

## Supplementary Information:

### Controlling triplet-triplet upconversion and singlet-triplet annihilation in organic light-emitting diodes for injection lasing

Atul Shukla,<sup>a,b,\*</sup> Monirul Hasan,<sup>a,b</sup> Gangadhar Banappanavar,<sup>c</sup> Viqar Ahmad,<sup>a,b</sup> Jan Sobus,<sup>a,b</sup>  
Evan G. Moore,<sup>d</sup> Dinesh Kabra,<sup>c,\*</sup> Shih-Chun Lo,<sup>a,d,\*</sup> Ebinazar B. Namdas<sup>a,b,\*</sup>

<sup>a</sup> Centre for Organic Photonics & Electronics, The University of Queensland, Brisbane,  
Queensland 4072, Australia

<sup>b</sup> School of Mathematics and Physics, The University of Queensland, Brisbane, Queensland  
4072, Australia.

<sup>c</sup> Department of Physics, Indian Institute of Technology Bombay, Mumbai 400076, India

<sup>d</sup> School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane,  
Queensland 4072, Australia.

\*Corresponding authors: Ebinazar B. Namdas ([e.namdass@uq.edu.au](mailto:e.namdass@uq.edu.au))

Shih-Chun Lo ([s.lo@uq.edu.au](mailto:s.lo@uq.edu.au))

Dinesh Kabra ([dkabra@iitb.ac.in](mailto:dkabra@iitb.ac.in))

Atul Shukla ([a.shukla@uq.edu.au](mailto:a.shukla@uq.edu.au))

**Keywords:** amplified spontaneous emission, triplet-triplet upconversion, anthracene derivatives, organic light-emitting diode, deep-blue emission

## Contents

### Supplementary Figures

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| <b>Supplementary Figure 1.</b> EL characteristics of doped and non-doped PCAN based OLEDs. Current density-luminance-voltage (J-V-L) characteristics of (a) non-doped and (b) doped OLED devices. (c) Comparison of PL and EL spectra from doped and non-doped PCAN based devices. Shoulder at 550 nm in neat film EL spectra was observed due to slight emission from Alq <sub>3</sub> .....                                                                                                                      | 4  |
| <b>Supplementary Figure 2.</b> PL decay of PCAN in toluene solution, non-doped and doped films. TCSPC decay curves for PCAN in (a) dilute toluene solution (b) neat films and (c) 10wt% doped in CBP. (Inset of all the figures showing TCSPC decay in 200 ns range).....                                                                                                                                                                                                                                          | 5  |
| <b>Supplementary Figure 3.</b> TRPL and fluence dependent studies (a) Time-resolved emission decay for neat and doped films, (b) emission spectra of neat films at different gate delays, (c) Normalised DF intensities vs normalised PF intensities at different fluence for neat films, linearly fitted with dual slopes .....                                                                                                                                                                                   | 6  |
| <b>Supplementary Figure 4.</b> Schematic of the triplet photosensitization mediated TTU in PCAN. In photosensitization, the absorption takes place via PtOEP, leading to generation of triplet excitons which are the transferred to PCAN by dexter energy transfer (DET) and subsequently upconverted to singlet excitons by triplet-triplet annihilation .....                                                                                                                                                   | 7  |
| <b>Supplementary Figure 5.</b> Steady-state absorption and emission for triplet photosensitization. (a) Absorption and (b) emission spectrum of the toluene solutions of only PtOEP (10 <sup>-5</sup> M) and PtOEP (10 <sup>-5</sup> M) with PCAN (10 <sup>-2</sup> M). (c) Comparison of emission spectrum of dilute PCAN solution (~10 <sup>-5</sup> M) when excited at 350 nm with upconverted PCAN emission. (d) Comparison of normalised emission from 550-800 nm obtained in both cases in (a) and (b) ..... | 8  |
| <b>Supplementary Figure 6.</b> Transient EL setup. Schematic of the experimental setup used to study transient EL response in PCAN based OLED devices .....                                                                                                                                                                                                                                                                                                                                                        | 8  |
| <b>Supplementary Figure 7.</b> Transient EL response of doped and non-doped PCAN based OLEDs. Transient current density and electroluminescence (EL) response of (a) non-doped and (b) doped PCAN based OLED at variable voltages.....                                                                                                                                                                                                                                                                             | 9  |
| <b>Supplementary Figure 8.</b> Transient absorption spectra of PCAN neat films. Transient absorption spectra for PCAN neat film with probe delays ranging from 0 to 2 $\mu$ s, showing triplet and singlet absorption band.....                                                                                                                                                                                                                                                                                    | 10 |
| <b>Supplementary Figure 9.</b> EL decay of doped and nondoped PCAN based OLEDs. EL turn-off characteristics for non-doped and doped devices showing the presence of prompt and delayed fluorescence .....                                                                                                                                                                                                                                                                                                          | 10 |
| <b>Supplementary Figure 10.</b> Light amplification characteristics of doped and non-doped PCAN thin films. Input–output–FWHM and emission spectra collected from the edge of the organic layer at different input excitation intensities for (a) neat film and (b) doped films.....                                                                                                                                                                                                                               | 11 |
| <b>Supplementary Figure 11.</b> Threshold current density as a function of STA and TTU. Increment in threshold current density in two scenarios when STA is fixed; TTU is reduced (black) and when TTU is fixed; STA is increased (red) .....                                                                                                                                                                                                                                                                      | 12 |
| <b>Supplementary Figure 12.</b> Schematic representation of the TTU mechanism in PCAN and C545T based host-guest system. The triplet excitons can be upconverted to singlet in PCAN                                                                                                                                                                                                                                                                                                                                |    |

and finally transferred to singlet excited state of C545T *via* Förster energy transfer. The triplet excitons on C545T can be funnelled back to PCAN *via* Dexter energy transfer. ....12

**Supplementary Figure 13.** Absorption and emission spectra of C545T in PCAN and CBP. Normalised absorption and PL spectra of 1, 3 and 5 wt% C545T doped in (a) PCAN and (b) CBP hosts.....13

**Supplementary Figure 14.** Comparison of triplet absorption and emission in neat PCAN and C545T:PCAN (1:99) blend. Triplet excited-state absorption spectrum of PCAN (time averaged spectrum from Supplementary Figure 8 overlapped with the emission of PCAN neat films and doped films of 1wt% C545T in PCAN .....14

**Supplementary Figure 15.** Performance characteristics of C545T OLEDs with PCAN and CBP hosts. (a) Schematic representation of solution-processed OLED device structure. Comparison of (b) *J-V-L* characteristics, (c) EQE vs current density, and (d) EL spectra of OLEDs based on 1wt% C545T doped in PCAN and CBP hosts matrices .....15

**Supplementary Figure 16.** Transient EL of C545T:CBP blend OLEDs. Normalised transient EL response of C545T: CBP (1:99 wt%) based OLED under variable voltage.....15

**Supplementary Figure 17.** Transient EL of C545T:PCAN blend OLEDs. (a) Absolute and (b) normalised transient EL response of C545T: PCAN (1:99 wt%) based OLED under variable voltages. ....16

