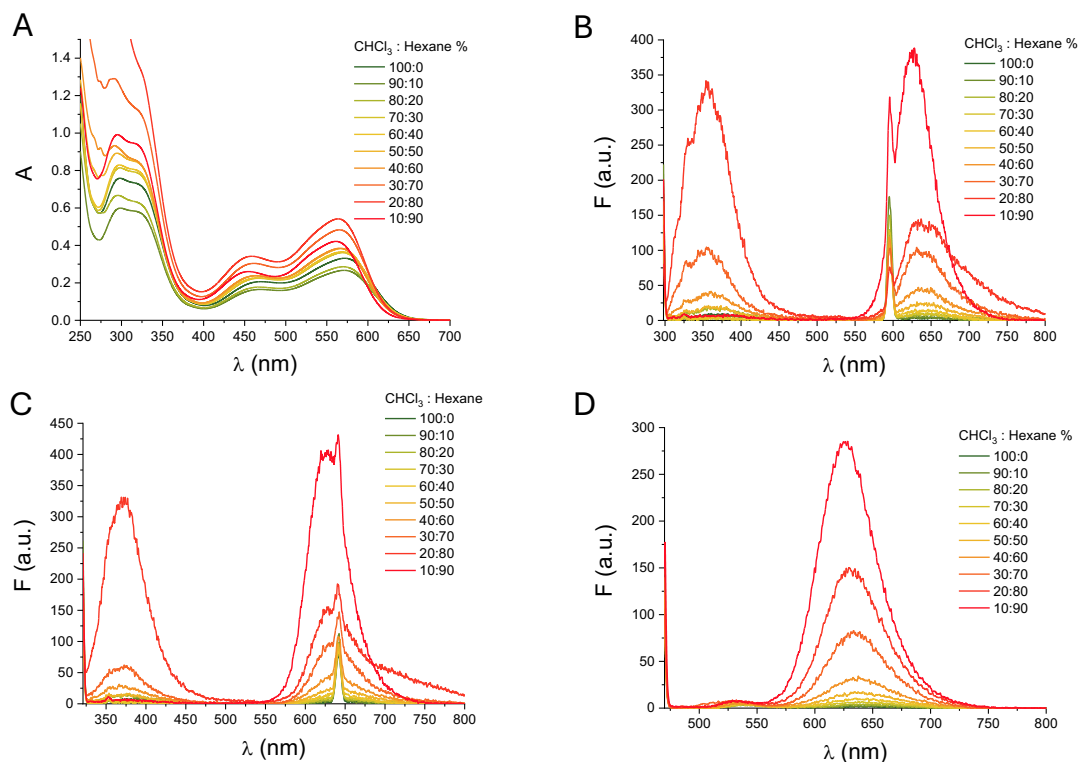
**Figure S4** | 3D spectrum of 1,7-DTPEPBI in toluene;  $C_D = 1.96 \times 10^{-5}$  M, 25.0 °C.



