

Supporting Information

The influence of directed π - π interactions in solution on thin film organic semiconductor devices properties of small molecule polymer blends

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Supporting Information Available: Details of Materials, Experimental Procedures, Optical Spectroscopy, Surface analysis, Isothermal Titration Calorimetry, Small Angle Neutron Scattering, Small Angle X-ray scattering.

Experimental Details.

Materials.

Anhydrous toluene, tetrahydronaphthalene and octadecyl trichlorosilane (99%), 1,2,3,4-tetrahydronaphthalene (tetralin, anhydrous 99%), amorphous polystyrene (PS, $M_n = 350$ kDa), semicrystalline isotactic polystyrene (iPS, $M_n = 400$ kDa), all obtained from Sigma-Aldrich UK and used as received. Physical properties of the polymers are given in Table S1. Deuterated n-hexane, cyclohexane and toluene (degree of deuteration > 99%) were obtained from Goss Scientific and used as received. 6, 13-bis (triisopropylsilylethynyl) pentacene (TIPS-pentacene) was synthesized according to the method previously described by Anthony [S1].

Separate stock solutions (1% w/w) of TIPS-pentacene and polymer were prepared and left 24 hours in the dark and in absence of oxygen before use. TIPS-pentacene stock solution was filtered using a 0.45 μm PTFE filter. Polymer dissolution was aided by using a Misonex ultrasonic probe at 30 W for 5 min and used unfiltered. After 5 min all polymer solution was clear. Polymer molecular weights were checked before and after sonication and no molecular weight degradation was observed. TIPS-pentacene – polymer solution blends were prepared fresh prior to use with the total mass content kept constant at 1 % w/w.

Optical spectroscopy.

UV-Vis absorption spectra were recorded on a Varian Eclipse 5000 between 200 and 800 nm. Solutions were placed in a quartz cuvette (1 cm path) and baseline correction was done by subtracting the signal for pure solvent. Fluorescence spectra were recorded on a Varian Eclipse, using a quartz cuvette, with emission recorded between the excitation wavelength and 800 nm. For each formulation the excitation was kept constant and extracted from the absorption data of the diluted solution (first maximum of absorption from the highest wavelength). To allow quantitative comparison of emission intensity between experiments, emission and excitation slits were kept identical throughout. They

were initially optimized for a concentration of 10^{-4} mol.l⁻¹. Once solutions were prepared optical activity was tested in the shortest possible time to avoid any oxidative degradation of the semiconductor in solution. [S2] Solutions were then diluted, enabling four data points decades: 1, 0.75, 0.5 and 0.25, and the characterisation repeated until no fluorescence signal could be recorded. The same process applies to prepare solution for Isothermal Titration Calorimetry.

Surface analysis.

Topography as well as phase image were recorded using a Scanning Force Microscopy (SFM), AFM XE100 (PSIA Inc, Seoul, Korea), in high resolution contact mode at 0.5 Hz. A commercial silicon cantilever with a nominal spring constant of about 40 N/m was used the back of which was coated with aluminum to increase signal feedback. Thin films were realized by drop casting and drawing a small volume of solution on both hydrophilic and hydrophobic glass microscope slides. Hydrophilic slides were prepared by immersing the slide in hydrochloric acid (12M) for one min followed by rinsing thoroughly with deionised water with sonication. Hydrophobic glass slides were prepared by first cleaning by sonication in de-ionised water for 15 minutes, then methanol for 15 minutes and finally acetone for 15 minutes, prior to immersion in a solution of 10 mM octadecyl trichlorosilane in anhydrous toluene for 30 min maintained at room temperature. Substrates were then rinsed with hexane and methanol, and dried on a hot plate for 2 hours at 120 °C in ambient conditions.

Isothermal Titration Calorimetry (ITC).

Titration were carried out using a VP-ITC Microcal. [S3] Before each experiment the reference cell was filled with clean solvent and left to equilibrate at 25 °C. The apparatus consisted of two cells (1.46 cm³) enclosed in an adiabatic jacket. All measurements were thermostated at 25 °C. Solution blends of TIPS-pentacene and polymer were titrated against pure solvent to observe de-aggregation of the mixture. 8 µl aliquots were injected into the measurement cell and the quantity of heat exchanged in the process was recorded. The system was left to stabilise for 400 s before the next injection with the enthalpy change occurring in the solution upon dilution recorded in real time

Small Angle Neutron Scattering (SANS).

