

Supporting Information for: Effect of  
Nanocrystalline Domains in Photovoltaic Devices  
with Benzodithiophene Based Donor-Acceptor  
Co-Polymers

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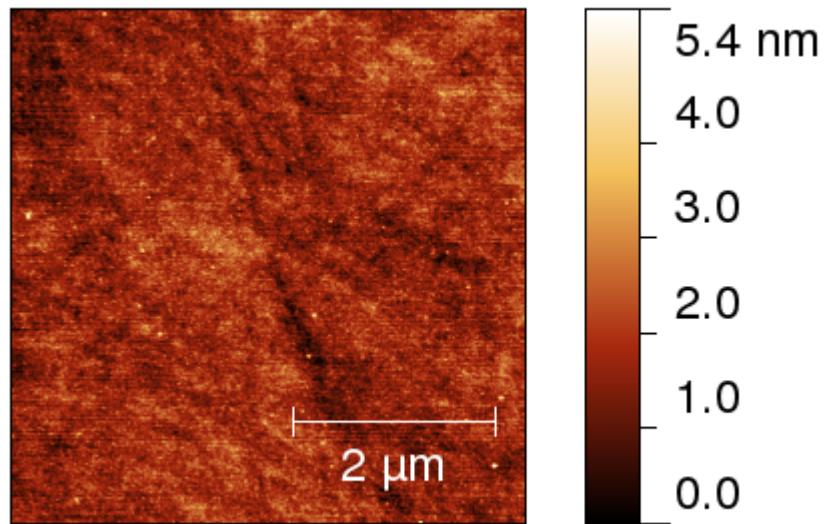
## 1 Sputtering and characterization of TiO<sub>2</sub> thin-films

For exciton diffusion measurements described in the main text, thin, uniform films of TiO<sub>2</sub> were deposited onto quartz substrates by RF magnetron sputter deposition in an ATC 2400-V system from AJA International. A three-inch TiO<sub>2</sub> target was sputtered in a 3 mTorr inert atmosphere, with Ar flowing at 20 sccm. 300 W RF power was supplied to the gun, producing a DC bias of about 170 V. No heating was applied to the substrate and the deposition time of 62 minutes was chosen to give a titania film thickness of 80 nm.

Rapid-thermal annealing (RTA) was subsequently carried out under Ar flowing at 2 L minute<sup>-1</sup>. The samples were placed on a Si wafer and annealed for two minutes at 450 °C. Due to the large thermal mass of the (~ten) quartz substrates, the initial ramp time was prolonged and the peak temperature was actually maintained for less than two minutes.

In addition, TiO<sub>2</sub> was concurrently deposited on a Si substrate, and the resulting sample used for spectroscopic ellipsometry. We found that before RTA, the titania was about 81 nm thick with a (real) refractive index of 2.39 at 633 nm. After RTA, the thickness had decreased to 78 nm and the index had increased to 2.47, suggesting that some densification had occurred.

Figure S1 shows an AFM image of the resulting films on quartz from which a surface roughness of ~2 nm was determined.



**Figure S1:** Atomic force microscopy image of a thin film of TiO<sub>2</sub> sputtered on the surface of a quartz substrate as described in the text.

## 2 Modelling of exciton diffusion to a quencher layer

The photoluminescence decay from a thin polymer film deposited on a TiO<sub>2</sub> quencher layer was modeled by calculating the number and distribution of excitons in the film  $n(x,t)$  according to the 1-D diffusion equation,

$$\frac{\partial n(x,t)}{\partial t} = D \frac{\partial^2 n(x,t)}{\partial x^2} - \frac{n(x,t)}{\tau} \quad (1)$$

where  $D$  is the diffusion coefficient and  $\tau$  is the intrinsic polymer PL lifetime, determined by fitting a monoexponential decay to the PL data measured from polymer layers in the absence of any quencher material. <sup>[S1]</sup> The effect of the quenching layer was included by assuming that all excitons which reach the interface are quenched with unit efficiency ( $n(L,t) = 0$ , where  $x=0$  at the glass/polymer interface and  $L$  is the polymer film thickness). As the excitation pulse was from the glass substrate side of the samples, the initial distribution of excitons was taken to be  $n(x,0) = n_0 \exp(-\alpha x)$ , where  $\alpha = A/L$  (absorbance at 450 nm / polymer layer thickness). In order to calculate the diffusion length  $L_D$ , the diffusion coefficient was varied to minimize the reduced chi-squared value,

