

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

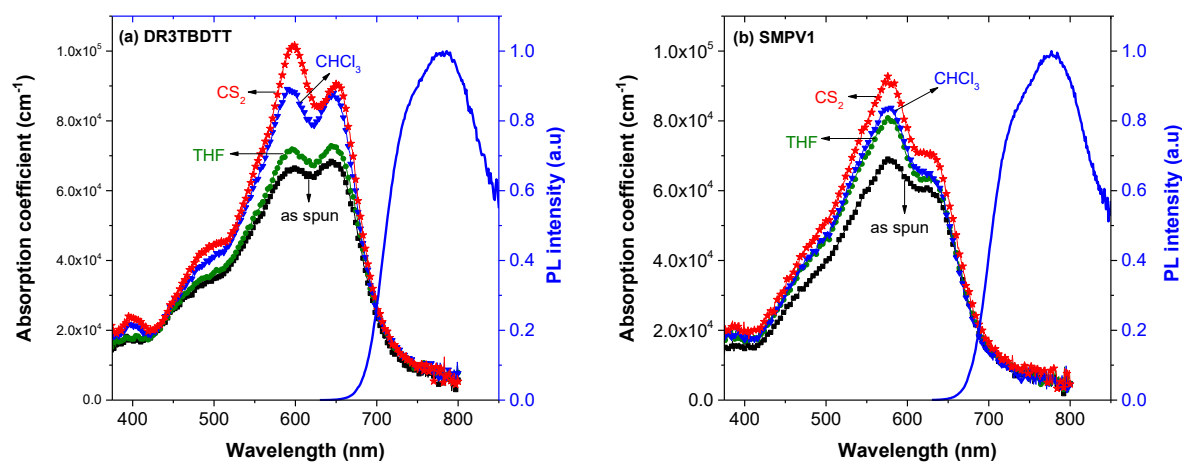
## Engineered exciton diffusion length enhances device efficiency in small molecule photovoltaics

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### Absorption and photoluminescence (PL) of neat donor molecules

The absorption spectra of neat films of DR3TBDDT and SMPV1 with and without solvent vapour annealing (SVA) are shown in Fig. S1a and S1b. The absorption spectra show that neat DR3TBDDT has a two peaks at 599 nm and at 646 nm, whereas SMPV1 has a strong peak at 578 nm with a shoulder around 632 nm. After solvent vapour annealing, the strong absorption peak becomes stronger for both molecules. This enhancement depends on the solvent used for annealing, the highest enhancement was observed for CS<sub>2</sub>, and the lowest for THF.

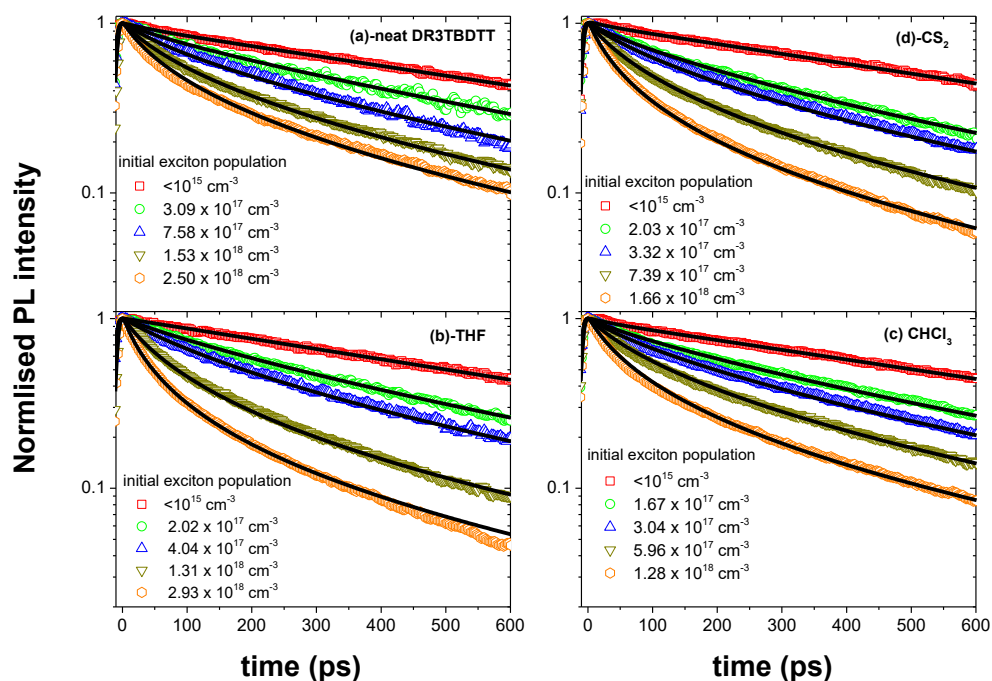
The photoluminescence (PL) of both molecules was measured by exciting the samples at 590 nm and emission was detected from 630 to 850 nm. The obtained PL spectra are shown in Fig. S1 (blue lines) which show that DR3TBDDT has PL peak around 783 nm and SMPV1 has PL peak around 776 nm. For both molecules PL spectra remain unchanged after solvent vapour annealing.