For neutron scattering experiments, stock solution at 3 wt-% and 1 wt-% in deuterated solvent were prepared fresh. Blank solution mixtures of 3 wt-% or 1 wt-% protonated solvent in deuterated solvent were also prepared. Solutions were prepared prior to measurement by mixing deuterated solvent with a fraction of protonated solvent corresponding to the proton load of the added compound in the deuterated solvent.

The SANS measurement were performed on the LOQ (N5 instrument) at ISIS at the Rutherford Appleton Laboratory in Didcot (UK). The wavelength range used has a Gaussian distribution between 2 and 10 Å, with wavelength resolution $\Delta\lambda/\lambda$ on LOQ of 3.8 % at 2 Å and 2.9 % at 10 Å. The solutions were measured in Hellma glass cells with a path length of 1 mm at room temperature with the distance of the sample from the detector fixed at 11 m. Measurements recorded over a q-range of 0.006 to 0.24 Å⁻¹. Data reduction was performed using onsite software (COLETTE). All measurements were background corrected to compensate for the incoherent cross section induced by concentration at several percent of polymer.

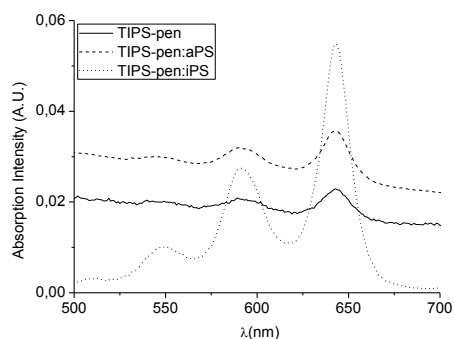
Small Angle X-ray scattering (SAXS).

Small angle X-ray Scattering measurements were carried out on a Hecus 3 micro with a Cu K_α source at 1.54 Å, beam energy 50 keV. Solution was measured in a borosilicate glass capillary 1mm cross section.

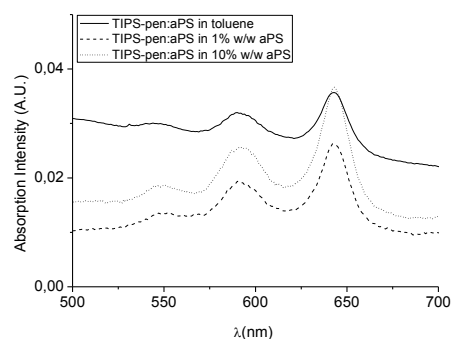
References

- S1 Anthony, J.E.; Eaton, D.L.; Parkin, S.R.; *Org. Lett.*, **2002**, *4*, 15.
- S2 Coppo, P.; S.G. Yeates, S.G. *Advanced Materials*, **2005**, *17(24)*, 3001.
- S3 Blandamer, M.J.; Cullis, P.M.; Engberts, B.F.N. *J. Chem. Soc., Faraday Trans.*, **1998**, *94(16)*, 2261.

(a)



(b)



(c)

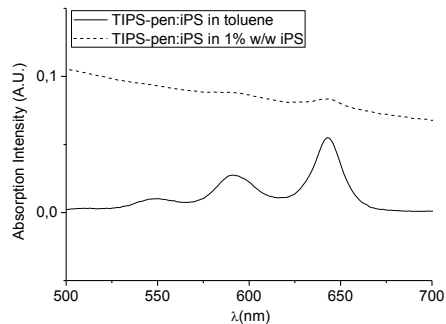


Figure S1: Normalised UV absorption of a 10^{-5} M solution of TIPS-pentacene under the following conditions blended with polystyrene (50:50 wt/wt) as (a) function of tacticity, (b) blended with atactic polystyrene as a function of concentration and (c) blended with isotactic polystyrene as a function of solvent (either pure toluene or 1 wt-% iPS stock solution).