$$\chi_r^2 = \frac{1}{(m-p-1)} \sum \frac{[y(t) - y_c(t)]^2}{y(t)} \quad (2)$$

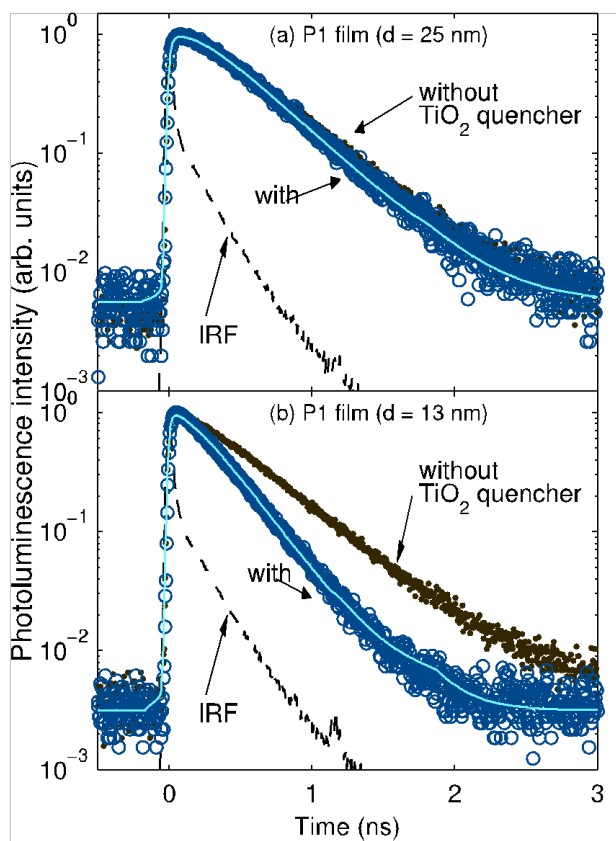
where  $y(t)$  and  $y_c(t)$  are the measured and calculated PL intensities at time  $t$ ,  $m$  is the number of data points and  $p$  is the number of fitting parameters. <sup>[S2]</sup> The equation was solved numerically using the Crank-Nicholson algorithm and the number of excitons integrated across the entire film in order to determine the total PL intensity at time  $t$ . Both the stretched exponential and 1-D diffusion models were fit to the experimental TCSPC data by iterative reconvolution with the

instrument response function (IRF) which was recorded separately, such that the observed PL intensity,

$$I(t) = \int g(t)f(t-t')dt \quad (3)$$

is the result of the real decay curve,  $f(t)$ , convolved with the IRF,  $g(t)$ .<sup>[S2]</sup> The average diffusion length  $L_D$  is given by  $\sqrt{D\tau}$  and the errors reported in the text account for errors in the fitting procedure and in sample thickness, with the latter providing the most significant contribution. The effect on the calculated  $L_D$  of reflections at the polymer/TiO<sub>2</sub> interface (approx. 2%) were determined and were found to be negligible, particularly compared with other sources of error in the experiment.