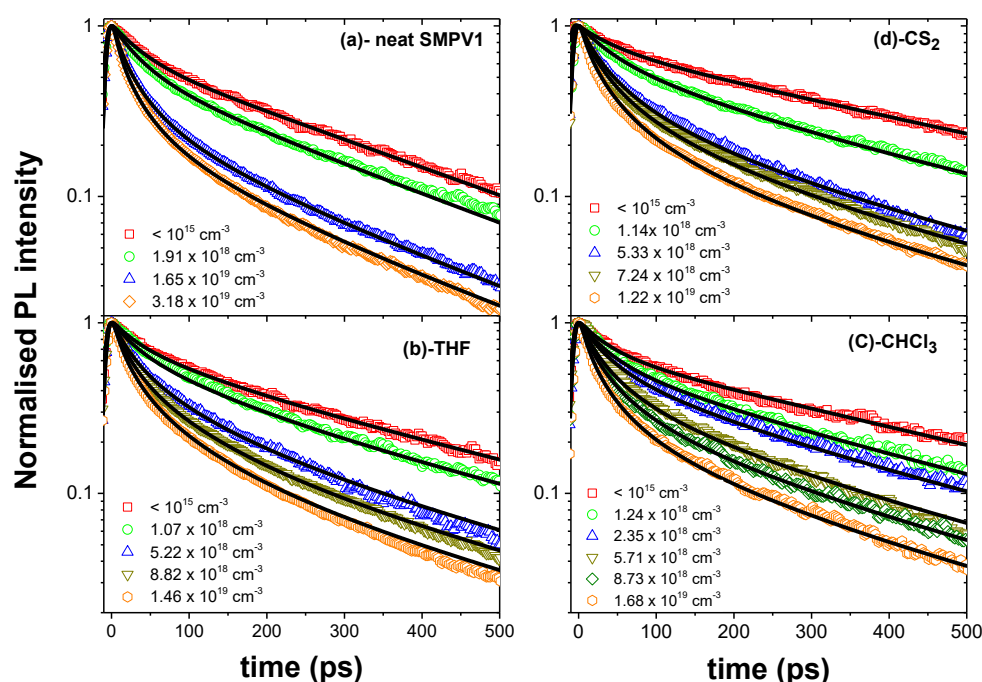
**Fig. S1:** (a) Absorption and photoluminescence spectra of DR3TBDDT films spin-coated from solutions in chlorobenzene and annealed using different solvents. The blue line represents the photoluminescence spectrum of an untreated film. (b) Absorption and photoluminescence spectra of SMPV1 films spin-coated from solutions in chlorobenzene and annealed using different solvents. The blue line represents the photoluminescence spectrum of an untreated film.

### Exciton-exciton annihilation: excitation dependent time-resolved fluorescence decays

The effect of solvent vapour annealing on exciton diffusion was studied by singlet exciton–exciton annihilation. For this we spin-coated thin films of ~ 35 nm and processed them using three different solvents (THF, CHCl<sub>3</sub> and CS<sub>2</sub>). We then measured time-resolved fluorescence of untreated and solvent vapour annealed films at different excitation densities as shown in Fig. S2 and S3.



**Fig. S2:** Time-resolved PL decays of DR3TBDTT measured at different excitation densities: Excitation density dependent time-resolved fluorescence measured in thin films of untreated DR3TBDTT (a) and solvent vapour annealed DR3TBDTT ((b)-THF, (c)-CHCl<sub>3</sub> and (d)-CS<sub>2</sub>).

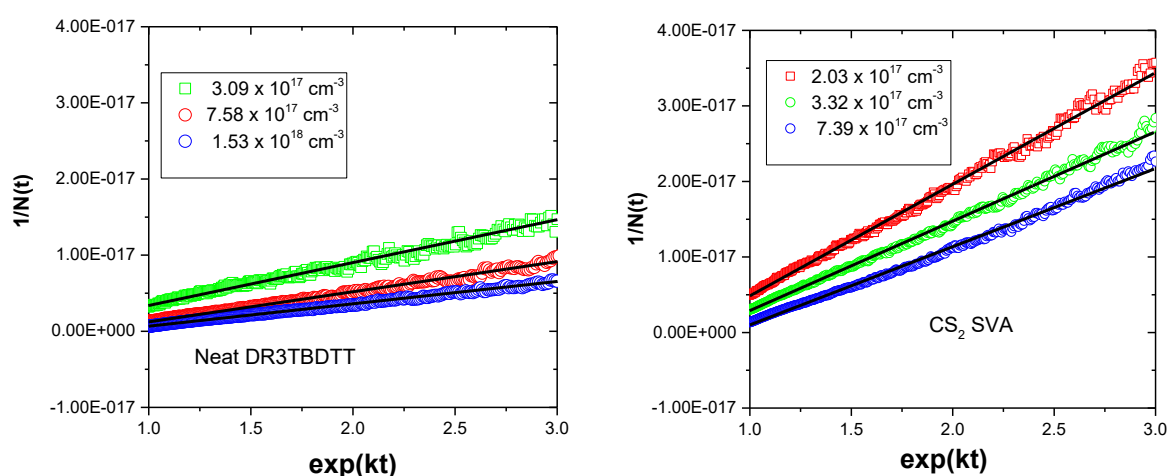


**Fig. S3:** Time-resolved PL decays of SMPV1 measured at different excitation densities: Excitation density dependent time-resolved fluorescence measured in thin films of untreated SMPV1 (a) and solvent vapour annealed SMPV1 ((b)-THF, (C)-CHCl<sub>3</sub> and (d)-CS<sub>2</sub>).

We modelled these PL decays using rate equation 1 of the main manuscript to extract time-dependent rate constant  $\gamma(t)$ . For this we first measured PL decays at very low intensity ( $<10^{15}$

$\text{cm}^{-3}$ ) which correspond to natural decay of the film (red dots) and used as reference to model the PL decays at high excitation density in order to extract the annihilation rate constant<sup>1</sup>. The obtained time-dependent annihilation rate constant  $\gamma(t)$  for all films (with and without SVA) of both DR3TBDTT and SMPV1 are given in Fig. 1c and 1d.