## **Supplementary Notes**

**Supplementary Note 1.** TTU through triplet photosensitization .....17

**Supplementary Note 2.** Numerical model to extract annihilation rate constants .....17

**Supplementary Note 3.** Estimation of threshold current density required for lasing .....18

## **Supplementary Tables**

**Supplementary Table 1.** Comparison of performance characteristics of doped and non-doped PCAN based OLEDs.....19

**Supplementary Table 2.** Summary of photophysical properties derived from PLQYs and TCSPC decay curves.....19

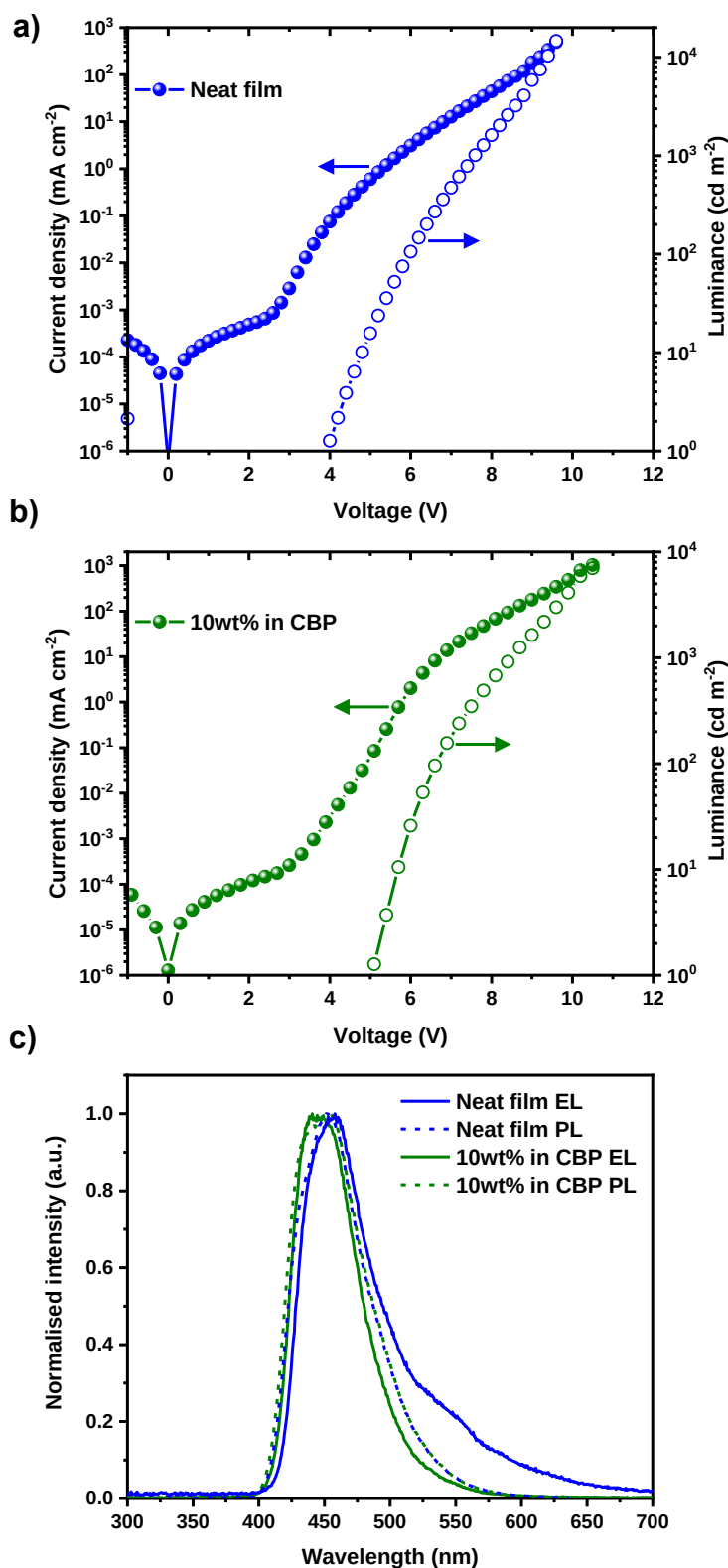
**Supplementary Table 3.** Summary of  $k_{STA}$  and  $k_{TTU}$  obtained from non-doped PCAN OLEDs at different voltage pulses with corresponding steady-state current densities .....20

**Supplementary Table 4.** Summary of  $k_{STA}$  and  $k_{TTU}$  obtained from doped PCAN OLEDs at different voltage pulses with corresponding steady-state current densities.....20

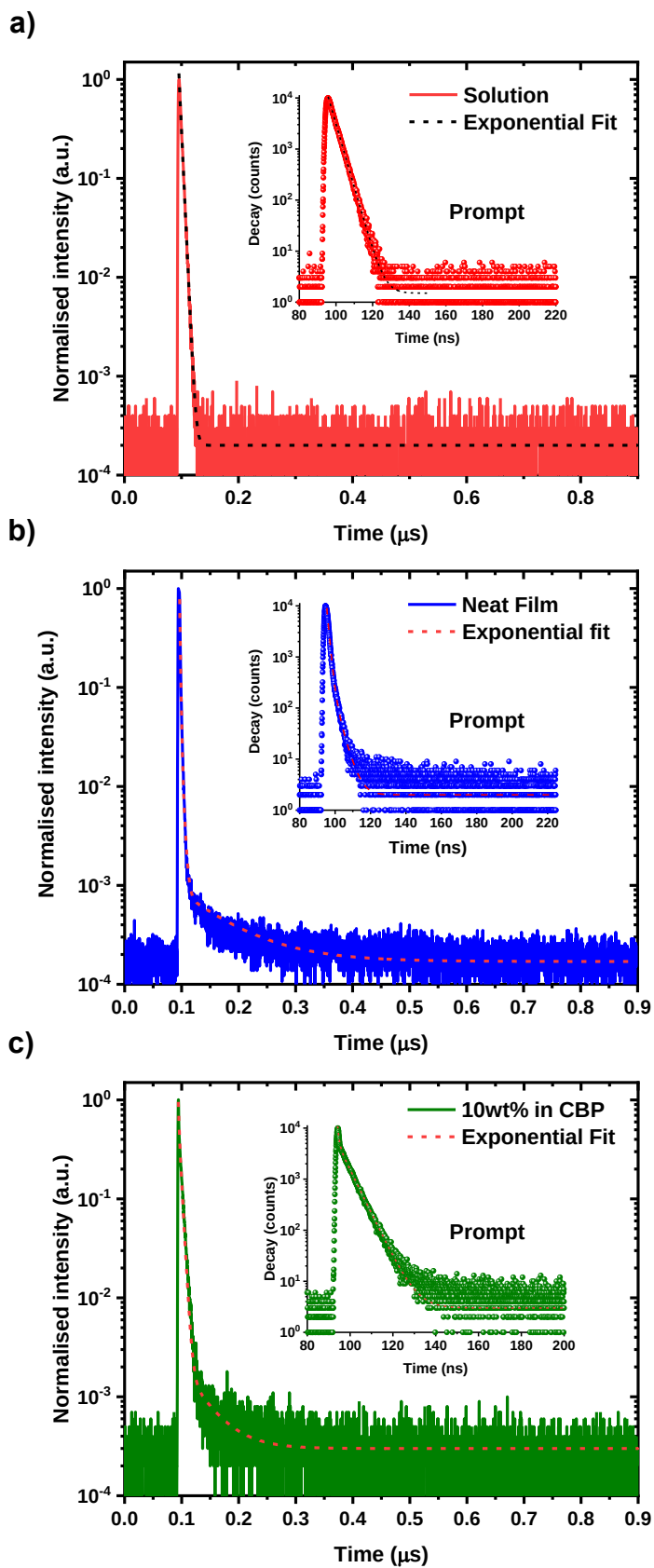
**Supplementary Table 5.** Summary of photophysical properties for variable doping ratio (1, 3, and 5 wt%) of C545T in PCAN and CBP.....20

