Electronic Supplementary Information

Structured Oligo(aniline) Nanofilms via Ionic Self-Assembly

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1. Calculation of solution concentration

Solutions were prepared of oligomers and oligomer-BEHP dopant complexes of a certain concentration so as to generate films of "thick" "thin" samples. These samples have nominal thickness of 350 nm and 35 nm, estimated assuming complete and even coverage of the silicon (Si) substrate. As an example, the length of one TANI molecule was estimated in ChemDraw3D® as 2.3 × 0.5 nm and BHEP 0.9 × 0.9 nm, giving a total area of complex of 2.7×10^{-18} m^2 for the $TANI(BEHP)_{0.5}$ system. Assuming the third dimension in the crystal packing corresponds to the π–π stacking distance (d ~ 0.35 nm) a total molecular volume of 9.4×10^{-28} m^3 is found. In order to cover a 10×10 mm Si substrate at a thickness of 350 nm, 3.7×10^{16} molecules of TANI are required and twice the number of BEHP molecules. Drop-casting of each film was performed using a 40 ml droplet which meant preparing a solution of 1.54 mM of $TANI(BEHP)_{0.5}$ complex. Practically, this was achieved by dissolving 6.8 mg of TANI(EB) and 9.9 mg of BEHP in 10 ml of THF. The $TANI(BEHP)_{0.5}$ "thin" films were prepared in the same manner, however the solution for the "thick" films was diluted at a ratio of 1:10 so as to generate a film of roughly 35 nm. The actual film thicknesses of the films were determined using AFM and ellipsometry as described in the main text.

2. AFM film thickness determination

AFM microscopy was used to determine the thickness of the oligo(ANI) films as described in the main text. The film preparation method was designed to produce "thick" and "thin" films of thickness ~350 nm and ~35 nm respectively. Due to the evaporation of volatile THF solvent the resultant air-film interface was rough and film thickness could vary from the predicted values. As such it was necessary to characterise in detail the topology (see main text and Fig. S1) and film thickness (summarised in Table S1).

Table S1 Summary film thickness as determined through AFM scratch profiling

Sample			**AFM Film thickness**	**Description**
"Thick"	TANI	EB	200 nm	Poor coverage, regular pitted drying effects
		$(BEHP)_{0.5}$	350-400 nm	Smooth even coverage, large aggregates >500 nm on surface
		$(BEHP)_{1.0}$	300-600 nm	Even coverage, varying thickness, large aggregates >1000 nm on surface
	OANI	EB		Rough, poor coverage, aggregation
		$(BEHP)_{0.5}$	200-2000 nm	Very rough surface
"Thin"	TANI	EB	8-16 nm	Dewetting into islands of thin film, surface aggregates (>300 nm)
		$(BEHP)_{0.5}$	15-30 nm	Dewetting into islands of thin film, surface aggregates (>80 nm)
		$(BEHP)_{1.0}$	10-50 nm	Even coverage with some dewetting, surface aggregates (>150 nm)
	OANI	$(BEHP)_{0.5}$	10-50 nm	Significant dewetting, surface aggregates

3. Comparison of AFM & ellipsometric film thickness measurements

Ellipsometry was performed on some films to compare with the findings from AFM. Due to the large footprint of the technique (as compared to the small area imaged with AFM) the resultant data are average values for the sampled area. As such the technique provides a useful indication that the results of AFM performed on a small sample area are consistent across the majority of the film which was confirmed by the macroscopic results from ellipsometry. Fresh films were prepared which were sent for ellipsometric analysis by R. Jacobs (University of Oxford), the films were subsequently returned and imaged with AFM for comparison. A summary of the results can be found in Table S2.

Table S2 Summary film thickness as determined through AFM scratch profiling

Sample			**Film thickness**	
			Ellipsometry	**AFM**
TANI	EB	"thin"	12.6 nm	8-16 nm
TANI	$(BEHP)_{0.5}$	"thin"	20.7 nm	15-30 nm
TANI	$(BEHP)_{0.5}$	"thick"	351.1 nm	150-300 nm[a]
TANI	$(BEHP)_{1.0}$	"thin"	17.1 nm	10-30 nm
OANI	$(BEHP)_{0.5}$	"thin"	16.0 nm	10-50 nm

[a]Note that this is a different sample to that presented in table S1.

4. Additional AFM micrographs

The topographical nature of oligo(ANI) films was found to vary significantly depending on the oligomer molecular architecture, oxidation state (*i.e.* EB state or ES state when treated with BEHP) and the film thickness. In addition to the results presented in the main text some further images can be found in Fig. S1.