The diffusion coefficient was extracted from  $\gamma(t)$  using equation 2 of the main manuscript. The resulting values of diffusion coefficients are shown in Fig. 1e. For the case of DR3TBDTT, a diffusion coefficient of  $1.5 \times 10^{-3} \text{cm}^2/\text{s}$  was obtained for untreated donor film (without SVA). This diffusion coefficient after SVA was  $3.0 \times 10^{-3} \text{cm}^2/\text{s}$  for THF,  $3.8 \times 10^{-3} \text{cm}^2/\text{s}$  for  $\text{CHCl}_3$  and  $4.5 \times 10^{-3} \text{cm}^2/\text{s}$  for  $\text{CS}_2$ . In SMPV1 the untreated donor film had a diffusion coefficient of  $0.47 \times 10^{-3} \text{cm}^2/\text{s}$ . The diffusion coefficient after SVA was  $0.66 \times 10^{-3} \text{cm}^2/\text{s}$  for THF,  $0.70 \times 10^{-3} \text{cm}^2/\text{s}$  for  $\text{CHCl}_3$  and  $1.0 \times 10^{-3} \text{cm}^2/\text{s}$  for  $\text{CS}_2$ .



**Figure S4:** Inverse exciton density ( $1/N(t)$ ) vs  $\exp(kt)$  of (a) as spun (untreated) and (b)  $\text{CS}_2$  SVA film with their associated linear fits.

The time-dependent part of  $\gamma$  represents direct annihilation by energy transfer onto an excited chromophore, whereas the time-independent part represents diffusion-mediated annihilation. For our analysis we fixed  $R_a$  as described in the main manuscript and fitted the one free parameter ( $D$ ) to the entire decay curves (with both time-dependent and time-independent components). For cross-check we have analysed our data at long times using just the time-independent part of  $\gamma$  as follows.

The annihilation equation 
$$\frac{dN}{dt} = -kN(t) - \gamma N^2(t)$$

can be solved for time-independent  $\gamma$  to obtain

$$N(t) = \frac{N(0)\exp(-kt)}{1 + \frac{\gamma}{k}[1 - \exp(-kt)]} \quad (\text{S1})$$

where  $N(0)$  is the initial exciton density. The eq.S1 can be rearranged into the linear form

$$\frac{1}{N(t)} = \left( \frac{1}{N(0)} + \frac{\gamma}{k} \right) \exp(kt) - \frac{\gamma}{k} \quad (\text{S2})$$

We obtained  $N(t)$  from the PL decays and  $N(0)$  from the excitation energy density. Then we plotted  $\frac{1}{N(t)}$  against  $\exp(kt)$  in the Figure S4. The time-independent annihilation rate  $\gamma$  was determined from the linear fit and was used to extract the diffusion coefficient using

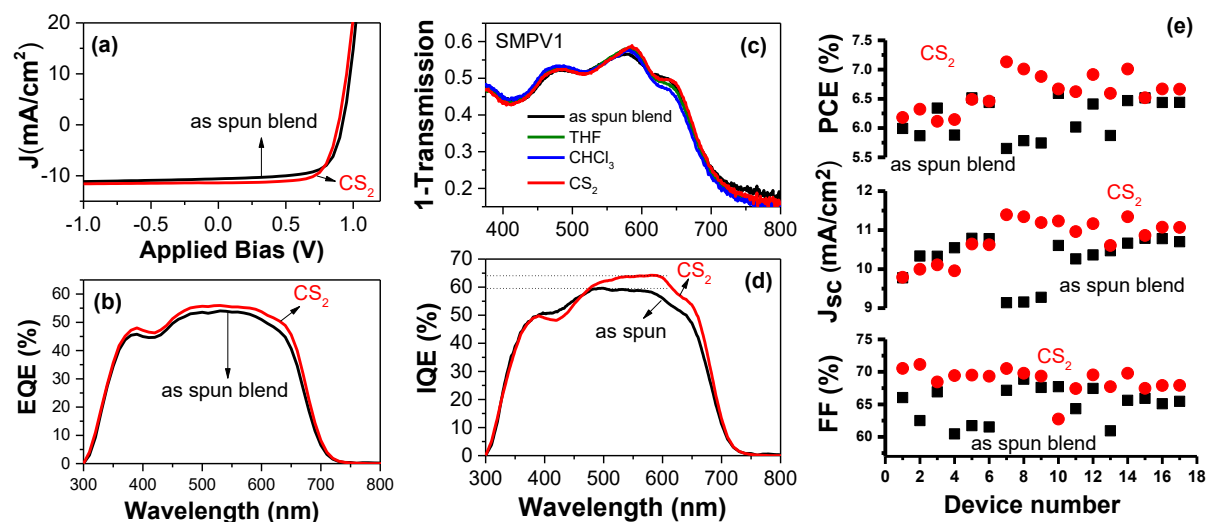
$$\gamma = 4\pi R_a D$$

A diffusion coefficient of  $D = (1.4 \pm 0.1) \times 10^{-3} \text{ cm}^2/\text{s}$  for as spun (untreated film) and  $D = (4.8 \pm 0.3) \times 10^{-3} \text{ cm}^2/\text{s}$  for  $\text{CS}_2$  SVA film was obtained. These values are comparable to the values obtained using equation 2 of the main manuscript.

The 3-dimensional exciton diffusion length was determined using the obtained value of  $D$  and lifetime. For untreated films of DR3TBDTT, a  $L_{3D}$  of 25.0 nm was achieved. Similar to  $D$ , we also observe the improvement in  $L_{3D}$  after SVA. The SVA films exhibited  $L_{3D}$  of 36, 41 and 45 nm for THF,  $\text{CHCl}_3$  and  $\text{CS}_2$  SVA treatment respectively. For the case of SMPV1,  $L_{3D}$  of 7.0, 9, 10 and 14 nm was achieved for untreated, THF,  $\text{CHCl}_3$  and  $\text{CS}_2$  treated films respectively.

### Device characterisation: SMPV1:PC<sub>71</sub>BM blend

Device characteristics of SMPV1:PC<sub>71</sub>BM blend are given in Fig. S5. Similar to DR3TBDTT, an enhancement in  $J_{sc}$ , FF, EQE and PCE was observed after SVA. However, the enhancement in overall device efficiency was low ( $\sim 8\%$ ) compared to DR3TBDTT where an average enhancement of about 24% was achieved. We believe that this is due to lower exciton diffusion length in SMPV1 compared to DR3TBDTT.