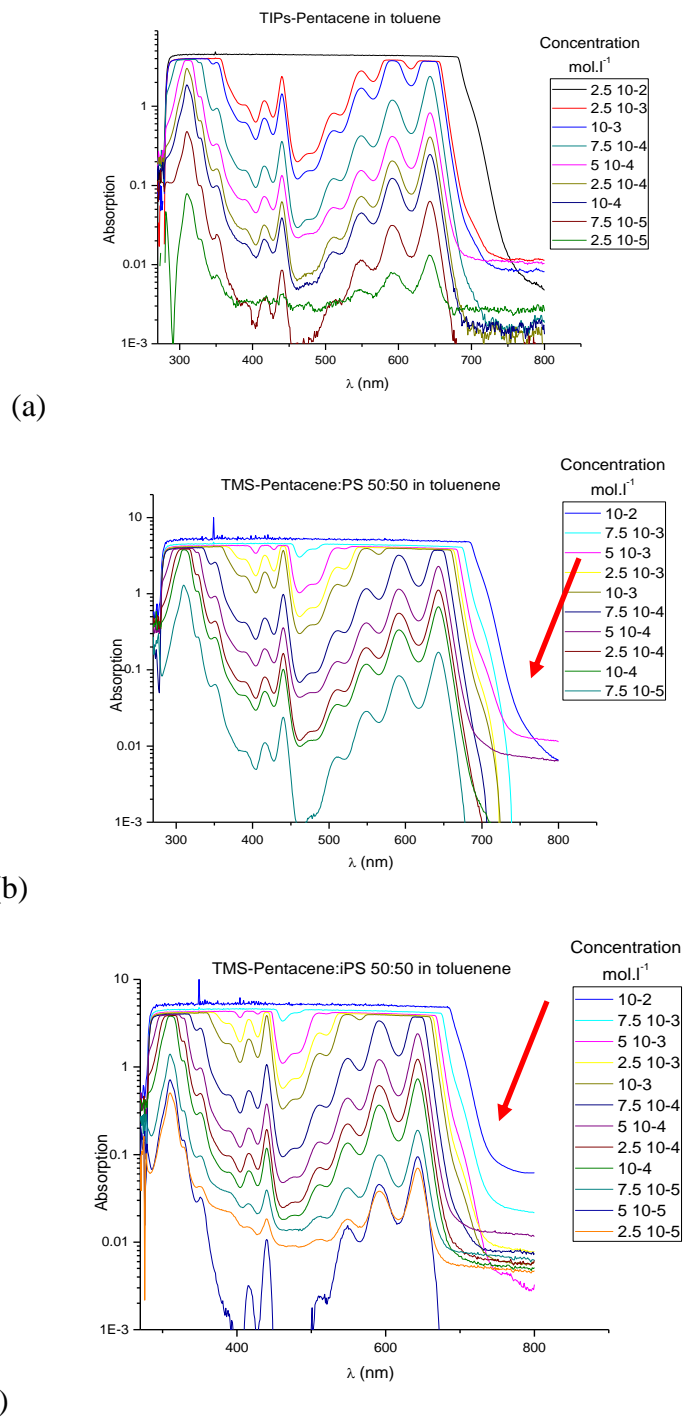
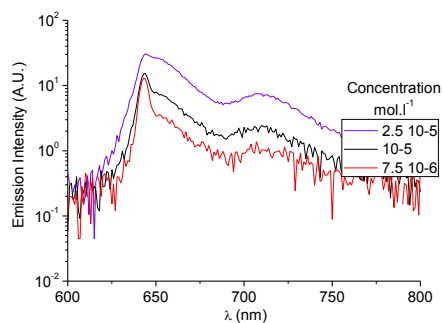
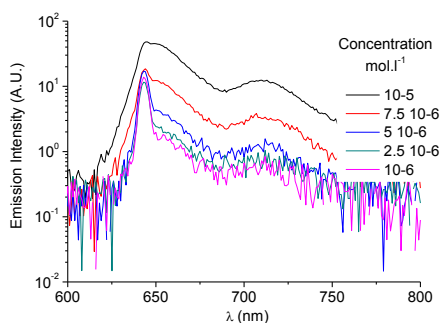


Figure S2: Non-normalised UV absorption of (a) TIPS-pentacene in toluene and (b) TIPS-pentacene: aPS (50:50 wt/wt) in toluene, (c) TIPS-pentacene: iPS (50:50 w/w) in toluene