**Supplementary References**.....21

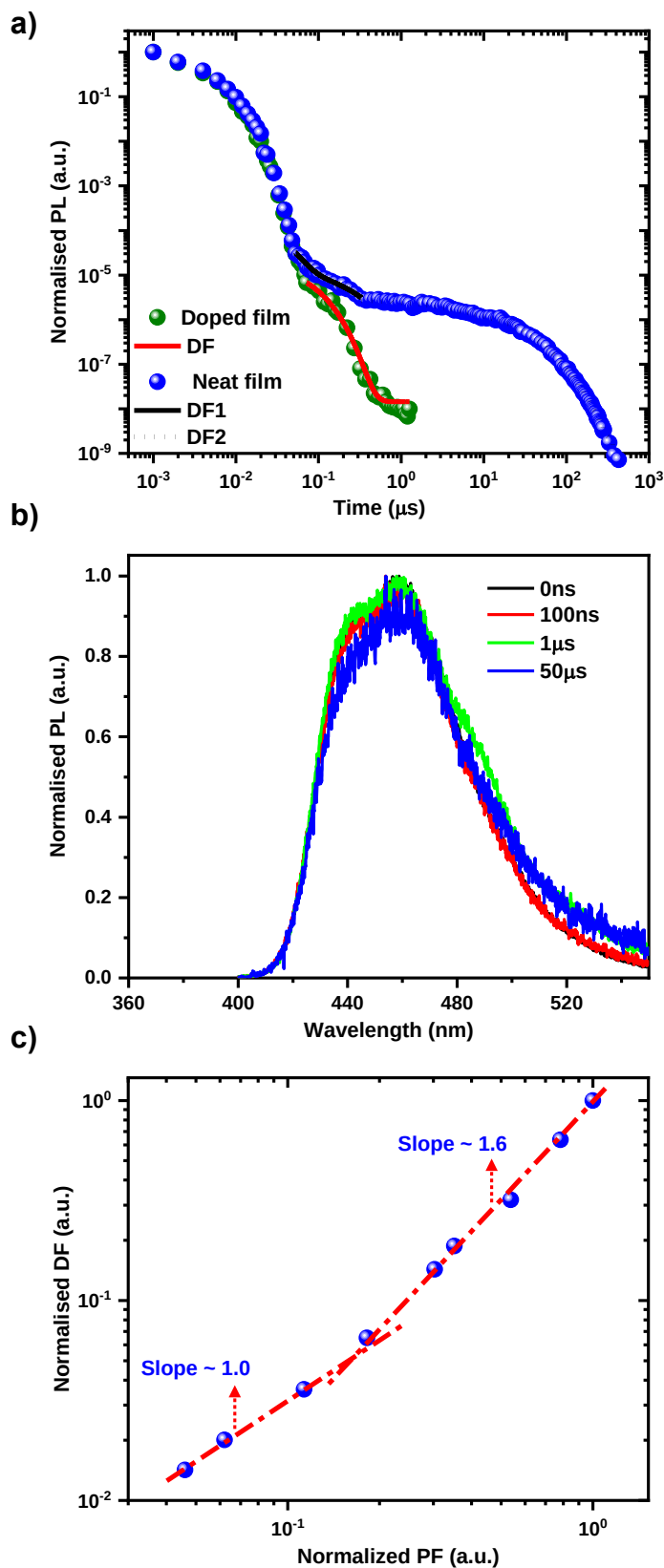
## Supplementary Figures



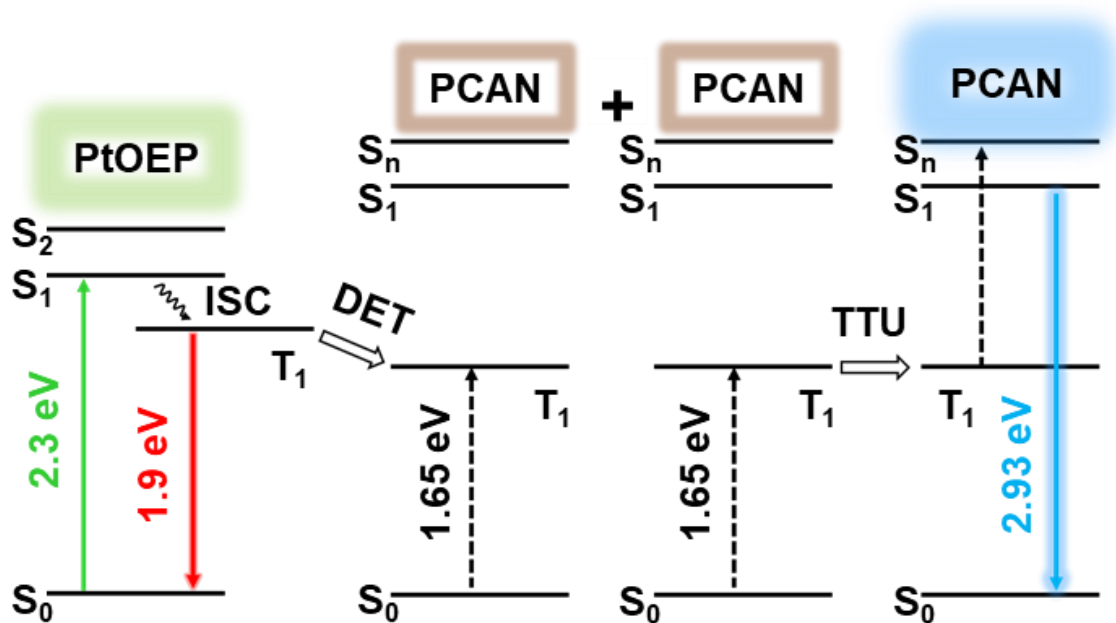
**Supplementary Figure 1. EL characteristics of doped and non-doped PCAN based OLEDs.** Current density-luminance-voltage (J-V-L) characteristics of (a) non-doped and (b) doped OLED devices. (c) Comparison of PL and EL spectra from doped and non-doped PCAN based devices. Shoulder at 550 nm in neat film EL spectra was observed due to slight emission from Alq<sub>3</sub>.



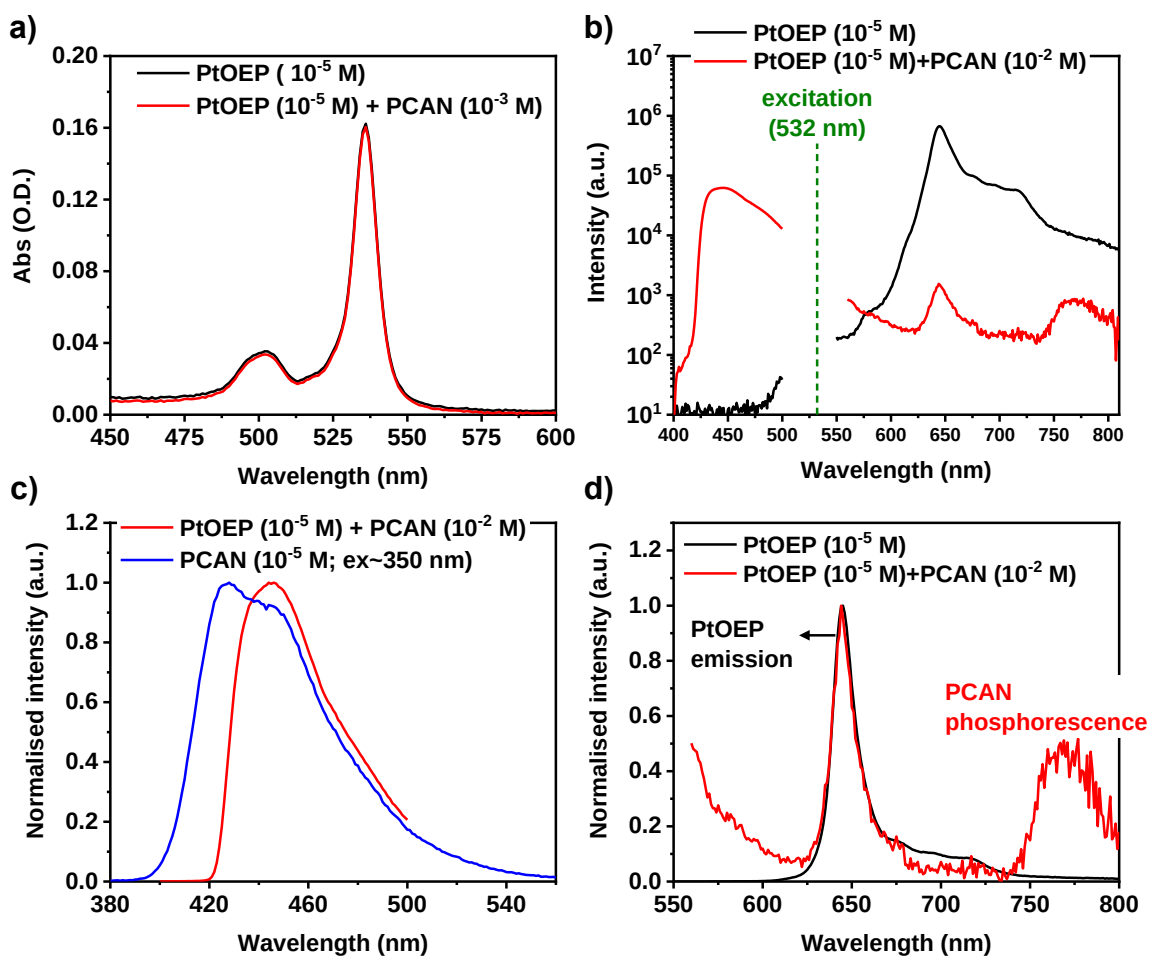
**Supplementary Figure 2. PL decay of PCAN in toluene solution, non-doped and doped films.** TCSPC decay curves for PCAN in (a) dilute toluene solution (b) neat films and (c) 10wt% doped in CBP. (Inset of all the figures showing TCSPC decay in 200 ns range)



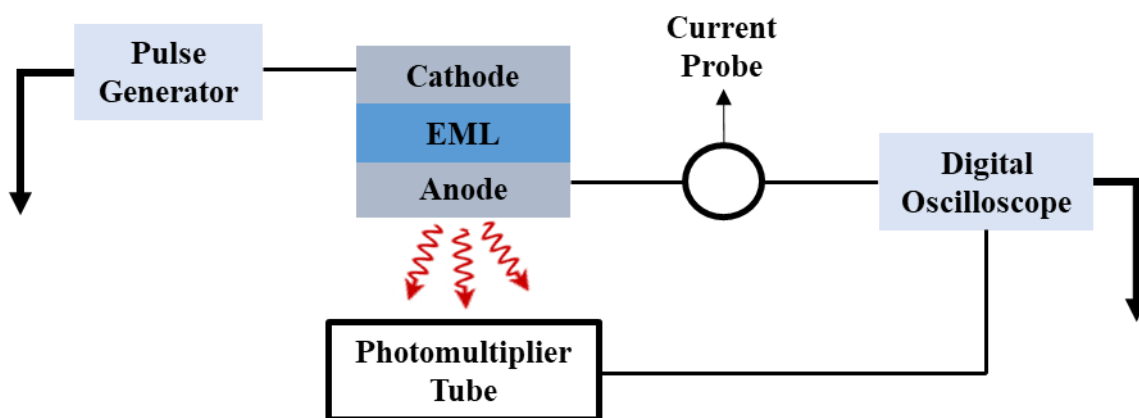
**Supplementary Figure 3. TRPL and fluence dependent studies** (a) Time-resolved emission decay for neat and doped films, (b) emission spectra of neat films at different gate delays, (c) Normalised DF intensities vs normalised PF intensities at different fluence for neat films, linearly fitted with dual slopes.