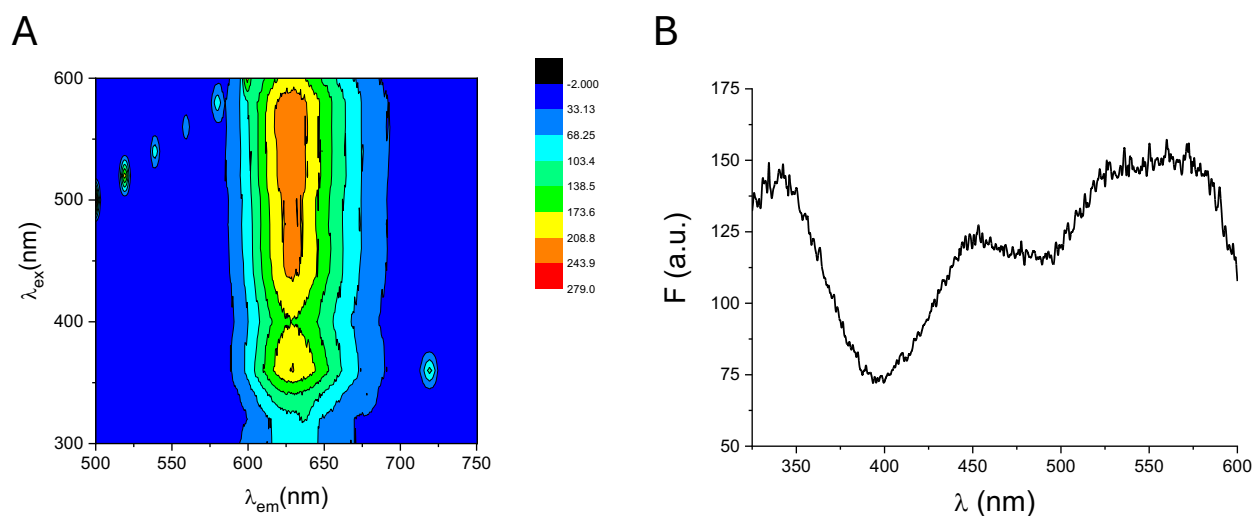
**Figure S5** | (A) Emission spectra of 1,7-DTPEPBI in toluene;  $\lambda_{ex} = 570$  nm,  $3.84 \times 10^{-7} \leq C_D \leq 1.96 \times 10^{-5}$  M, 25 °C; (B) Linear interpolation of fluorescence signal read in toluene for 1,7-DTPEPBI as a function of concentration;  $\lambda_{ex} = 570$  nm,  $3.84 \times 10^{-7} \leq C_D \leq 1.96 \times 10^{-5}$  M, 25.0 °C.



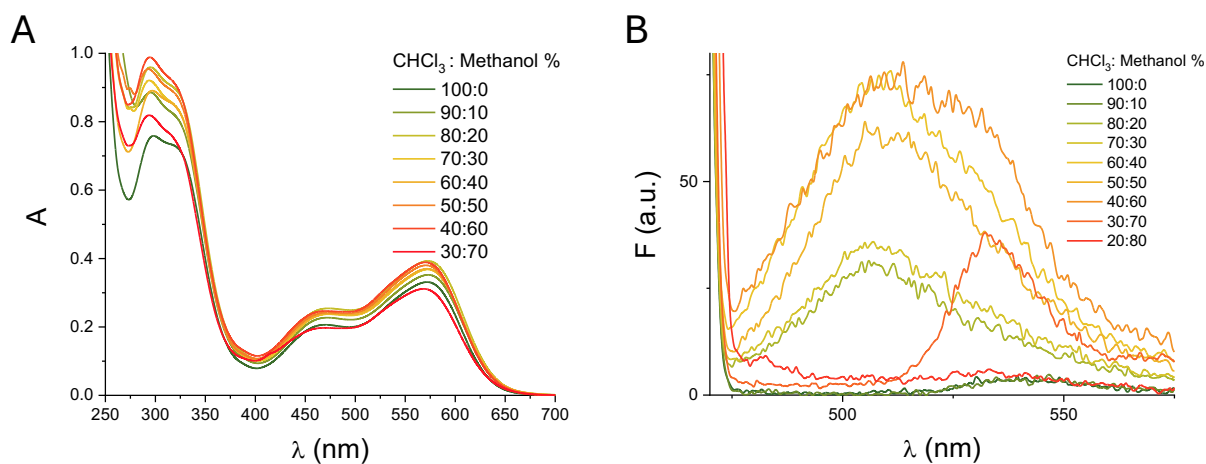
**Figure S6** | Absorption spectra of 1,7-DTPEPBI in solutions at different percentage of nonsolvent (H<sub>2</sub>O) versus solvent (THF, v/v %)  $C_D = 1.75 \times 10^{-5}$  M, 25.0 °C (A). Emission spectra of 1,7-DTPEPBI in solutions with different percentage of non-solvent (H<sub>2</sub>O) versus solvent (THF, v/v%);  $C_D = 1.75 \times 10^{-5}$  M;  $C_D$  (THF/H<sub>2</sub>O 60:40) =  $3.43 \times 10^{-7}$  M;  $\lambda_{ex}$  = 295 nm (B) - 323 nm (C) - 453 nm (D); 25.0 °C.