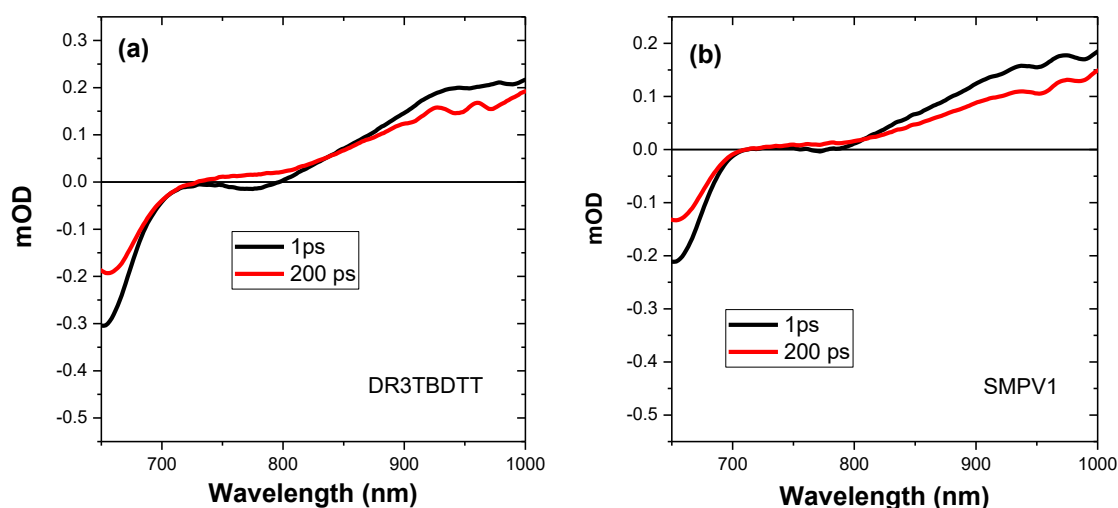


**Fig. S5: Device characteristics of SMPV1:PC<sub>71</sub>BM blend:** (a) Current density-voltage ( $J$ - $V$ ) curves (b) External quantum efficiency (EQE) of devices with and without  $\text{CS}_2$  SVA. (c) Absorption spectra of blend films of SMPV1:PC<sub>71</sub>BM before and after SVA using different solvents. (d) Internal quantum efficiency (IQE) of devices with and without  $\text{CS}_2$  SVA. (e) Short circuit current ( $J_{sc}$ ), fill factor (FF) and power conversion efficiency (PCE) of all devices with and without  $\text{CS}_2$  SVA.

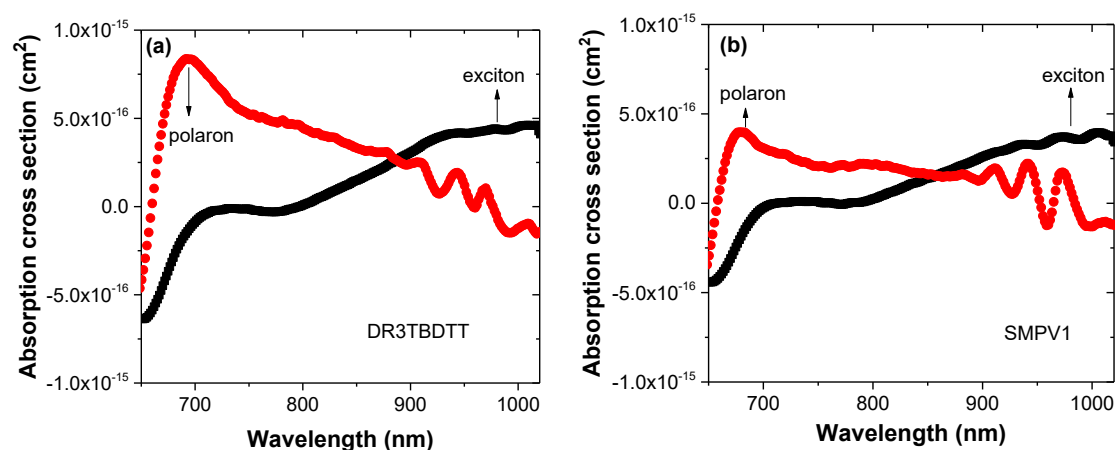
We calculated the IQE using the optical constants and it is shown in Fig. S5d. The enhancement in IQE of SVA blend is a combined effect of enhanced absorption as well as better charge extraction which is also reflected in improved  $J_{sc}$  and FF.

### Charge photogeneration study using transient absorption spectroscopy

We investigated the efficiency of charge generation in DR3TBDTT:PC<sub>71</sub>BM and SMPV1:PC<sub>71</sub>BM blends using transient absorption (TA) spectroscopy. First we measured the absorption spectrum of the singlet exciton from the TA signal in neat donor films at 1 ps (Fig. S6). The shape of the TA spectra did not change significantly with time which indicates the dominance of a single excited species, i.e. the singlet exciton in neat donor materials. Then we determined the absorption cross section of the singlet exciton as a function of wavelength (Fig. S7) using the known excitation density, the amount of absorbed light and film thickness.