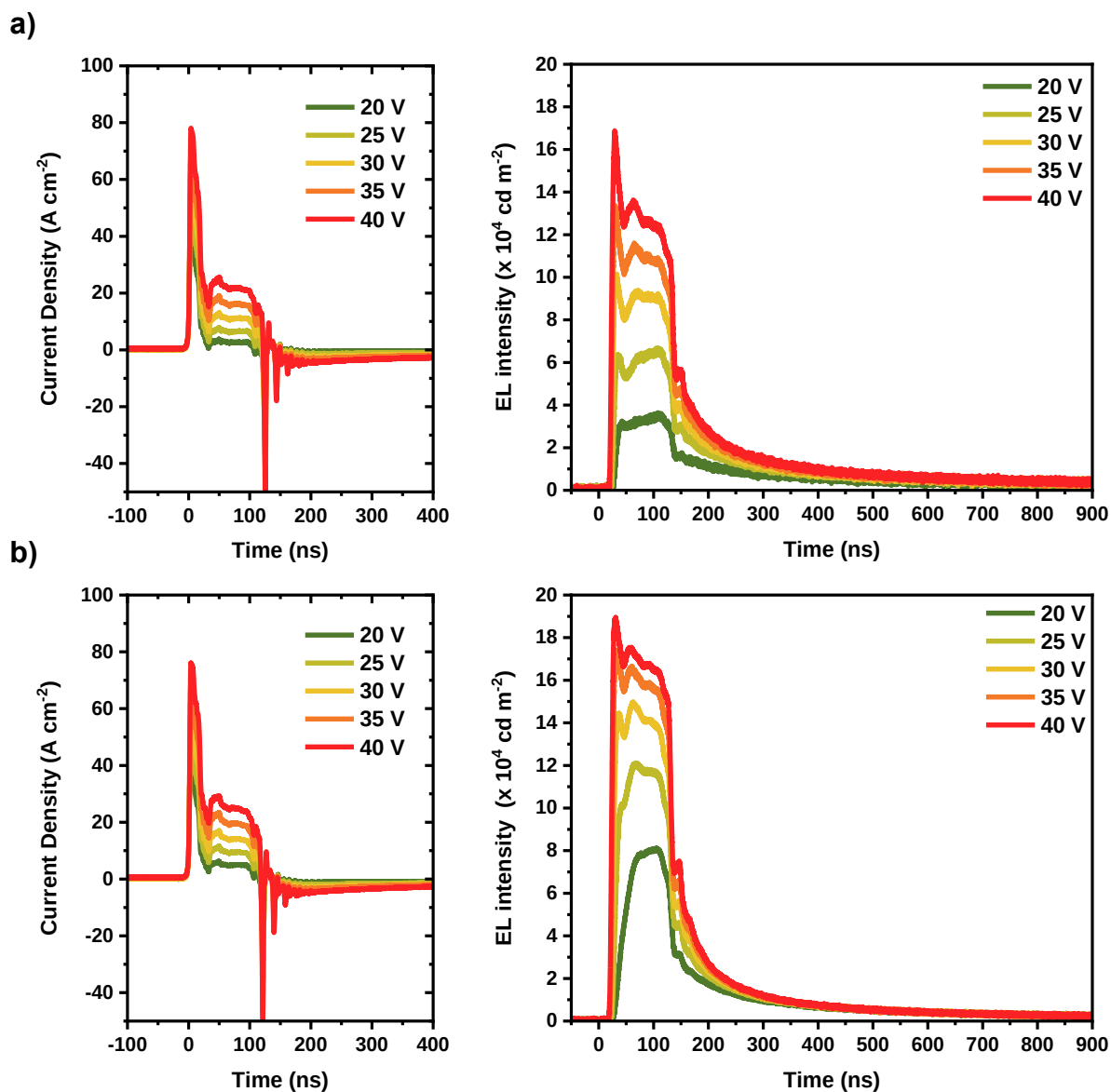
**Supplementary Figure 4. Schematic of the triplet photosensitization mediated TTU in PCAN.** In photosensitization, the absorption takes place via PtOEP, leading to generation of triplet excitons which are the transferred to PCAN by dexter energy transfer (DET) and subsequently upconverted to singlet excitons by triplet-triplet annihilation.



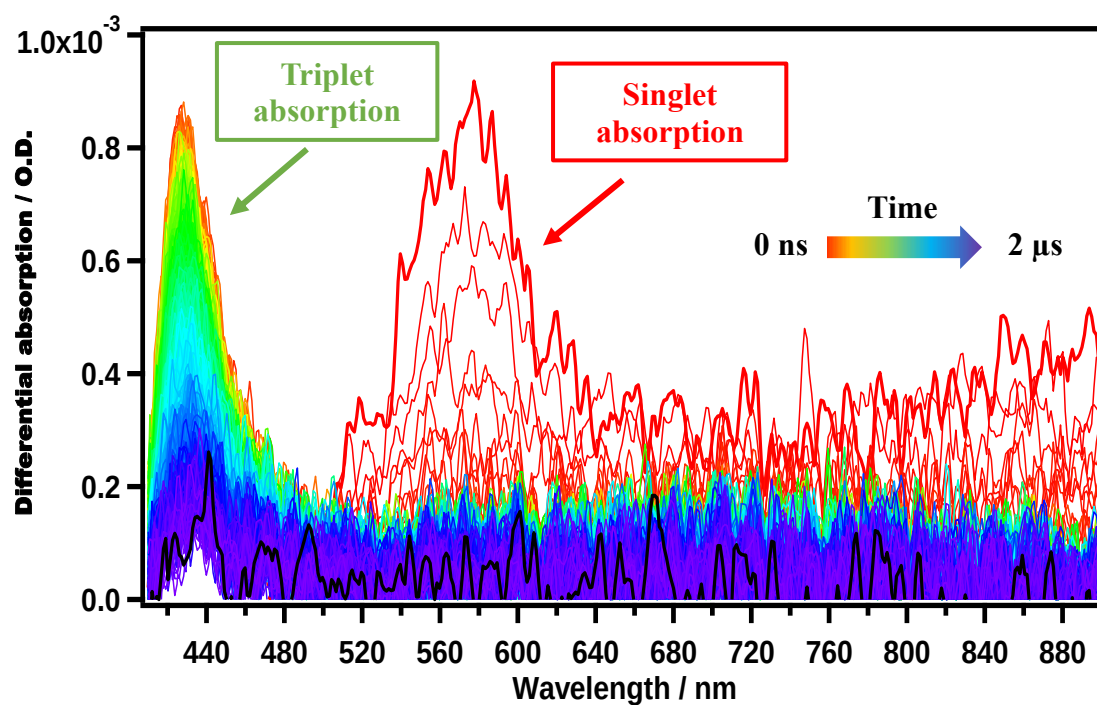
**Supplementary Figure 5. Steady-state absorption and emission for triplet photosensitization.** (a) Absorption and (b) emission spectrum of the toluene solutions of only PtOEP ( $10^{-5}$  M) and PtOEP ( $10^{-5}$  M) with PCAN ( $10^{-2}$  M). (c) Comparison of emission spectrum of dilute PCAN solution ( $\sim 10^{-5}$  M) when excited at 350 nm with upconverted PCAN emission. (d) Comparison of normalised emission from 550-800 nm obtained in both cases in (a) and (b).



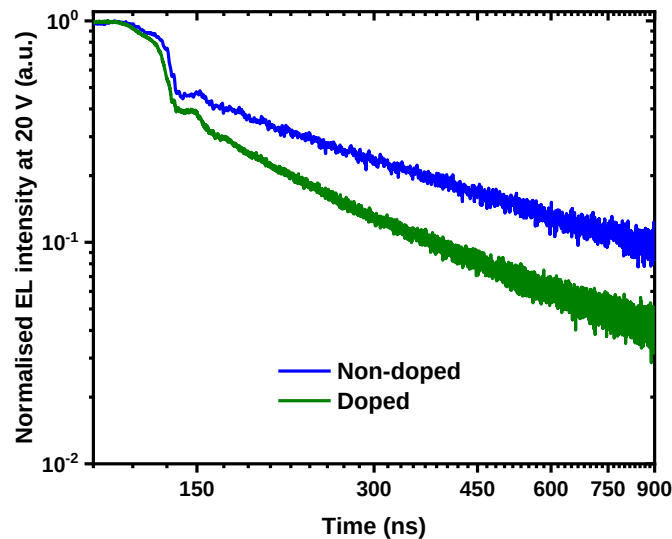
**Supplementary Figure 6. Transient EL setup.** Schematic of the experimental setup used to study transient EL response in PCAN based OLED devices.