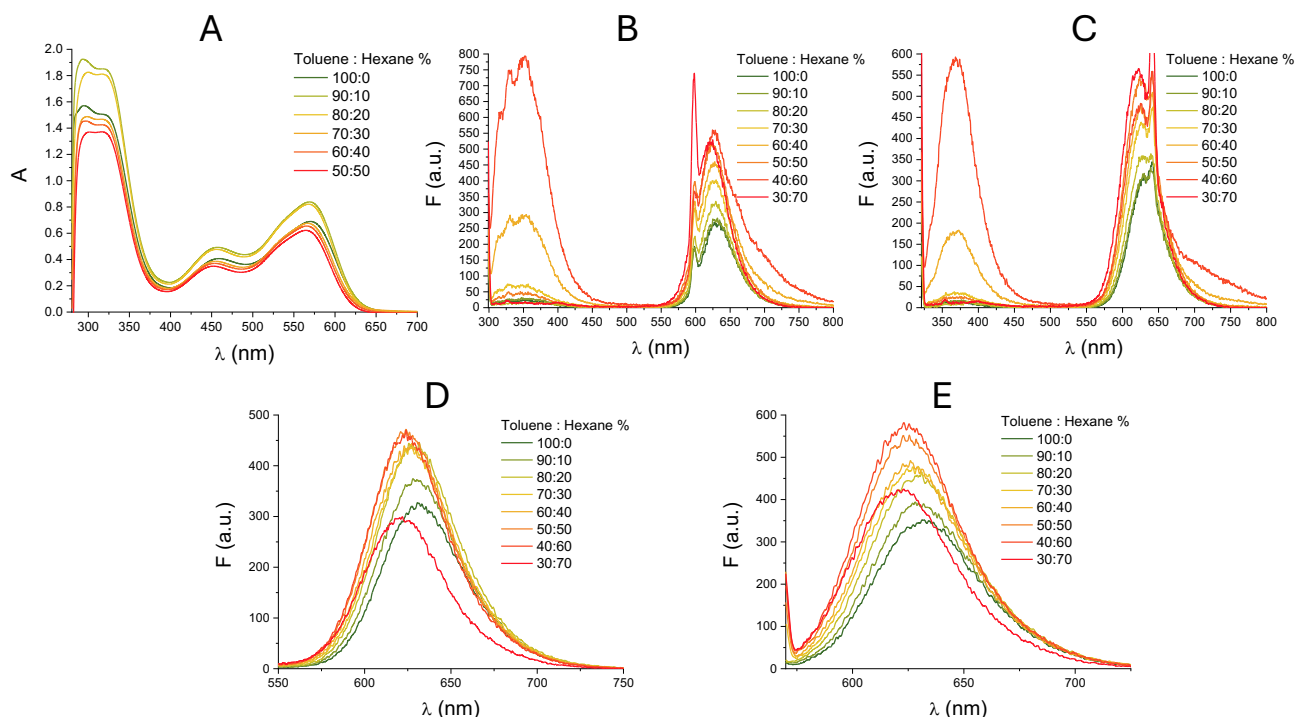
**Figure S7**: Absorption spectra of 1,7-DTPEPBI in solutions at different percentage of nonsolvent (hexane) versus solvent (CHCl<sub>3</sub>, v/v %)  $C_D = 1.66 \times 10^{-5}$  M, 25.0 °C (A). Emission spectra of 1,7-DTPEPBI in solutions with different percentage of non-solvent (hexane) versus solvent (CHCl<sub>3</sub>, v/v%);  $C_D = 1.66 \times 10^{-5}$  M;  $\lambda_{ex}$  = 298 nm (B) - 321 nm (C) - 470 nm (D); 25.0 °C.



**Figure S8** | (A) 3D spectrum of 1,7-DTPEPBI in  $\text{CHCl}_3$ -Hexane 10:90 solution;  $C_D = 1.66 \times 10^{-5} \text{ M}$ ;  $25.0^\circ \text{C}$ ; (B) Excitation spectrum ( $\lambda_{\text{em}} = 630 \text{ nm}$ ) of 1,7-DTPEPBI in the 90% solution of nonsolvent (hexane) versus solvent ( $\text{CHCl}_3$ , v/v%);  $C_D = 1.66 \times 10^{-5} \text{ M}$ ;  $25.0^\circ \text{C}$ .



