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### Supplementary Information

## Mission Immiscible: Overcoming the Miscibility Limit of Semiconducting:Ferroelectric

#### **Polymer Blends via Vitrification**

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### Materials and processing

Regio-regular poly(3-hexylthiophene-2,5-diyl) (P3HT) with a weight-average molecular weight,  $M_w$ , of 130 kg/mol was obtained from Dr. James Bannock, Dr. Martin Heeney, and Dr. John de Mello at Imperial College London. Low molecular weight P3HT of 60 kg/mol was purchased from Ossila. Poly(vinylidene fluoride) (PVDF) of various weight-average molecular weight (60 kg/mol, 180 kg/mol, and 530 kg/mol) were purchased from Sigma Aldrich. The solvents cyclohexanone and xylene were purchased from Sigma Aldrich and used as received.

P3HT:PVDF solutions were prepared at 7 mg mL<sup>-1</sup> using a 3:1 cyclohexanone:xylene volume ratio of solvents to control the solidification sequence of the two components. All solutions were stirred at 100 °C for 1-2 hours to dissolve the polymers. The blends were mixed at different weight percentages (e.g. 75:25 corresponds to 75% component I by weight and 25% component II). Solution-processed films were prepared via wire-bar coating on glass substrates at a speed of 14 cm s<sup>-1</sup> (speed 6) at 50°C. A K 101 control coater from Printcoat Instruments with a heated bed (temperature-controlled stage) was used for this purpose. The

solution was directly poured onto the bar, allowing a gap of around 150  $\mu$ m in between the bar and the substrate. Melt processed films were prepared by heating solution processed films to 300 °C till a melt state was achieved. These films were then cooled down to room temperature. The heating/cooling rates were chosen to be 20 °C min<sup>-1</sup>, to match the thermal history of samples analyzed via DSC.

# Differential scanning calorimetry (DSC)

Samples for differential scanning calorimetry (DSC) were prepared by drop-casting solutions onto cleaned glass substrates at 50 °C. After solvent evaporation at ambient pressure, the films were placed in a desiccator under vacuum overnight. They were then scraped off as flakes/powder, and  $\sim$ 1.5–2 mg was transferred into hermetic aluminum DSC pans, which were sealed with punctured lids. The measurements were performed under nitrogen using a Mettler Toledo STARe System DSC 3+ instrument. Two heating and two cooling cycles were recorded at a 20 °C min<sup>-1</sup> rate. The first heating cycle represents the solution processed film, while the second cycle mimics the melt processed state. The endotherm endset temperatures and exotherm onset temperatures were used to report melting and crystallization temperatures, respectively.

# Vapor phase infiltration (VPI)

The VPI process was conducted in a Veeco Savannah S200 system. The samples were exposed to 30 alternating cycles of DEZ and H<sub>2</sub>O at 60 °C. During each cycle, the samples were exposed to two consecutive DEZ pulses for 120 sec, followed by a purge process of 30 sec after each pulse. After the DEZ pulses, the samples were exposed to two consecutive H<sub>2</sub>O pulses for 120 sec, followed by a purge processes of 40 sec. The VPI process condition were carefully adjusted to minimize morphological changes during process.

# High resolution scanning electron microscopy (HRSEM)

The HRSEM micrographs were acquired using a Zeiss Ultra-Plus FEG-SEM operated at 1.5 kV accelerating voltage with a working distance of 2.4 mm. For cross-section HRSEM imaging, the films on silicon substrates were cleaved in liquid nitrogen.

# Measurement of specific viscosity

The viscosity of P3HT and PVDF solutions were measured at 25°C using a RheoSense *micro*VISC<sup>™</sup> viscometer. The P3HT solution was prepared by dissolving the polymer at 7 mg mL<sup>-1</sup> in chlorobenzene at 50°C for 2 hours. The solution was

then cooled to 25°C for 3 hours before beginning viscosity measurements. The PVDF was dissolved at 10 mg mL -1 in dimethylsulfoxide at 60°C for 2 hours, then cooled to 25°C for 3 hours.