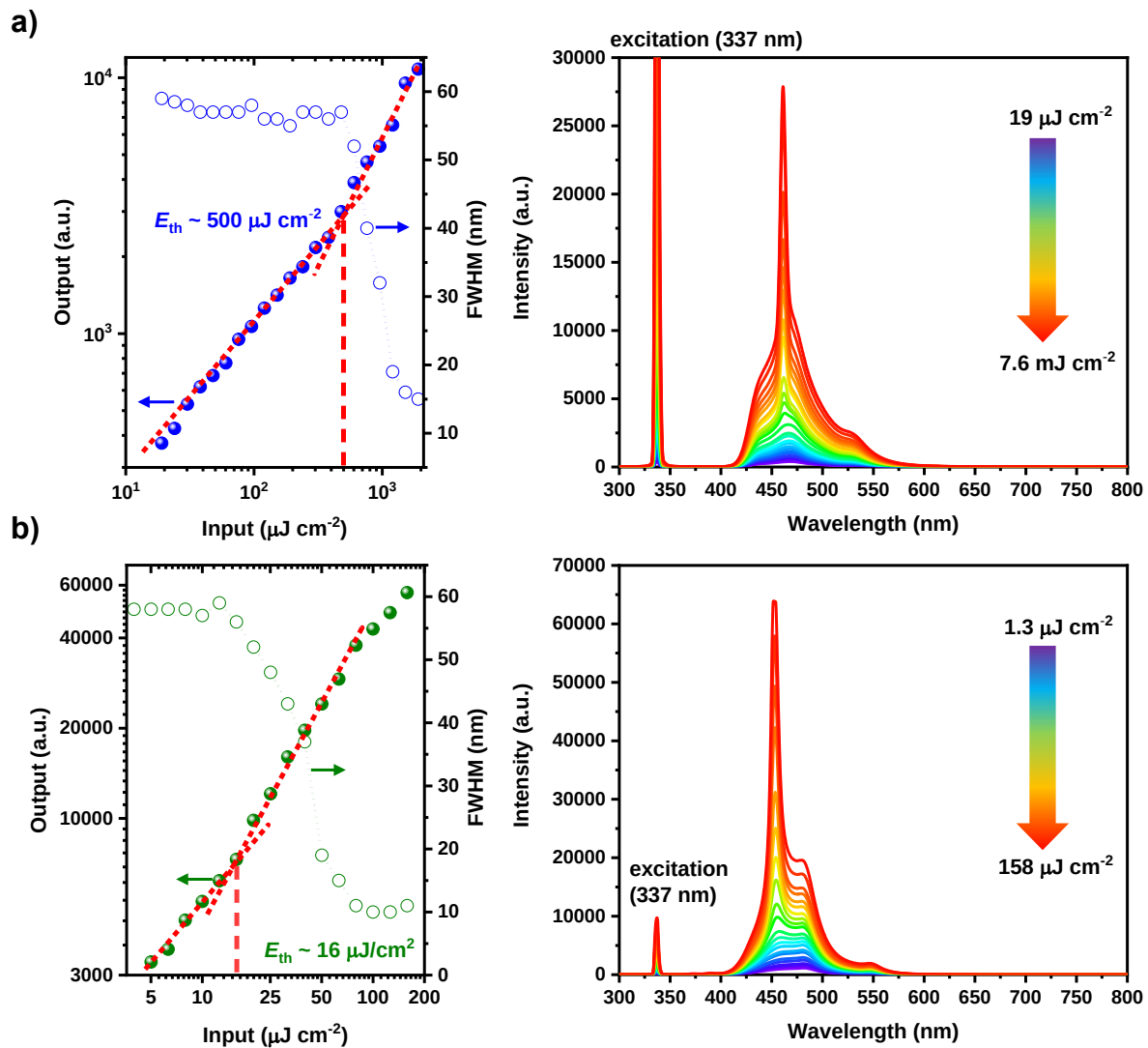
**Supplementary Figure 7. Transient EL response of doped and non-doped PCAN based OLEDs.** Transient current density and electroluminescence (EL) response of (a) non-doped and (b) doped PCAN based OLED at variable voltages.



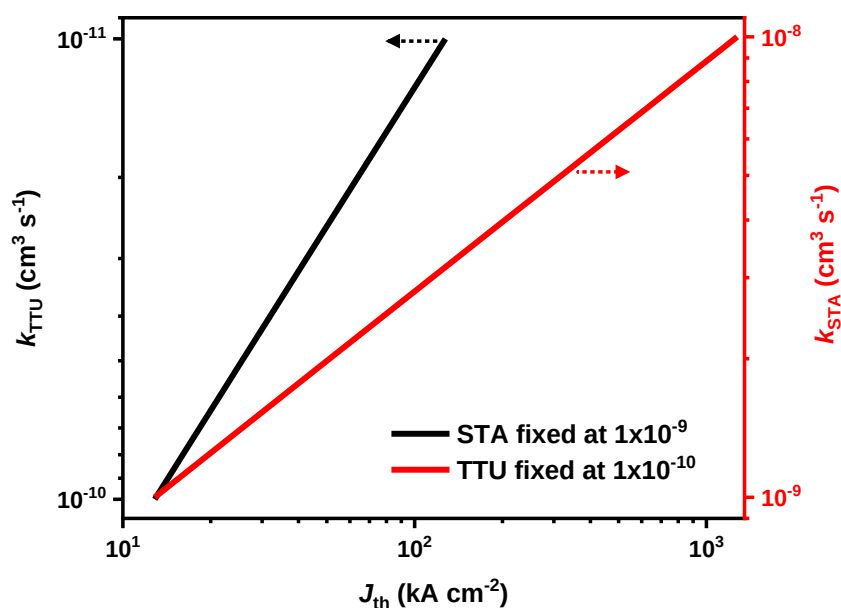
**Supplementary Figure 8. Transient absorption spectra of PCAN neat films.** Transient absorption spectra for PCAN neat film with probe delays ranging from 0 to 2  $\mu$ s, showing triplet and singlet absorption band.



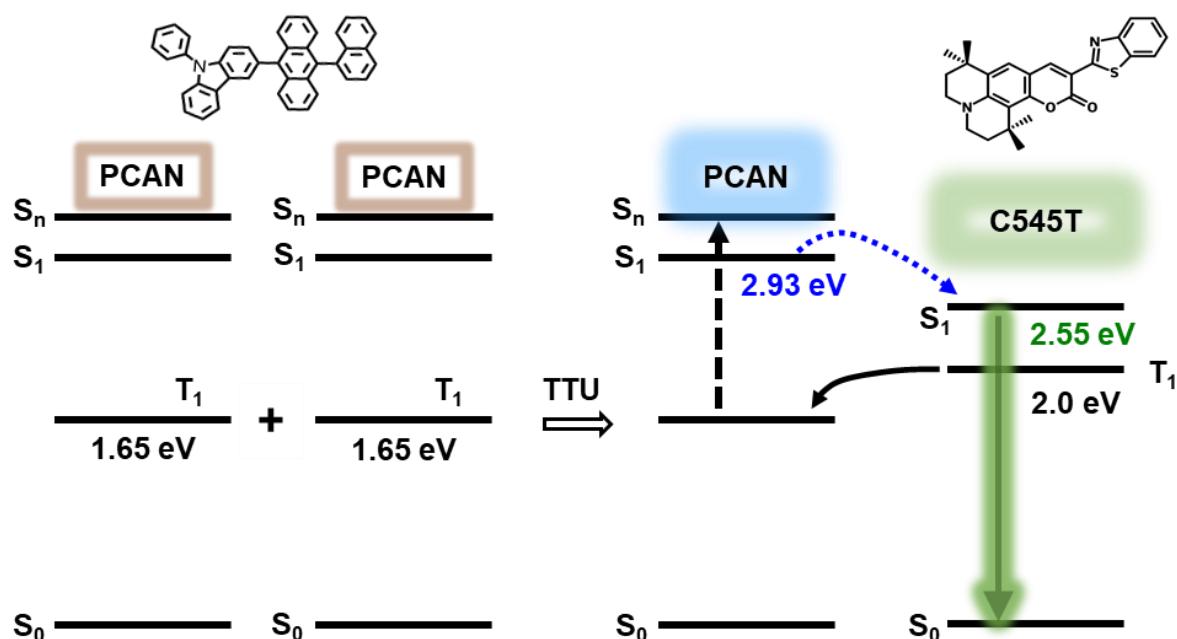
**Supplementary Figure 9. EL decay of doped and nondoped PCAN based OLEDs.** EL turn-off characteristics for non-doped and doped devices showing the presence of prompt and delayed fluorescence.