**Figure S9** | Absorption spectra of 1,7-DTPEPBI in solutions at different percentages of nonsolvent (methanol) versus solvent ( $\text{CHCl}_3$ , v/v%);  $C_D = 1.67 \times 10^{-5} \text{ M}$ ;  $25.0^\circ \text{C}$  (A). Emission spectra of 1,7-DTPEPBI in solutions at different percentages of nonsolvent (methanol) versus solvent ( $\text{CHCl}_3$ , v/v%);  $C_D = 1.67 \times 10^{-5} \text{ M}$ ;  $\lambda_{\text{ex}} = 470 \text{ nm}$ ;  $25.0^\circ \text{C}$  (B).



**Figure S10** | Absorption spectra of 1,7-DTPEPBI in solutions at different percentages of non-solvent (hexane) versus solvent (toluene, v/v%);  $C_D = 3.92 \times 10^{-5}$  M; 25.0 °C (A). Emission spectra of 1,7-DTPEPBI in solutions at different percentages of non-solvent (hexane) versus solvent (toluene, v/v%);  $C_D = 3.92 \times 10^{-5}$  M;  $\lambda_{ex} = 299$  nm (B) - 323 nm (C) - 458 nm (D) - 570 nm (E); 25.0 °C.

### LSC Performance determination

An LCS-100 94011A solar simulator (S/N: 322, AM filter 1.5G std:  $69 \text{ mW cm}^{-2}$  at 254 mm, Oriel Instruments, USA) was used as a light source. The incident, transmitted and edge-emitted irradiance spectra were recorded by using a commercially available Arkeo instrument (Cicci research s.r.l., Italy) containing a CMOS-based spectrometer (CCARK.A.4 Spectroradiometer, Fiber Optic VIS/NIR spectrometer, 2048 pixels, grating VA 360-1100nm, slit-50, OSC, DCL- UV/VIS), with a symmetrical Czerny-Turner optical bench connected to an integrating sphere. The spectrally-resolved edge output photon count was collected from the CMOS-based spectrometer, converted into optical power (W) and then in irradiance ( $\text{W m}^{-2}$ ). The cylindrical integrating sphere has a circular aperture with a diameter of 1 cm. By placing the integrating sphere directly under the light of a solar simulator at the correct distance to obtain an irradiance of about 1 Sun, the incident irradiance spectrum ( $E_{in}$ ) is acquired. Subsequently, by placing the sample over the integrating sphere hole, the transmitted irradiance spectrum ( $E_{\lambda, tr}$ ) is acquired. The transmitted irradiance spectrum used in the calculations is the average of three transmittance spectra acquisitions in different positions of the same LSC.

Four edge-emitted irradiance spectra are then acquired by placing the integrating sphere horizontally, in contact with each edge of the LSC one at a time, under the light of the solar simulator. The average edge-emitted irradiance spectrum ( $\bar{E}_{\lambda, tr}$ ) is then calculated. A black adhesive tape layer has been applied to the uncovered aperture portion of the LSC to minimize the detection of stray light. For all the irradiance acquisitions, an absorbing matte black background was placed in contact with the LSC rear side to limit reflections of unabsorbed light.

Since the photon density flux is the number of photons passing through a surface in the unit of time, we define the density flux of incident photons ( $F_{ph, in}$ ), the density flux of absorbed photons ( $F_{ph, abs}$ ), and the average density flux of photons emitted from the edges ( $F_{ph, out}$ ) as follows (in  $\text{m}^{-2} \text{s}^{-1}$ ):

$$F_{ph,in} = \int_{\lambda_1}^{\lambda_2} E_{\lambda,in}(\lambda) \frac{\lambda}{hc} d\lambda$$

$$F_{ph,abs} = \int_{\lambda_1}^{\lambda_2} E_{\lambda,abs}(\lambda) \frac{\lambda}{hc} d\lambda = \int_{\lambda_1}^{\lambda_2} [E_{\lambda,in}(\lambda) - E_{\lambda,tr}(\lambda)] \frac{\lambda}{hc} d\lambda$$

$$\bar{F}_{ph,out} = \int_{\lambda_1}^{\lambda_2} \bar{E}_{\lambda,out}(\lambda) \frac{\lambda}{hc} d\lambda$$

where  $\lambda$  is the wavelength of photons (in nm),  $h$  is Planck's constant (in J s),  $c$  is the speed of light (in nm s<sup>-1</sup>),  $\lambda_1$  and  $\lambda_2$  the extremes of the wavelength acquisition range. The units for all the irradiance spectra are W m<sup>-2</sup> nm<sup>-1</sup>. The incident light irradiance spectrum was integrated in the 350 - 1100 nm range. The absorbed irradiance spectrum was derived subtracting the incident and transmitted irradiance spectra and integrating the result, covering only the absorption range. The edge-emitted irradiance spectrum was integrated covering the emission range exclusively, where possible, to minimize overestimates due to the scattering of the incident light.