## Grazing incidence wide angle X-ray spectroscopy (GIWAXS)

X-ray scattering patterns were collected at the National Synchrotron Light Source II (NSLS-II) beamline 11BM-CMS. Patterns were collected by a Photon Science CCD (1042 × 1042 pixels, 101.7  $\mu$ m × 101.7  $\mu$ m pixel size) area detector at a beam energy of 11 keV in a vacuum environment with 15 s exposure time and an angle of incidence of 0.14°. Calibration was performed with a silver behenate standard. The 2D scattering patterns and 1D line cuts obtained from in-plane and out-of-plane sector slices, are denoted as q<sub>z</sub> and q<sub>xy</sub> respectively.



**Figure S1.** Specific viscosity measurements of neat P3HT and PVDF solutions as a function of molecular weight.  $M_c$  corresponds to the critical molecular weight, where a drastic increase in specific viscosity is observed, as indicated in the graphs. The high molecular weight components used in this work (P3HT of  $M_w = 130$  kg/mol and PVDF of  $M_w = 530$  kg/mol; indicated with green circles) are well above the  $M_c$  of the two polymers. (Note: P3HT was dissolved in chlorobenzene at a concentration of 7 mg/ml, and PVDF in DMSO at a concentration of 10 mg/ml).



Figure S2. DSC heating thermographs of a. solution-processed and b. melt-processed PVDF and P3HT of various M<sub>w</sub>.

**Table S1**. Melting temperatures of neat P3HT and PVDV of various  $M_{w}$ , deduced from the end-set of their melting endotherms (see Fig S2).

Neat component	M <sub>w</sub> [kg/mol]	Melting temperature [°C]	
		Solution processed	Melt processed
PVDF	60	175	173
	130	171	171
	530	166	165
РЗНТ	60	234	239
	130	228	233



**Figure S3.** Cross-section HRSEM BSE micrographs of neat P3HT (top) and PVDF (bottom) after  $DEZ/H_2O$  VPI process demonstrating the selective deposition of ZnO in P3HT films bright appearance. In contrast, the PVDF inhibits ZnO deposition, and hence PVDF domains are generally appear dark. This behavior is detected for low and high Mw polymers. The scale bar for all micrographs is 500 nm.



**Figure S4.** Cross-section HRSEM BSE micrographs of solution-processed P3HT:PVDF blends of different molecular weights (given in kg/mol) after a  $DEZ/H_2O$  VPI process. The blends comprising at least one high-molecular-weight material allow for a partially or fully vitrified intermixed phase to form, as a result of chain entanglements hindering mass transport. The scale bar for all micrographs is 500 nm.



**Figure S5.** *a.* DSC thermograms of first heating scans for solution-processed P3HT:PVDF blends ( $M_w$  130 and 530 kg/mol for P3HT and PVDF, respectively) as a function of blend composition. The CC exotherms (shaded in grey) are prevalent for a substantial range of blending ratios for this high molecular weight blend, supported by the homogeneous intermixed phases observed in their cross-section HRSEM BSE micrographs (b.- e.). The scale bar for all micrographs is 500 nm. f. Comparison of  $\Delta H_{cc}$  to the combined melting enthalpies of the individual blend components,  $\Delta H_m^{P3HT} + \Delta H_m^{PVDF}$ , to determine the extent of vitrification of the different composition blends.



**Figure S6.** The effect of processing temperature on the phase behavior of neat P3HT and PVDF and P3HT:PVDF blend (*M*<sub>w</sub> 130 and 530 kg/mol for P3HT and PVDF, respectively), showing varied cold crystallization behavior for the blend.

We compared three casting temperatures: 25, 50, and 100 °C, to explore the influence on the blend vitrification. DSC thermograms for the neat materials and blends cast at different temperatures are displayed in Figure S6. At room temperature (25 °C), where the solvent evaporation and mass transport are low, a notable CC exotherm is observed, indicating a certain degree of vitrification. Casting at 50 °C leads to more rapid quenching and, consequently, a more pronounced CC exotherm, i.e., more significant vitrification. Selecting a higher casting temperature (100°C), increases mass transport, assisting the two components to phase-separate and molecularly order. No cold crystallization is, thus, observed.