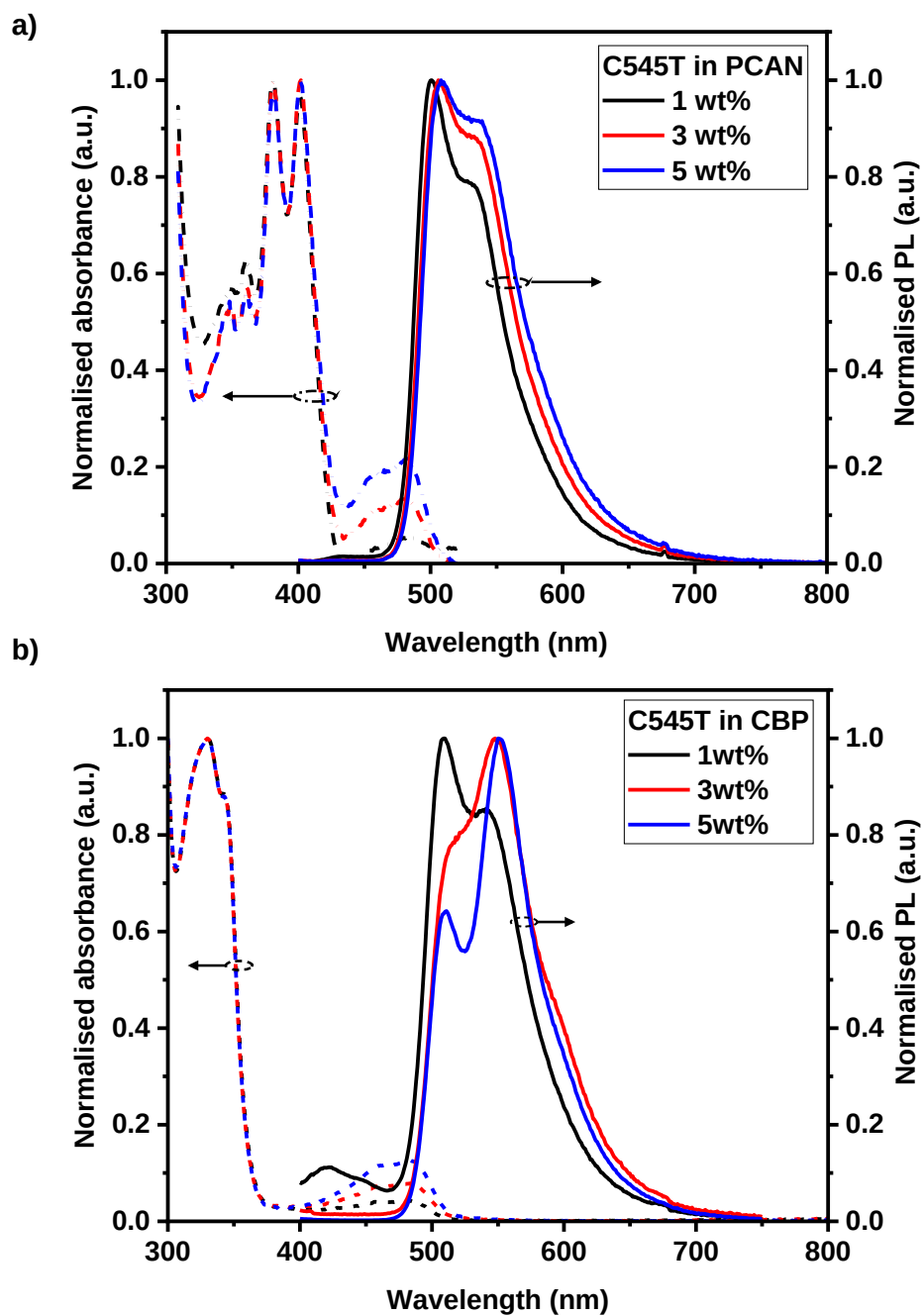
**Supplementary Figure 10. Light amplification characteristics of doped and non-doped PCAN thin films.** Input–output–FWHM and emission spectra collected from the edge of the organic layer at different input excitation intensities for (a) neat film and (b) doped films.



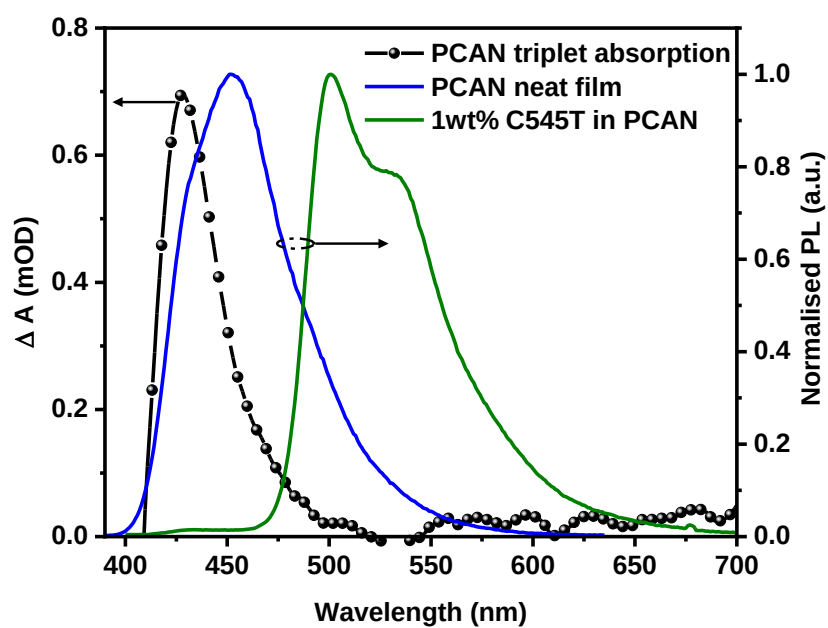
**Supplementary Figure 11. Threshold current density as a function of STA and TTU.** Increment in threshold current density in two scenarios when STA is fixed; TTU is reduced (black) and when TTU is fixed; STA is increased (red).



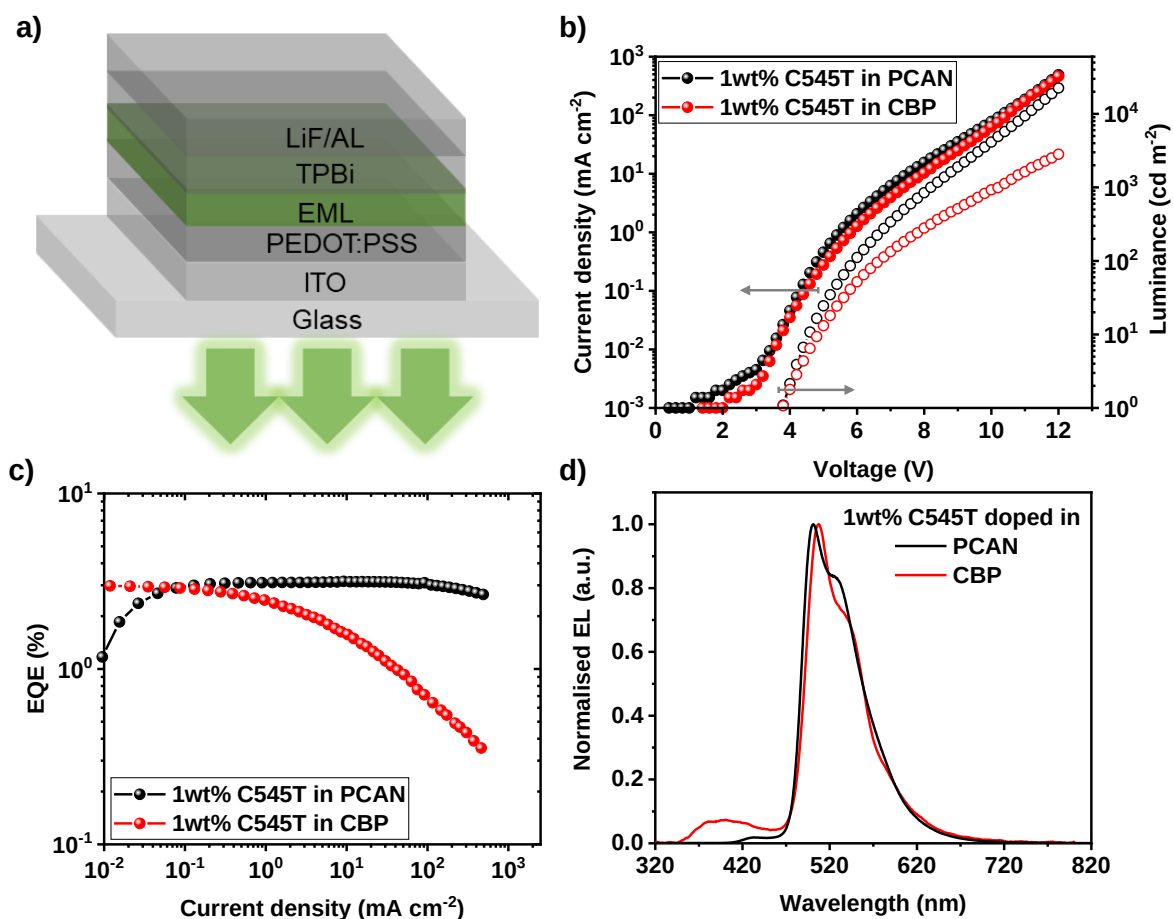
**Supplementary Figure 12. Schematic representation of the TTU mechanism in PCAN and C545T based host-guest system.** The triplet excitons can be upconverted to singlet in PCAN and finally transferred to singlet excited state of C545T via Förster energy transfer.<sup>3</sup> The triplet excitons on C545T can be funnelled back to PCAN via Dexter energy transfer.