LSC photonic efficiencies were then calculated as follows:

$$\eta_{int} = \frac{N_{out}}{N_{abs}} = \frac{4 A_{edge} F_{ph,out}}{A_{top} F_{ph,abs}}$$

$$\eta_{ext} = \frac{N_{out}}{N_{in}} = \frac{4 A_{edge} F_{ph,out}}{A_{top} F_{ph,in}}$$

where  $A_{edge}$  is the surface area of the single edge (the LSC side length multiplied by the average thickness),  $A_{top}$  is the area of the top surface of the LSC,  $N_{in}$  is the total flux of photons incident on the top surface of the LSC,  $N_{out}$  is the total flux of edge-emitted photons summed over all LSC edges and  $N_{abs}$  is the total flux of photons absorbed by the LSC. All the photon fluxes are expressed in s<sup>-1</sup> unit.

I-V curves for the electric device efficiency determination of lab-scale devices were obtained by coupling the LSC edge with two silicon PV cells (IXOLAR KXOB25- 12X1F solar cell 20.0 × 5.65 mm<sup>2</sup>,  $V_{oc} = 0.69$  V,  $I_{sc} = 46.7$  mA, FF > 70%, nominal  $\eta = 25\%$ , AnySolar Ltd, South Korea) in series, connected to a B2901A precision source/measure unit (Keysight Technologies, USA). The stray light emitted by the solar simulator and directed towards the PV cell was obscured by the application of a strip of black adhesive tape. Silicone grease was used to ensure optical contact between the LSC and the PV cell. The other three edges of the LSC were covered with reflective aluminum tape. A black matte layer was placed beneath the LSC with an air gap of about 1.5 cm.

$\eta_{dev}$  gives a quantification of the potential usefulness of an LSC as an auxiliary device to PVs. It can be obtained experimentally as follows:

$$\eta_{dev} = \frac{P_{max}}{A_{top} E_{in}} = \frac{I_{MPP} V_{MPP}}{A_{top} \int_{\lambda_1}^{\lambda_2} E_{\lambda,in}(\lambda) d\lambda}$$

where  $E_{\lambda,in}$  is the incident spectral irradiance acquired as described earlier (in W m<sup>-2</sup> nm<sup>-1</sup>),  $E_{in}$  is the total incident irradiance (in W m<sup>-2</sup>),  $I_{MPP}$  is the current at the maximum power point (in A),  $V_{MPP}$  is the voltage at the maximum power point (in V),  $A_{top}$  is the illuminated top surface (in m<sup>2</sup>),  $\lambda$  is the wavelength of photons (in nm),  $\lambda_1$  and  $\lambda_2$  the extremes of the wavelength acquisition range.  $P_{max}$ , which is the maximum power generated by the LSC-PV system (in W), is derived from the J-V curve.

The probability, designated  $P_0$ , that a first-generation fluorescence photon will successfully reach the detector without undergoing reabsorption was calculated according to the following formula:

$$P_0 = \frac{\int PL'_s(\lambda) d\lambda}{\int PL_{Zr}(\lambda) d\lambda}$$

where  $PL_{Zr}(\lambda)$  represents a photoluminescence spectrum with zero reabsorption (or negligible reabsorption). This was obtained from an edge-emission spectrum acquired by exciting solely in a spot very close to the edge ( $\lambda_{exc} = 405$  nm)  $PL'_s(\lambda)$  is the edge-emission spectrum, scaled to match at long wavelengths where reabsorption is negligible. Please refer to the work of Wilson et al. [43] for more information about the scaling method.  $PL'_s(\lambda)$  was obtained exciting the sample in the center of the LSC, considering, for square LSC modules, the average path length for trapped fluorescence light as approximately half the side length.