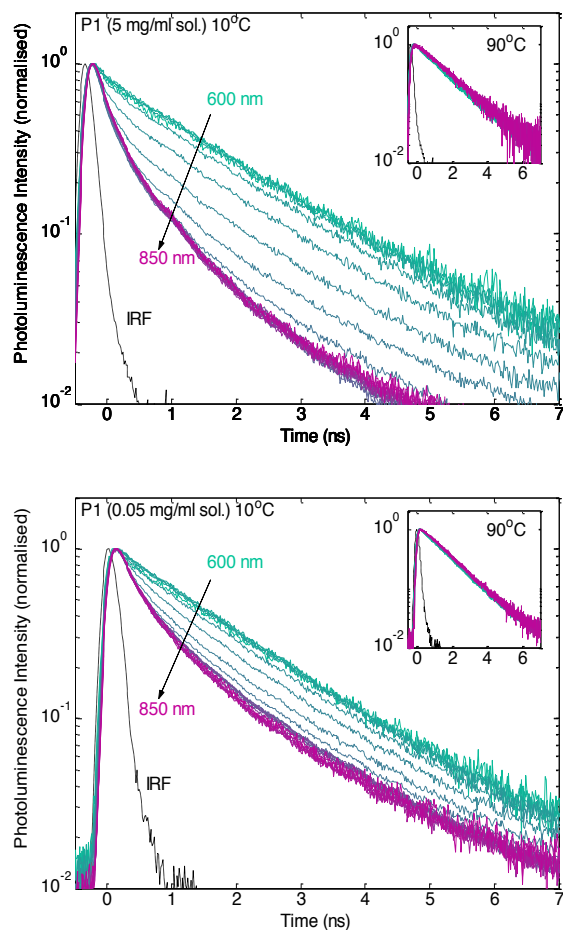
Figure S2S2 shows an example of PL transients and fits taken for thin films of polymer P1 for two different film thicknesses.



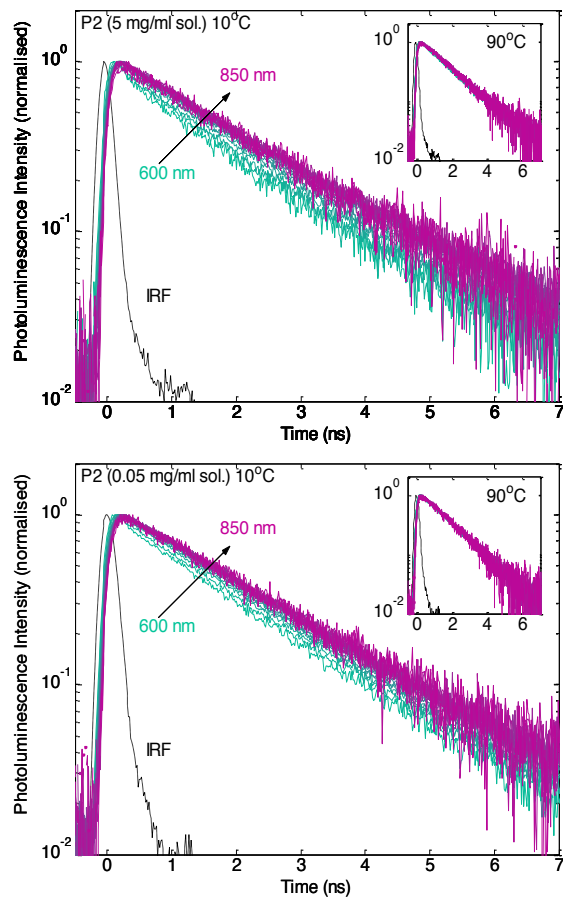
**Figure S2:** Photoluminescence decay transients measured for P1 polymer films deposited on quartz substrates with (dark blue circles) and without (black dots) an 80-nm-thick coating of sputtered TiO<sub>2</sub>. Data were taken with the TCSPC technique using a small-area silicon avalanche photodiode – the dashed line is the instrument response function (IRF) showing 35 ps FWHM. The light blue line is a one-dimensional exciton diffusion model fit to the data by iterative re-convolution with the IRF. The sole fitting parameter was  $D$ , the diffusion coefficient. Curves are shown for two different polymer film thicknesses, (a) 25 nm and (b) 13 nm. In each case, samples were excited from the front with pulses of 100 fs duration and 450 nm wavelength and the PL was detected at a wavelength of 690 nm.

### 3 Time-resolved emission transients for polymer solutions

Photoluminescence transients of dilute and concentrated solutions of all 5 polymers are shown in Figures S3 to S7 for temperatures of at 10°C (main) and 90°C (inset), supplementary to Fig. 6 of the main text.