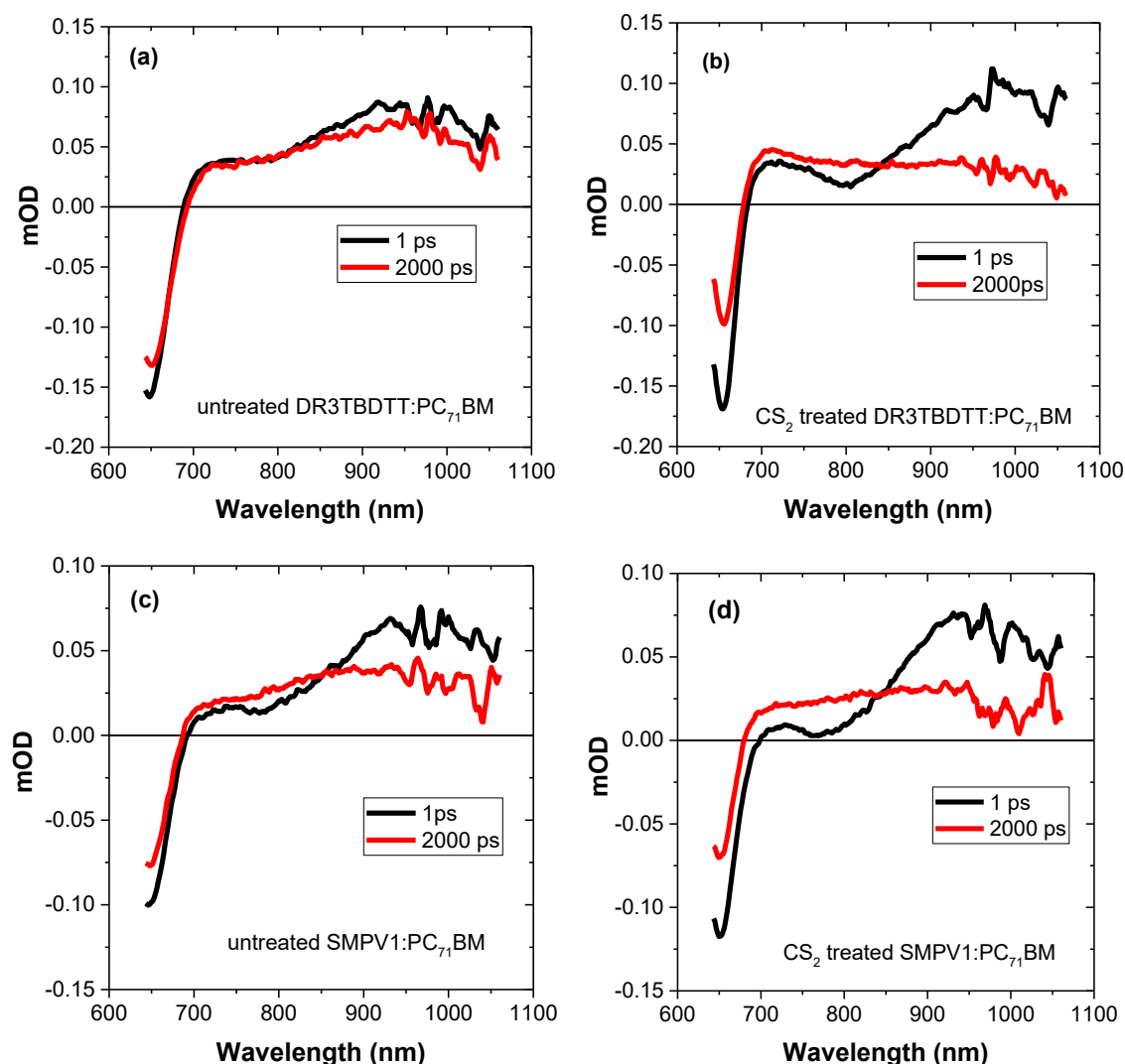
**Fig. S6:** Transient absorption spectra of neat donor films at different times after excitation. (a) DR3TBDTT. (b) SMPV1



**Fig. S7:** Absorption cross section of exciton and polaron. (a) Cross sections of exciton and polaron (charge) determined using neat DR3TBDTT and its blend with PC<sub>71</sub>BM. (b) Cross sections of exciton and polaron determined using neat SMPV1 and its blend with PC<sub>71</sub>BM.

Some representative TA spectra of photovoltaic blends DR3TBDTT:PC<sub>71</sub>BM and SMPV1:PC<sub>71</sub>BM which were used in devices are given in Fig. S8. The TA spectra at 1 ps are different from the spectra in neat films indicating that some charge (polaron) pairs are generated in 1 ps. They can be reproduced by a sum of a scaled absorption cross-section of singlet exciton (Fig. S7) and the long time TA spectra of the SVA blends (2000 ps, Fig. S8b and S8d). Using the known excitation density and the amount of absorbed light in blends and

assuming that each absorbed photon generated either one singlet exciton or one charge pair we determined the absorption cross-section of a charge (polaron) pair (Fig. S7).



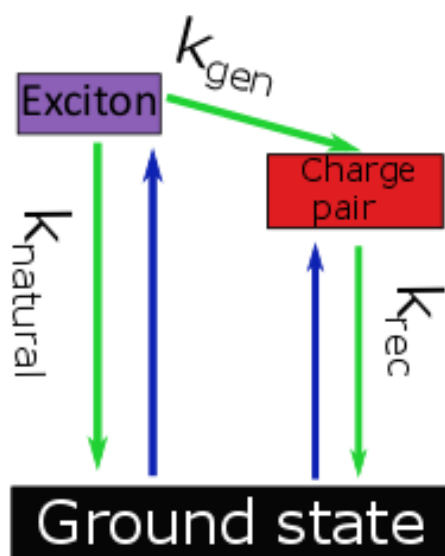
**Fig. S8: Transient absorption spectra of blends of DR3TBDDT: PC<sub>71</sub>BM and SMPV1: PC<sub>71</sub>BM before and after solvent vapour annealing.** Time evolution of transient absorption spectra of a blend of DR3TBDDT: PC<sub>71</sub>BM before (a) and after CS<sub>2</sub> SVA blend (b) taken at 1 ps (black line) and at 2000 ps (red line). (c,d) are time evolution of transient absorption spectra of a blend of SMPV1: PC<sub>71</sub>BM before (c) and after CS<sub>2</sub> SVA blend (d) taken at 1 ps (black line) and at 2000 ps (red line).