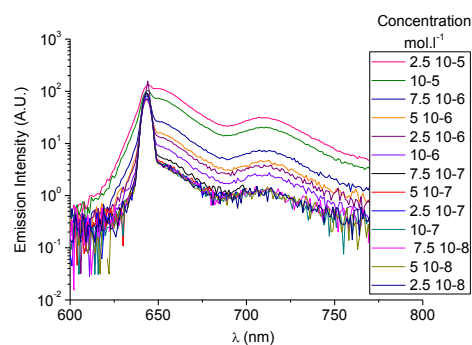
TIPS-pentacene in toluene



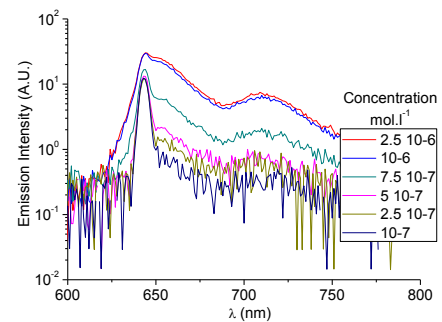
TIPS-pentacene:aPS in toluene



TIPS-pentacene:aPS in 1 wt-% aPS



TIPS-pentacene:iPS in toluene



TIPS-pentacene:iPS in 1 wt-% iPS

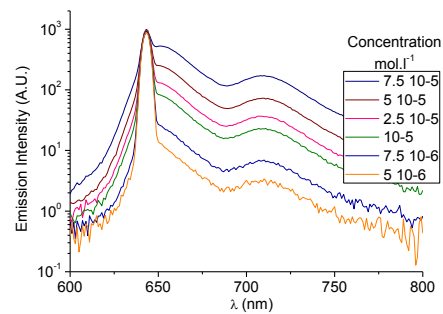


Figure S3: Emission spectra for TIPS-pentacene in toluene solution in the absence and presence of atactic and isotactic polystyrene binder. Note the peak corresponding to unimeric TIPS-pentacene at $\lambda = 643$ nm persists at higher concentration when formulated with isotactic polystyrene.

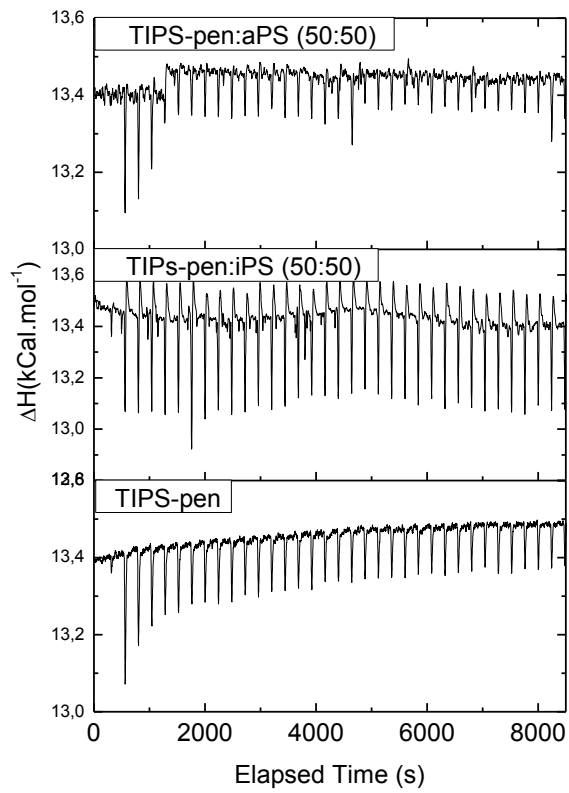
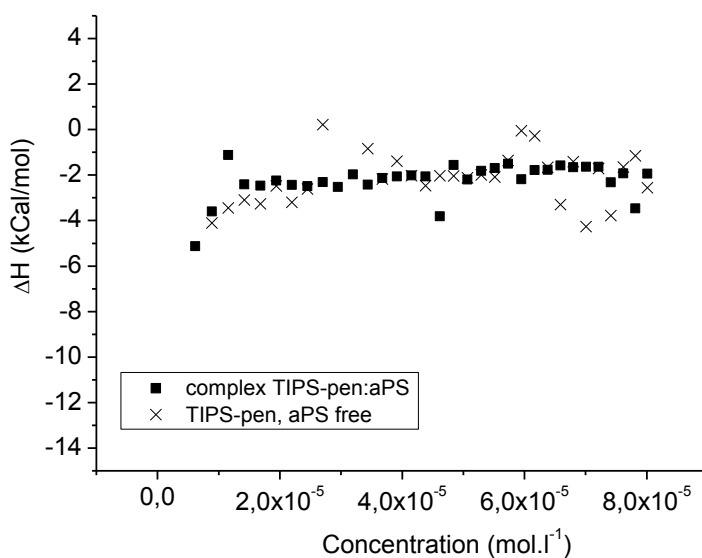


Figure S4: ITC injection profile for (a) TIPS-pentacene:aPS (50:50 wt/wt), (b) TIPS-pentacene: iPS (50:50 wt/wt), and (c) TIPS-pentacene in toluene solution.