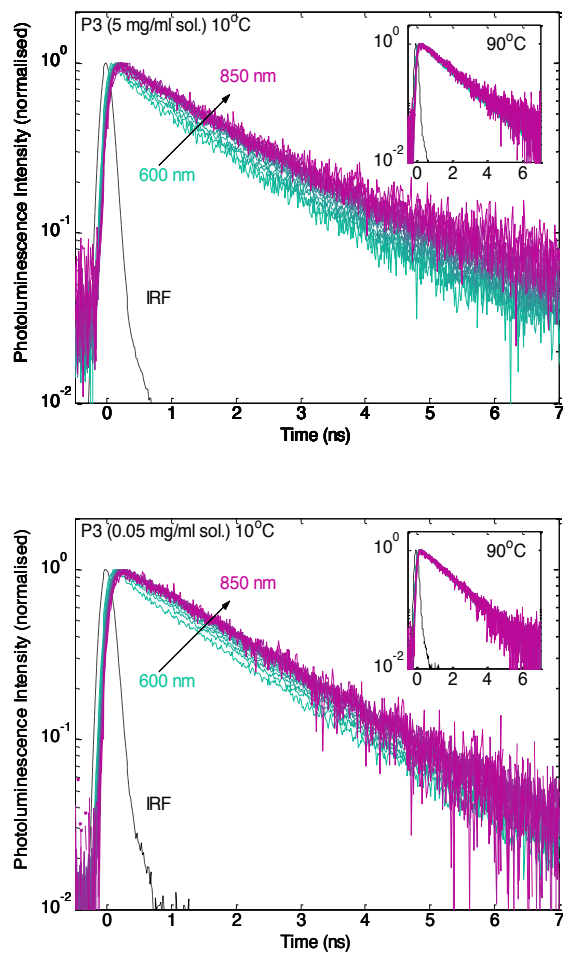


**Figure S3:** Photoluminescence decay transients for polymer P1 at 5 mg ml<sup>-1</sup> (top) and 0.05 mg ml<sup>-1</sup> (bottom) concentration in o-DCB, for solution temperature of 10°C (main figure) and 90°C (inset). In each case, the excitation wavelength was held constant at 450 nm, and the time resolved PL intensity measured at emission wavelengths ranging from 600 nm to 850 nm in 10-nm steps.