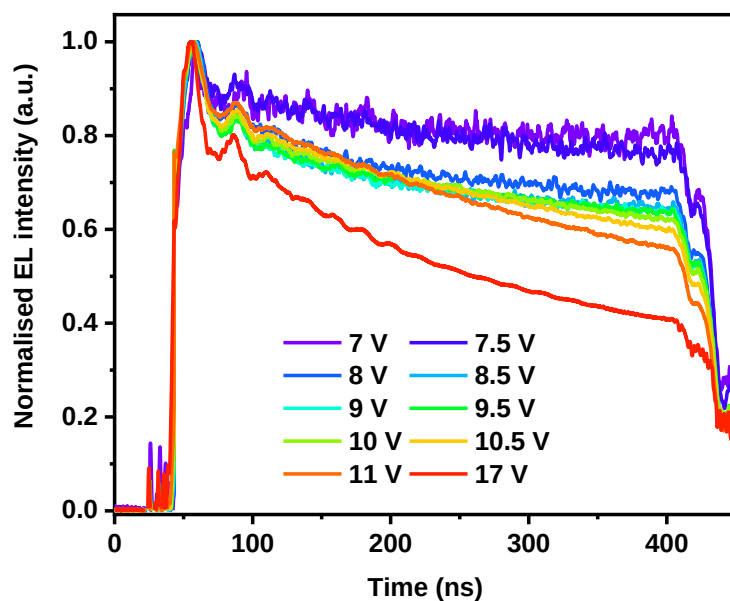
**Supplementary Figure 13. Absorption and emission spectra of C545T in PCAN and CBP.** Normalised absorption and PL spectra of 1, 3 and 5 wt% C545T doped in (a) PCAN and (b) CBP hosts.



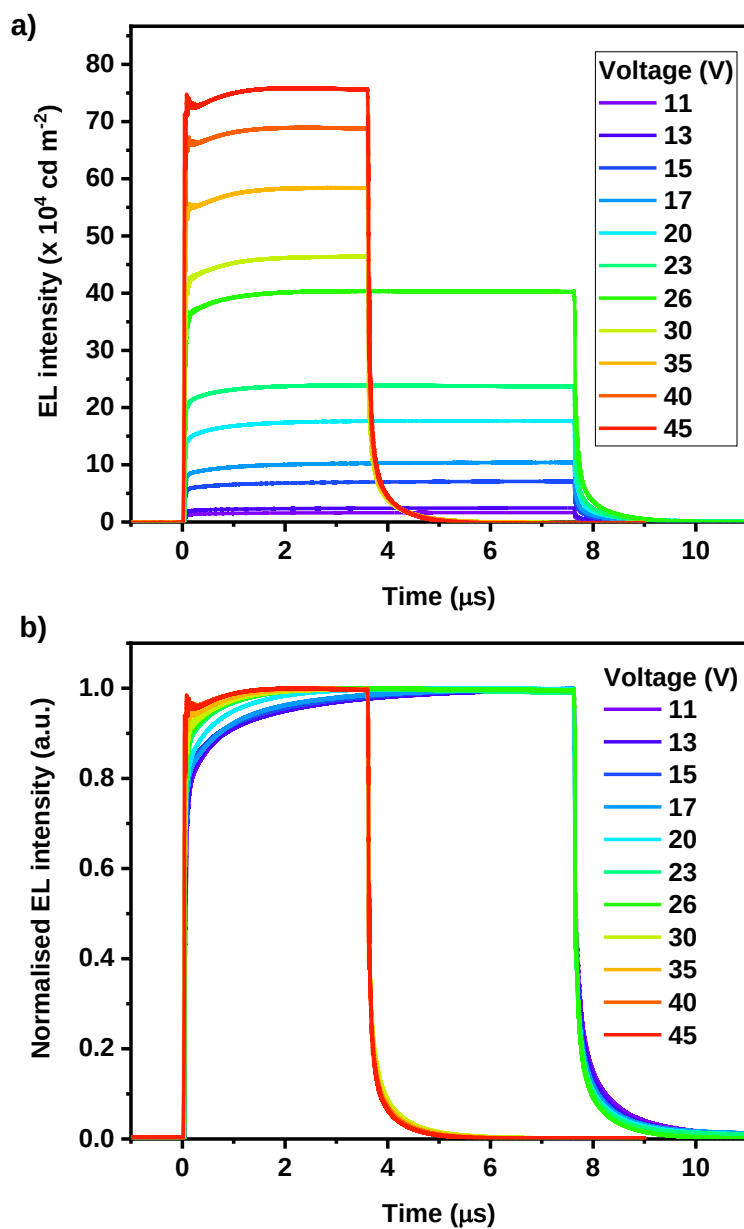
**Supplementary Figure 14. Comparison of triplet absorption and emission in neat PCAN and C545T:PCAN (1:99) blend.** Triplet excited-state absorption spectrum of PCAN (time averaged spectrum from Supplementary Figure 8 overlapped with the emission of PCAN neat films and doped films of 1wt% C545T in PCAN).



**Supplementary Figure 15. Performance characteristics of C545T OLEDs with PCAN and CBP hosts.** (a) Schematic representation of solution-processed OLED device structure. Comparison of (b)  $J$ - $V$ - $L$  characteristics, (c) EQE vs current density, and (d) EL spectra of OLEDs based on 1wt% C545T doped in PCAN and CBP hosts matrices.



**Supplementary Figure 16. Transient EL of C545T:CBP blend OLEDs.** Normalised transient EL response of C545T:CBP (1:99 wt%) based OLED under variable voltage.



**Supplementary Figure 17. Transient EL of C545T:PCAN blend OLEDs.** (a) Absolute and (b) normalised transient EL response of C545T: PCAN (1:99 wt%) based OLED under variable voltages.

## Supplementary Notes

### **Supplementary Note 1: TTU through triplet photosensitization**

The measurements were performed for deoxygenated toluene solution of PCAN ( $10^{-2}$  M) with PtOEP ( $10^{-5}$  M). Samples with only PCAN ( $10^{-2}$  M) and only PtOEP ( $10^{-5}$  M) were also measured for comparison. All measurements were performed by exciting the samples at 532 nm. Since PCAN does not absorb at this wavelength, all the pump power is absorbed by PtOEP. The triplet exciton of PtOEP is transferred to PCAN through Dexter energy transfer (DET). Due to the high concentration of PCAN in the solution, these triplet excitons can then undergo TTU to generate singlet exciton.

As seen in **Supplementary Figure 5b**, a clear emission band in the range 400–500 nm can be observed in the solution of PCAN ( $10^{-2}$  M) with PtOEP ( $10^{-5}$  M). This band can be attributed to the singlet emission of PCAN. The comparison of normalised emission of PCAN in the dilute solutions ( $10^{-5}$  M,  $\lambda_{\text{ex}} = 350$  nm) and in concentrated solutions used in photosensitisation studies ( $\lambda_{\text{ex}} = 532$  nm) are shown in **Supplementary Figure 5c**. The slight difference in spectrum can be attributed to ground-state self-absorption of PCAN at high concentrations. On the other hand, the PtOEP emission was found to be significantly quenched in the presence of PCAN. The indication of triplet sensitization can also be observed from contribution arising from PCAN's phosphorescence emission in 700–800 nm wavelength range.