We used the model shown in Fig. S9 to extract the populations of excitons and charges from the TA spectra of the photovoltaic blends. We have determined  $k_{\text{natural}}$  and  $k_{\text{gen}}$  from the PL decays measured in neat donor films and in photovoltaic blends using

$$k_{PL} = k_{\text{Natural}} + k_{\text{gen}} \quad (\text{S3})$$

Here  $k_{PL}$  – the rate constant for PL decay of the blend,  $k_{\text{Natural}}$  is the natural rate constant of untreated donor film measured from TA spectroscopy and  $k_{\text{gen}}$  the rate constant for charge generation from excitons and is determined using equation S3. For both molecules, the PL quenching of the untreated blend is higher compared to the SVA treated blend. In the case of SVA blends, the PL quenching is strongly dependent on the nature of the solvent used for

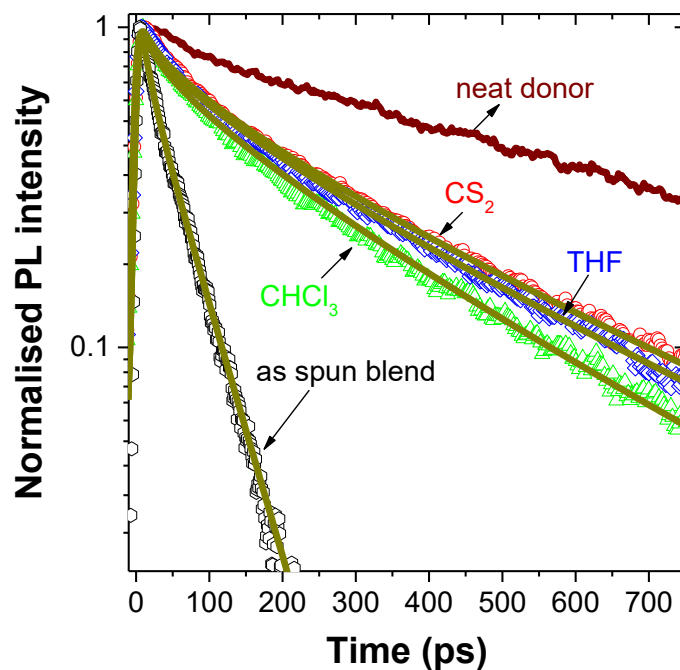
example the highest PL quenching is observed for the highest boiling point solvent like THF and the lowest is observed for the case of the lowest boiling point solvent CS<sub>2</sub> for both molecules. The fixed and fitted parameters used for modelling TA spectra are given in Table S1.



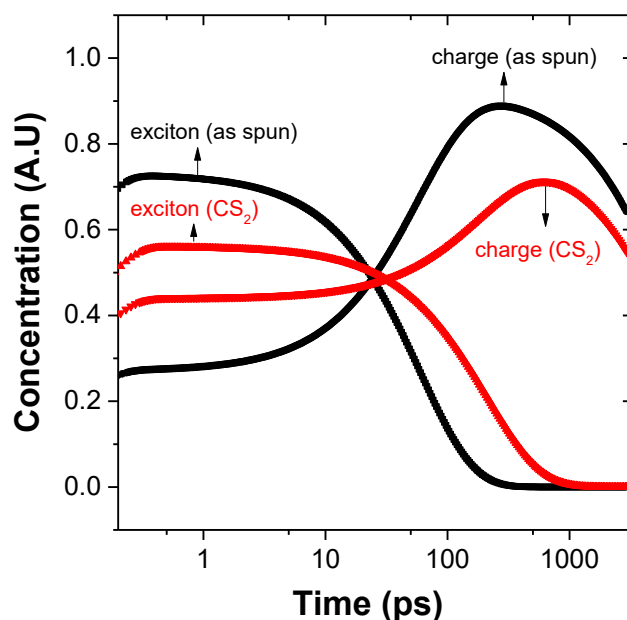
**Fig. S9: Model to fit TA spectra of the blends.** Blue arrows represent photogeneration of excitons and charge pairs within a response time of the apparatus (200 fs) from absorbed photons. Green arrows have three time constants;  $k_{\text{natural}}$  – the rate constant for natural decay of untreated donor film obtained from TA spectroscopy,  $k_{\text{gen}}$  – the rate constant for charge generation from excitons extracted using equation S3 and  $k_{\text{rec}}$  – a free parameter used for slow charge recombination.

**Table S1: Parameters used in the model shown in Fig. S9 for modelling TA spectra :**  $k_{\text{natural}}$  – the rate constant for natural decay of singlet exciton in untreated neat donor film (i.e. without PC<sub>71</sub>BM) measured using TA spectroscopy,  $k_{\text{PL}}$  – the rate constant for PL decay of blend determined from PL quenching,  $k_{\text{gen}}$  – the rate constant for charge generation from excitons extracted using equation S3 and  $k_{\text{rec}}$  – a free parameter used for slow charge recombination

Molecule blended with PC <sub>71</sub> BM	$k_{\text{natural}} (s^{-1})$	$k_{\text{PL}} (s^{-1})$	$k_{\text{gen}} (s^{-1})$	$k_{\text{rec}} (s^{-1})$
DR3TBDTT (untreated)	$1.80 \times 10^9$	$2.50 \times 10^{10}$	$2.33 \times 10^{10}$	$1.25 \times 10^8$
DR3TBDTT (CS <sub>2</sub> treated)	$1.80 \times 10^9$	$6.49 \times 10^9$	$4.70 \times 10^9$	$1.25 \times 10^8$
SMPV1 (untreated)	$1.82 \times 10^9$	$1.67 \times 10^{10}$	$1.49 \times 10^{10}$	$1.25 \times 10^8$
SMPV1 (CS <sub>2</sub> treated)	$1.82 \times 10^9$	$4.65 \times 10^9$	$2.84 \times 10^9$	$1.25 \times 10^8$



**Fig. S10:** Time-resolved PL quenching of SMPV1 in a blend with PC<sub>71</sub>BM before and after solvent vapour annealing. For comparison, the PL decay of neat donor (purple line) is also shown. Dark yellow lines are fits to experimental data using equation S4.