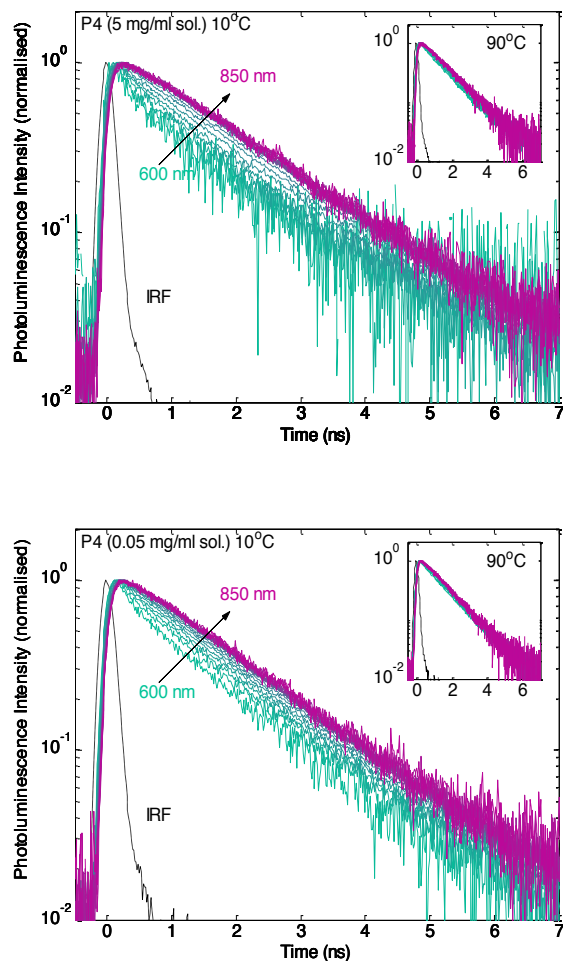


**Figure S4:** Photoluminescence decay transients for polymer P2 at  $5 \text{ mg ml}^{-1}$  (top) and  $0.05 \text{ mg ml}^{-1}$  (bottom) concentration in o-DCB, for solution temperature of  $10^\circ\text{C}$  (main figure) and  $90^\circ\text{C}$  (inset). In each case, the excitation wavelength was held constant at  $450 \text{ nm}$ , and the time resolved PL intensity measured at emission wavelengths ranging from  $600 \text{ nm}$  to  $850 \text{ nm}$  in  $10\text{-nm}$  steps.

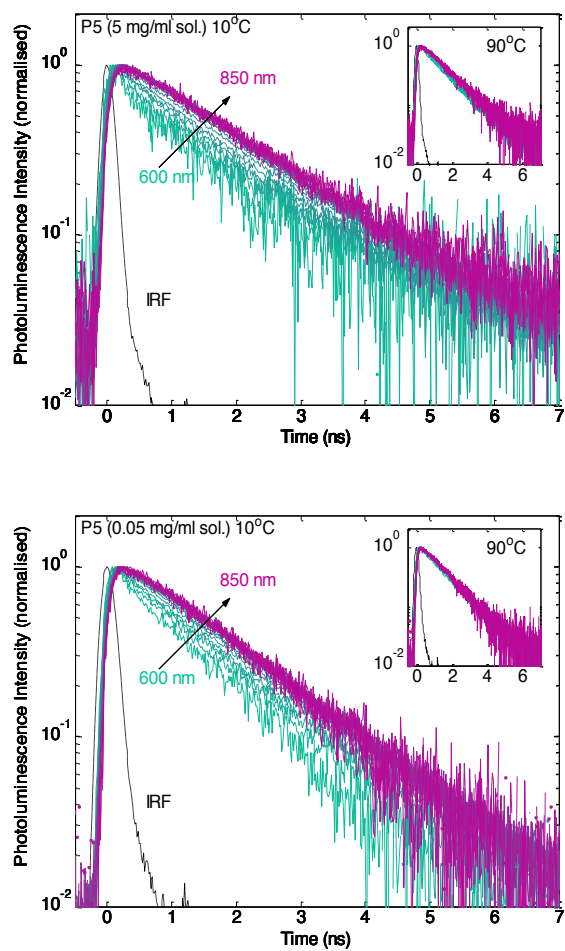




**Figure S5:** Photoluminescence decay transients for polymer P3 at 5 mg ml<sup>-1</sup> (top) and 0.05 mg ml<sup>-1</sup> (bottom) concentration in o-DCB, for solution temperature of 10°C (main figure) and 90°C (inset). In each case, the excitation wavelength was held constant at 450 nm, and the time resolved PL intensity measured at emission wavelengths ranging from 600 nm to 850 nm in 10-nm steps.



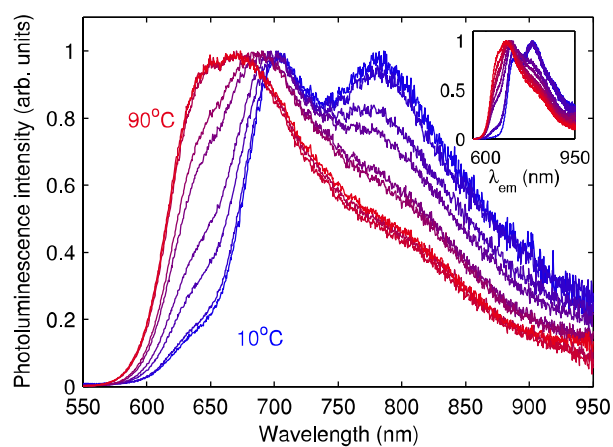
**Figure S6:** Photoluminescence decay transients for polymer P4 at 5 mg ml<sup>-1</sup> (top) and 0.05 mg ml<sup>-1</sup> (bottom) concentration in o-DCB, for solution temperature of 10°C (main figure) and 90°C (inset). In each case, the excitation wavelength was held constant at 450nm, and the time resolved PL intensity measured at emission wavelengths ranging from 600nm to 850nm in 10-nm steps.