### **Supplementary Section 2: Numerical model to extract annihilation rate constants**

In fluorescent OLEDs, non-radiative bimolecular processes such as singlet-triplet annihilation (STA) and triplet-triplet upconversion (TTU) influence the dynamics of singlet and triplet exciton densities under electrical excitation. By taking these processes into account, the equations describing the singlet and triplet populations can be given as<sup>1, 2</sup>

$$\frac{dn}{dt} = \frac{J(t)}{ed} - \gamma n^2, \quad (\text{S1})$$

$$\frac{dS}{dt} = \alpha \gamma n^2 - (k_r + k_{nr})S - k_{STA}ST + \frac{\alpha}{2} k_{TTU}T^2, \quad (\text{S2})$$

$$\frac{dT}{dt} = (1 - \alpha)\gamma n^2 - k_tT - \frac{1+\alpha}{2} k_{TTU}T^2, \quad (\text{S3})$$

where  $n$ ,  $S$ , and  $T$  are the polaron, singlet and triplet densities, respectively;  $J(t)$  is the current density as a function of time;  $e$  is the elementary charge,  $d$  is the width of the recombination zone;  $\gamma$  is the Langevin recombination rate;  $\alpha = 0.25$  is the singlet exciton generation ratio

under electrical excitation from spin-statistics;  $k_r$  and  $k_{nr}$  are the radiative and nonradiative decay constants, respectively;  $k_t$  is the triplet decay constant extracted from ns-TAS (triplet lifetime  $\sim 1.2 \mu\text{s}$  from global fitting). The other terms  $k_{TTA}$  and  $k_{STA}$  denotes the annihilation rate constants of STA and TTU, respectively. For the simplicity of the model, we have not considered triplet generation through intersystem crossing from singlet state to triplet state as the triplet exciton generation was mainly dominated by charge injection under electrical excitation.

The Langevin recombination rate was calculated from the charge mobilities and given by  $\gamma = e(\mu_h + \mu_e)/\varepsilon_r \varepsilon_0$ , where  $\mu_h(\mu_e)$  is the hole (electron) mobility,  $\varepsilon_r$  is the relative permittivity of the material, and  $\varepsilon_0$  is the vacuum permittivity. The hole mobilities of non-doped and doped PCAN devices were measured experimentally with a value of  $3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $2.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. We neglected the electron mobility in our calculation as the recombination zone was assumed to be close to the cathode side in the devices. By assuming  $d = 10 \text{ nm}$  and  $\varepsilon_r = 3.0$ , time-resolved EL data obtained from doped and non-doped devices were fitted using Equation (S1)–(S3) to obtain STA and TTU rate constants (summarised in **Supplementary Table 3** and **4**).

### **Supplementary Section 3: Estimation of threshold current density required for lasing**

The experimentally measured optical pumping ASE thresholds can be translated into threshold singlet exciton density required to attain lasing emission. Assuming uniform absorption in 200 nm thickness of the gain medium for 3.5 ns pump pulse, we obtained photon density of  $1.22 \times 10^{28}$  and  $3.9 \times 10^{26}$  photons per  $\text{cm}^3$  per second required to achieve population inversion in case of neat and doped films, respectively. To calculate the threshold singlet exciton density rate equations similar to ones described in **Supplementary Section 2** were used, however under optical excitation all the polaron density terms were omitted and the concentration of the triplet excitons was assumed to be zero.

For simulating the current density required to achieve lasing threshold under electrical pumping equations (S1)–(S3) as specified above in **Supplementary Section 2** were used. Herein, the threshold current density was calculated by considering the current required to be injected into the device to reach the threshold singlet exciton population at saturation in 100 ns current pulse. The peak singlet populations in temporal EL signals in **Section 2.5** (in main text) were not

taken into consideration for threshold current density calculations to take into account the clear effects of STA and TTU.

### Supplementary Tables

**Supplementary Table 1.** Comparison of performance characteristics of doped and non-doped PCAN based OLEDs.

| <b>EML</b>              | <b>Turn-on voltage<br/>(V)<sup>a</sup></b> | <b>Maximum brightness<br/>(cd m<sup>-2</sup>)</b> | <b>Maximum current<br/>density (mA cm<sup>-2</sup>)</b> | <b>EQE<sub>max</sub><br/>(%)</b> |
|-------------------------|--------------------------------------------|---------------------------------------------------|---------------------------------------------------------|----------------------------------|
| <b>Non-doped</b>        | 4.0                                        | 14 610±450                                        | 490±100                                                 | 2.9±0.2                          |
| <b>10wt% in<br/>CBP</b> | 5.0                                        | 7 020±210                                         | 1 004±70                                                | 2.3±0.1                          |

<sup>a</sup> at 1 cd m<sup>-2</sup>.

**Supplementary Table 2.** Summary of photophysical properties derived from PLQYs and TCSPC decay curves.

|                  | <b>PLQY<br/>(%)</b> | <b>Lifetime<br/>(ns)</b>              | <b>k<sub>r</sub><br/>(×10<sup>8</sup> s<sup>-1</sup>)</b> | <b>k<sub>nr</sub><br/>(×10<sup>8</sup> s<sup>-1</sup>)</b> |
|------------------|---------------------|---------------------------------------|-----------------------------------------------------------|------------------------------------------------------------|
| Toluene solution | 64±7                | 3.5<br>1.1 (81.2%)<br>3.5 (14.1%)     | 1.83<br>0.68 <sup>a</sup>                                 | 1.03<br>1.17                                               |
| Neat film        | 37±6                | 85 (4.7%)<br>1.1 (13%)<br>4.0 (84.4%) | 1.73 <sup>a</sup>                                         | 0.43                                                       |
| 10wt% in CBP     | 54±6                | 41 (2.6%)                             |                                                           |                                                            |

<sup>a</sup>calculated using average lifetimes

**Supplementary Table 3.** Summary of  $k_{STA}$  and  $k_{TTU}$  obtained from non-doped PCAN OLEDs at different voltage pulses with corresponding steady-state current densities.

| Voltage<br>[V] | Steady-state<br>current density<br>[A cm <sup>-2</sup> ] | $k_{STA}$<br>[ $\times 10^{-9}$ cm <sup>3</sup> s <sup>-1</sup> ] | $k_{TTU}$<br>[ $\times 10^{-10}$ cm <sup>3</sup> s <sup>-1</sup> ] |
|----------------|----------------------------------------------------------|-------------------------------------------------------------------|--------------------------------------------------------------------|
| 20             | 2.60                                                     | 8.01                                                              | 3.10                                                               |
| 25             | 6.70                                                     | 9.89                                                              | 3.17                                                               |
| 30             | 11.13                                                    | 9.80                                                              | 2.69                                                               |
| 35             | 16.07                                                    | 5.70                                                              | 1.62                                                               |
| 40             | 21.95                                                    | 3.49                                                              | 1.03                                                               |
|                |                                                          | 7.37 (average)                                                    | 2.32 (average)                                                     |

**Supplementary Table 4.** Summary of  $k_{STA}$  and  $k_{TTU}$  obtained from doped PCAN OLEDs at different voltage pulses with corresponding steady-state current densities.

| Voltage<br>[V] | Steady-state<br>current density<br>[A cm <sup>-2</sup> ] | $k_{STA}$<br>[ $\times 10^{-9}$ cm <sup>3</sup> s <sup>-1</sup> ] | $k_{TTU}$<br>[ $\times 10^{-11}$ cm <sup>3</sup> s <sup>-1</sup> ] |
|----------------|----------------------------------------------------------|-------------------------------------------------------------------|--------------------------------------------------------------------|
| 20             | 5.60                                                     | 0.90                                                              | 6.19                                                               |
| 25             | 10.04                                                    | 1.20                                                              | 5.55                                                               |
| 30             | 14.43                                                    | 1.53                                                              | 6.84                                                               |
| 35             | 19.96                                                    | 2.10                                                              | 7.90                                                               |
| 40             | 25.66                                                    | 1.51                                                              | 6.91                                                               |
|                |                                                          | 1.44 (average)                                                    | 6.67 (average)                                                     |

**Supplementary Table 5.** Summary of photophysical properties for variable doping ratio (1, 3, and 5 wt%) of C545T in PCAN and CBP.

| C545T wt% | PCAN       |              |                     |                        |
|-----------|------------|--------------|---------------------|------------------------|
|           | PLQY (%)   | $\tau_{avg}$ | $k_r (\times 10^8)$ | $k_{nr} (\times 10^8)$ |
| 1wt%      | 88 $\pm$ 9 | 2.0          | 4.35                | 0.59                   |
| 3wt%      | 64 $\pm$ 4 | 1.6          | 3.94                | 2.22                   |
| 5 wt%     | 49 $\pm$ 7 | 1.2          | 4.18                | 4.35                   |
|           | CBP        |              |                     |                        |
| 1wt%      | 91 $\pm$ 7 | 1.9          | 4.77                | 0.47                   |
| 3wt%      | 72 $\pm$ 5 | 2.3          | 3.11                | 1.21                   |
| 5 wt%     | 64 $\pm$ 9 | 2.1          | 3.06                | 1.72                   |

### Supplementary References:

1. Zhang, Y. & Forrest, S.R. Triplets contribute to both an increase and loss in fluorescent yield in organic light emitting diodes. *Phys. Rev. Lett.* **108**, 267404 (2012).
2. Ieuji, R., Goushi, K. & Adachi, C. Triplet-triplet upconversion enhanced by spin-orbit coupling in organic light-emitting diodes. *Nat. Commun.* **10**, 5283 (2019).
3. Karunathilaka, B.S.B. et al. Suppression of external quantum efficiency rolloff in organic light emitting diodes by scavenging triplet excitons. *Nat. Commun.* **11**, 4926 (2020).