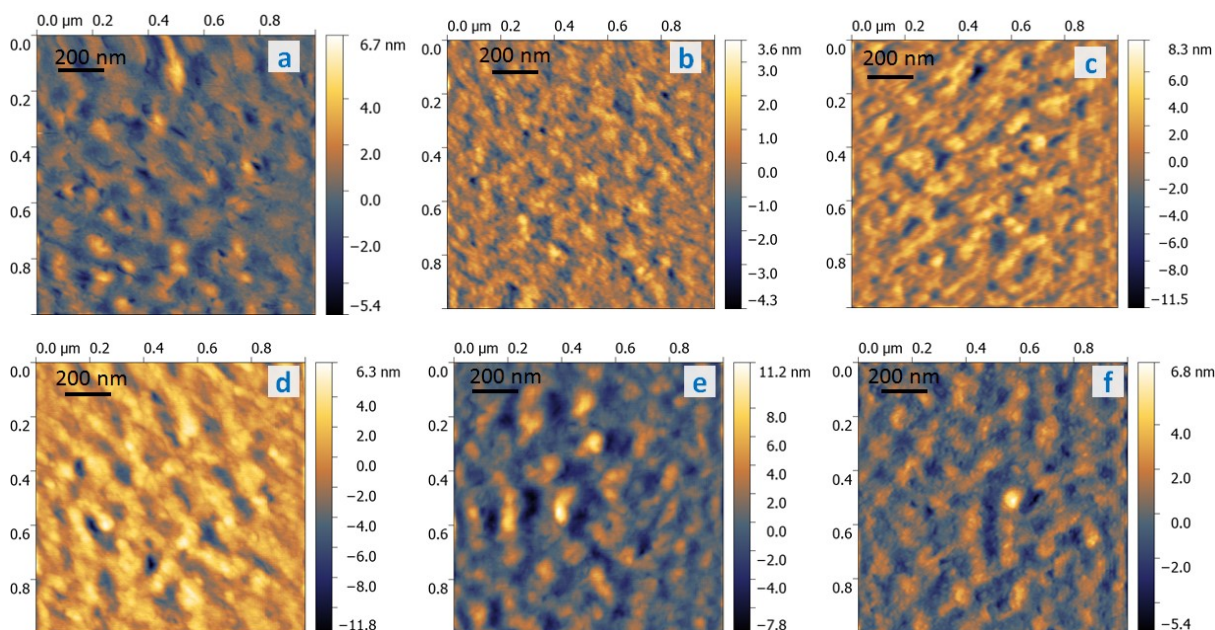


**Fig. S11:** Concentration of excitons and charges in the blend of SMPV1: PC<sub>71</sub>BM before and after solvent vapour annealing: (a) Concentration of excitons and charges in untreated and CS<sub>2</sub> blend of SMPV1:PC<sub>71</sub>BM extracted from the fitting of transient absorption spectra of untreated and CS<sub>2</sub> treated blend using model given in Fig. S9.



## Blend morphology and domain size

Atomic force microscopy images (Fig. S12) of blends show the change in morphology after being treated with different solvents i.e. feature size becomes large after solvent annealing.



**Fig. S12:** Atomic force microscopy images of DR3TBDTT: PC<sub>71</sub>BM SVA blend with (a) CHCl<sub>3</sub> (b) THF. AFM images of SMPV1: PC<sub>71</sub>BM blend before (c) and after SVA with (d) THF (e) CHCl<sub>3</sub> and (f) CS<sub>2</sub>.

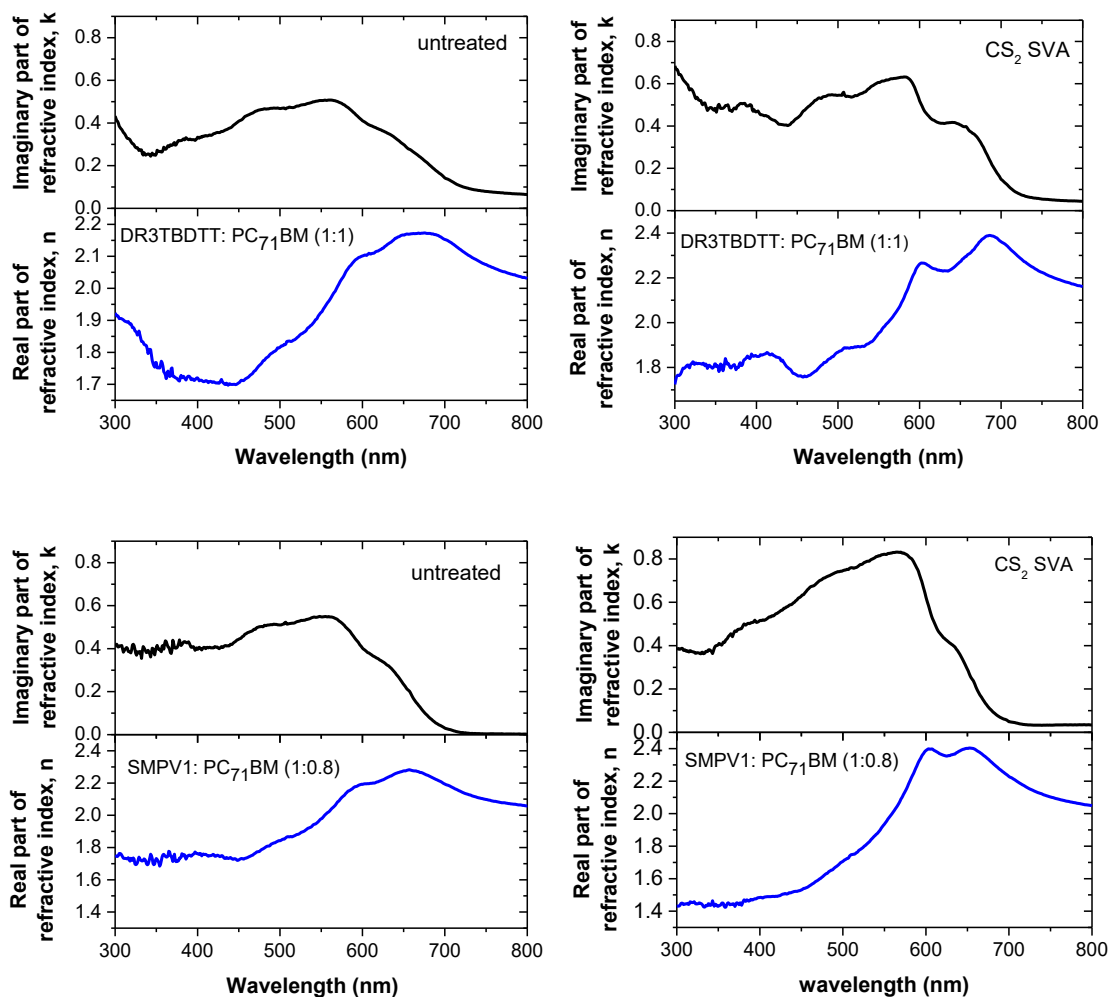
We extracted the size of PC<sub>71</sub>BM domains using a similar approach to Ruseckas et al<sup>2</sup> by considering that the PL quenching of the donor in the blend is mediated by exciton diffusion. Furthermore we also assume that the excitons diffuse by random walk and quench at the interface with PC<sub>71</sub>BM spheres. The rate of quenching is given by