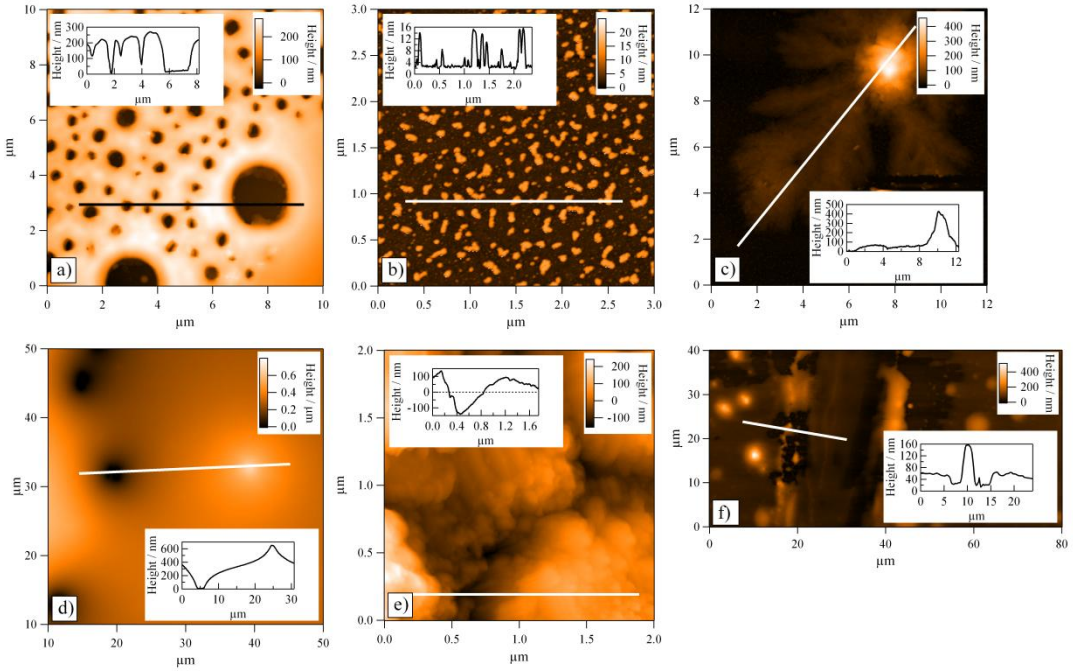

Fig. S1 AFM micrographs for a) TANI(EB) "thick"; b) TANI(EB) "thin" showing islands of 10-25 nm film; c) TANI(EB) "thin" showing larger aggregated deposits; d) $TANI(BEHP)_{1.0}$ "thick"; e) OANI(EB) "thick"; f) $TANI(BEHP)_{1.0}$ "thin".

5. Surface diffraction peak fitting

Bragg peaks observed in XRR surface diffraction curves were characterised using the "Multi-Peak" fitting operation in IgorPro®. The procedures we take are as follows. The segment of XRR curve with the Bragg peaks was selected, and an example is shown in the middle figure of Fig. S2. The background reflectivity was fit to a 3rd polynomial function (blue dotted curve in the figure) and the Bragg peak to a Voigt function. The red dashed curve in the figure is the fitted Voigt

function including the polynomial background fit. The solid red curve in the bottom figure of Fig. S2 shows the fitted Bragg peak after the background subtraction from which our FWHM (ΔQ / Å^{-1}) values were obtained used in the analysis (Eqs. 1 and 2 in the main text), with the residue shown in the top figure (empty circles). The example peak fitting shown in Fig. S2 is for the first Bragg peak observed for the TANI(BEHP)$_{0.5}$ "thick" sample.

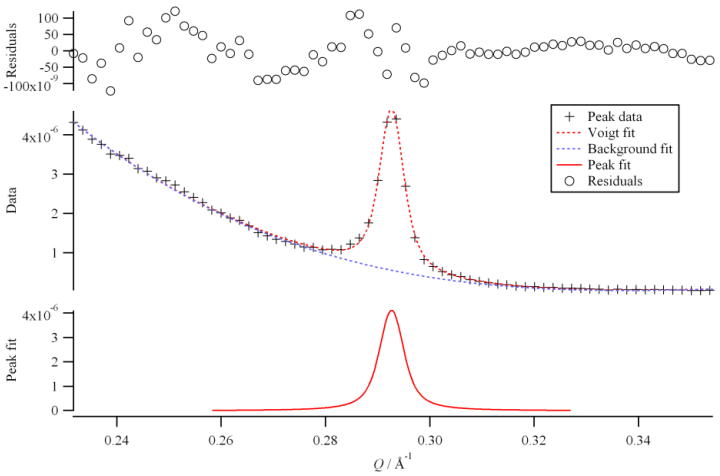

Fig. S2 Plot of peak fitting for the TANI(BEHP)$_{0.5}$ "thick" n = 1 Bragg diffraction peak.