TIPS-pentacene:aPS (50/50 wt/wt).



TIPS-pentacene :iPS (50/50 wt/wt)

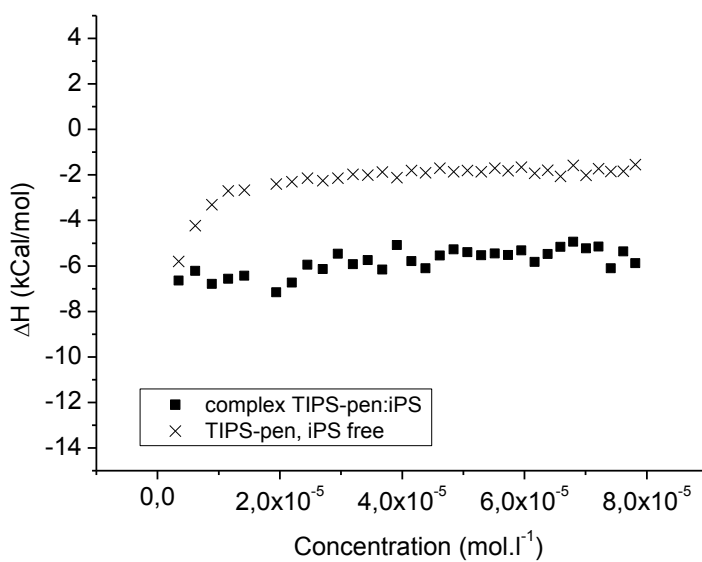


Figure S6: Comparison of TIPS-pentacene: polymer in toluene considered both as an associated complex (■) or as the sum of free molecules in solution (x).

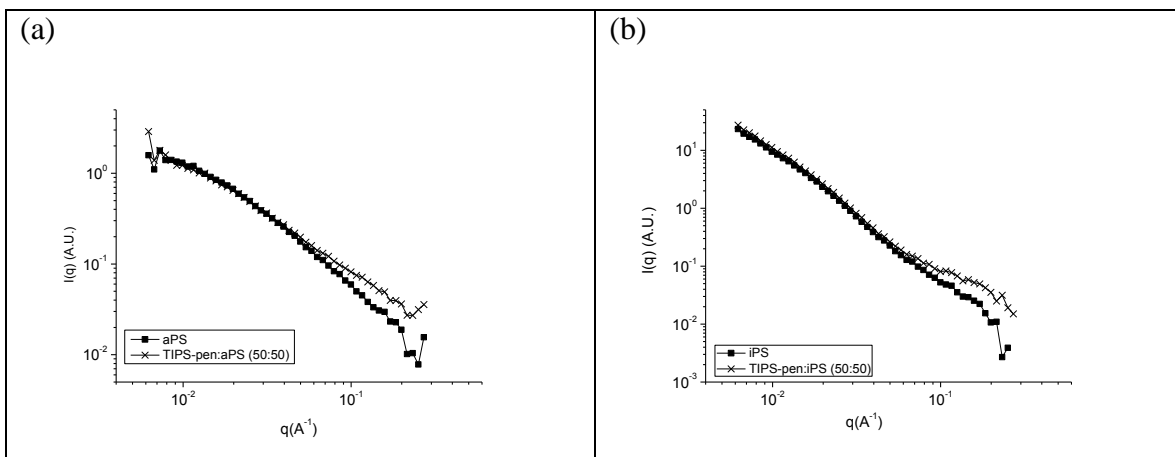


Figure S7: Guinier representation of scattered intensity as a function of q in case of (a) atactic polystyrene and TIPS-pentacene:aPS (50/50), and (b) isotactic polystyrene and TIPS-pentacene:iPS (50/50), used to estimated polymer radius of gyration at low q

Table S1: Exponential factor at medium-high q range extracted from Porod

Polymer or blend	a factor
aPS	-1.6
iPS	-2.5
TIPS-pen:aPS	-1.3
TIPS-pen:iPS	-2.5