$$k_q = \frac{3\pi Df(r+d)}{\pi r^3} \left(1 + \frac{r+d}{\sqrt{\pi Dt}}\right) \quad (S4)$$

where  $f$  is the fraction of PC<sub>71</sub>BM in the blend,  $D$  is the exciton diffusion coefficient,  $r$  is the radius of the sphere and  $d$  is the distance for direct transfer which is negligible as quenching is diffusion limited. For domain size, we multiplied equation S4 with the fluorescence intensity of neat film (without quencher) and then used it to fit the PL decays (shown in Fig. 3d and S10). The extracted domain sizes of acceptor molecules are plotted in Fig. 3e.

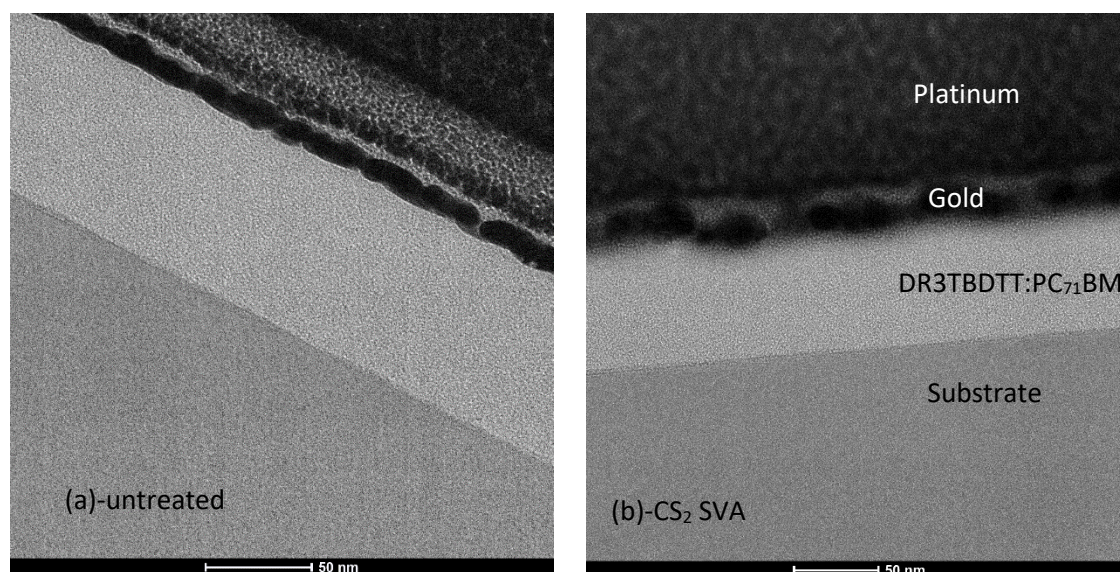
## Optical Constants

The films of blends (untreated and solvent vapour annealed) were measured using spectroscopic ellipsometry in the reflection mode. The angle was varied from 45° to 65° and data was modelled to obtain the refractive indices (given in Fig. S13).



**Fig. S13:** *Optical constants of blends determined using spectroscopic ellipsometry: The imaginary and real part of the refractive index of the untreated and treated with CS<sub>2</sub>. SVA (a) untreated DR3TBDDT (b) CS<sub>2</sub> SVA DR3TBDDT (c) untreated SMPV1 (d) CS<sub>2</sub> SVA SMPV1.*

#### Cross-sectional TEM of DR3TBDDT:PC<sub>71</sub>BM blends



**Figure S14:** *Cross-sectional TEM of (a) untreated and (b) CS<sub>2</sub> SVA blends of DR3TBDDT:PC<sub>71</sub>BM.*

- (1) M. Chowdhury, M. T. Sajjad, V. Savikhin, N. Hergue, K. Sutija, S. Oosterhout, M. F. Toney, A. Ruseckas and I. D. W. Samuel, *Phys. Chem. Chem. Phys.*, 2017, **19**, 12441-12451.
- (2) A. Ruseckas, P. E. Shaw and I. D. W. Samuel, *Dalton Transactions*, 2009, (45), 10040-10043.