6. Molecular dimensions of TANI and BEHP

The interpretation of the lamellar structure for oligo(aniline) thin films was based on the bulk unit cell assignment[1] and the dimensions of the dimension of the constituent molecules which were calculated using the 3D viewer function in ACD/Labs ACD/ChemSketch software.

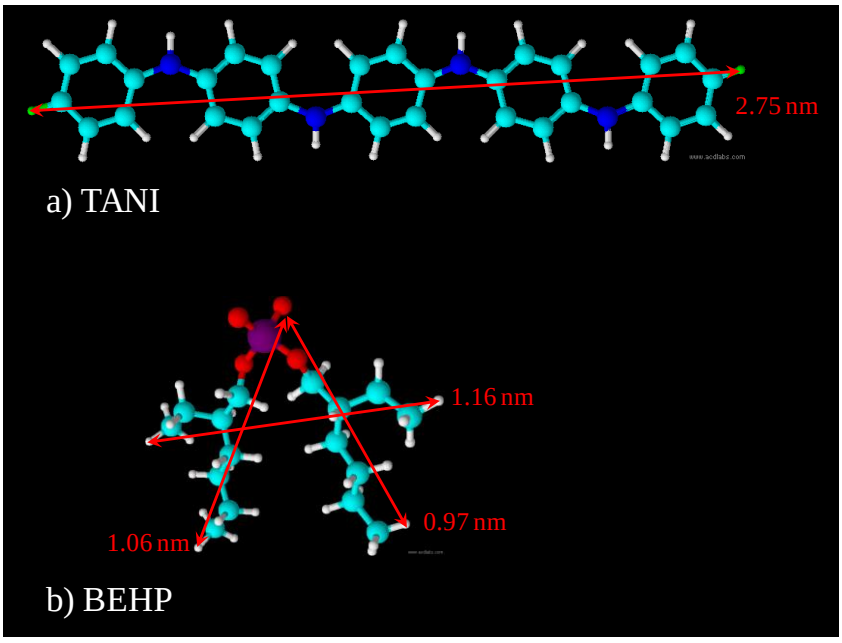

Fig. S3 Molecular dimensions of a) TANI and b) BEHP

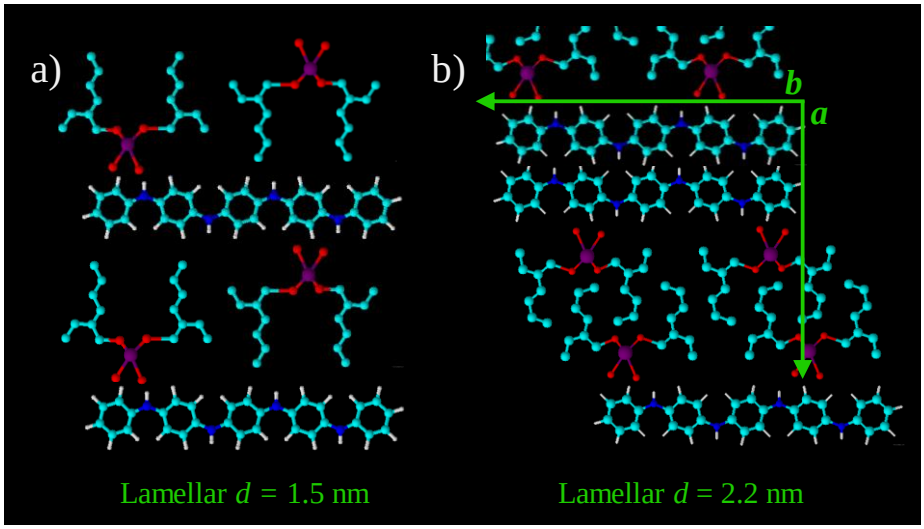

Fig. S4 Graphical representation of two possible lamellar structures for the TANI(BEHP)$_{0.5}$ complex with resulting *d*-spacing values; a) 'monolayer' structure; b) 'bilayer' structure which is assumed to be the most probable. Associated lattice vectors are labelled; the ***c*** lattice vector is perpendicular to the ***a***-***b*** plane and is assumed to have a *d*-spacing of 0.36 nm arising from the π–π stacking of the TANI molecules.

Reference:

1. Z. X. Wei, T. Laitinen, B. Smarsly, O. Ikkala and C. F. J. Faul, *Angew. Chem. Int. Ed.*, 2005, **44**, 751-756.