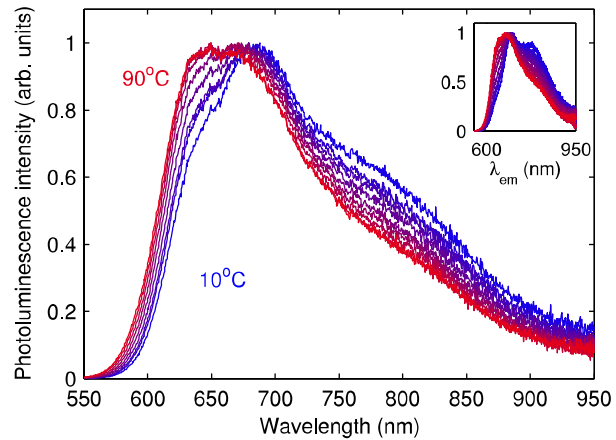
**Figure S7:** Photoluminescence decay transients for polymer P5 at 5 mg ml<sup>-1</sup> (top) and 0.05 mg ml<sup>-1</sup> (bottom) concentration in o-DCB, for solution temperature of 10°C (main figure) and 90°C (inset). In each case, the excitation wavelength was held constant at 450 nm, and the time resolved PL intensity measured at emission wavelengths ranging from 600 nm to 850 nm in 10-nm steps.

#### 4 Time-integrated emission spectra for polymer solutions

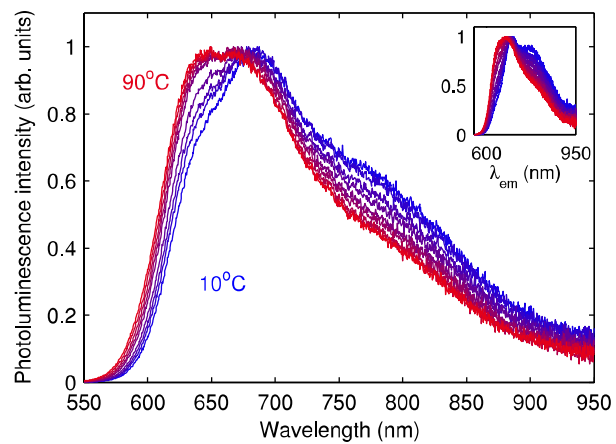
Figures S8 to S12 show time-integrated photoluminescence spectra as a function of temperature for dilute (main) and concentrated (inset) solutions of all five polymers, supplementary to Figure 7 in the main text.



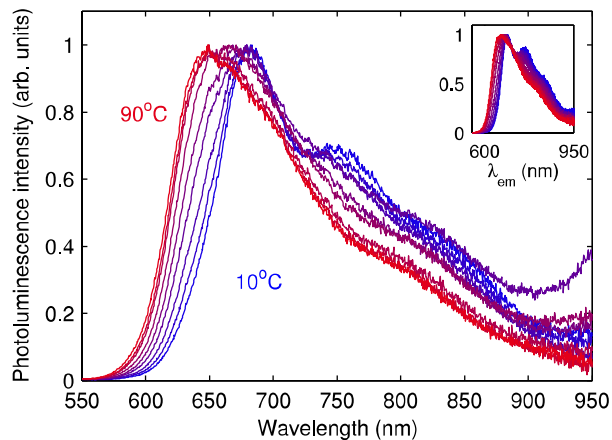
**Figure S8:** Temperature dependence of the P1 polymer PL spectrum in dilute ( $0.05 \text{ mg ml}^{-1}$ , main figure) and concentrated ( $5 \text{ mg ml}^{-1}$ , inset) o-DCB solutions.



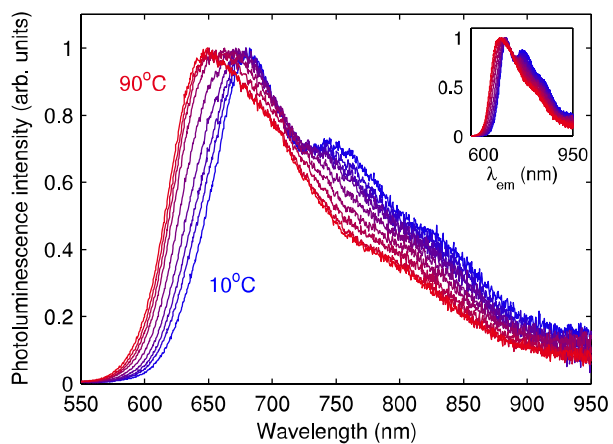
**Figure S9:** Temperature dependence of the P2 polymer PL spectrum in dilute (0.05 mg ml<sup>-1</sup>, main figure) and concentrated (5 mg ml<sup>-1</sup>, inset) o-DCB solutions.



**Figure S10:** Temperature dependence of the P3 polymer PL spectrum in dilute (0.05 mg ml<sup>-1</sup>, main figure) and concentrated (5 mg ml<sup>-1</sup>, inset) o-DCB solutions.



**Figure S11:** Temperature dependence of the P4 polymer PL spectrum in dilute (0.05 mg ml<sup>-1</sup>, main figure) and concentrated (5 mg ml<sup>-1</sup>, inset) o-DCB solutions.



**Figure S12:** Temperature dependence of the P5 polymer PL spectrum in dilute (0.05 mg ml<sup>-1</sup>, main figure) and concentrated (5 mg ml<sup>-1</sup>, inset) o-DCB solutions.

## 5 Polymer Physical Characteristics

The weight-average molecular weight,  $M_w$ , the number-average molecular weight,  $M_n$ , and the polydispersity,  $PDI$ , of each of the polymers P1-5 are given in **Table ST1**.

	$M_n$	$M_w$	$PDI$
	[g mol <sup>-1</sup> ]	[g mol <sup>-1</sup> ]	
<b>P1</b>	21.6	42.0	1.94
<b>P2</b>	22.6	42.1	1.86
<b>P3</b>	15.3	50.4	3.29
<b>P4</b>	29.7	53.0	1.78
<b>P5</b>	28.4	61.5	2.16

**Table ST1.** The weight-average molecular weight, number-average molecular weight and polydispersity of polymers P1-5.

## 6 Separating Optical Parameters from measured $J_{SC}$

In order to confirm that differences in measured  $J_{SC}$  did not arise solely from increased absorption in the synthesised PV devices, normalised  $J_{SC}$  values were calculated, where the measured  $J_{SC}$  is scaled by the total number of photons absorbed. This was given by

$$S = \int F_{AM1.5} (1 - \log_{10}(\epsilon d)) d\lambda \quad (4)$$

Where  $F_{AM1.5}$  is the photon flux with 1 nm bandwidth of the AM1.5 standard,  $\epsilon$  is the absorption coefficient and  $d$  is the active layer thickness (200 nm). The scaling factors  $S$ , were normalised to that of a 200 nm thick film of P1. The normalised and measured  $J_{SC}$  values are given in **Table ST2**.

	$J_{SC}$ [mA cm <sup>-2</sup> ]	$SJ_{SC}$ [mA cm <sup>-2</sup> ]
<b>P1</b>	5.33	5.33
<b>P2</b>	9.58	10.03
<b>P3</b>	5.34	4.91
<b>P4</b>	12.04	11.17
<b>P5</b>	9.25	8.14

**Table ST2.** The experimentally determined  $J_{SC}$  and normalised  $J_{SC}$  ( $SJ_{SC}$ ) values taking into account the difference in absorption between active layers with different polymers.

(S1) P. E. Shaw, A. Ruseckas, I. D. W. Samuel, Exciton Diffusion Measurements in poly(3-hexylthiophene), *Adv. Mater.* **2008**, *20*, 3516-3520.

(S2) Lakowicz, J. R. *Principles of fluorescence spectroscopy*, 3<sup>rd</sup> ed.; Springer, **2007**, 130-135.