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Supporting Information

Two-dimensional charge transport in molecularly ordered polymer field-effect transistors

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Table S1

Sample	As LS deposited		Melt-annealed	
	μ_{sat} (cm^2/Vs)	V_{Th} (V)	μ_{sat} (cm^2/Vs)	V_{Th} (V)
1 layer	0.02	21.8	0.01	65.6
2 layers	0.02	16.2	0.04	70.7
3 layers	0.02	16.2	0.07	69.7

Figure S1

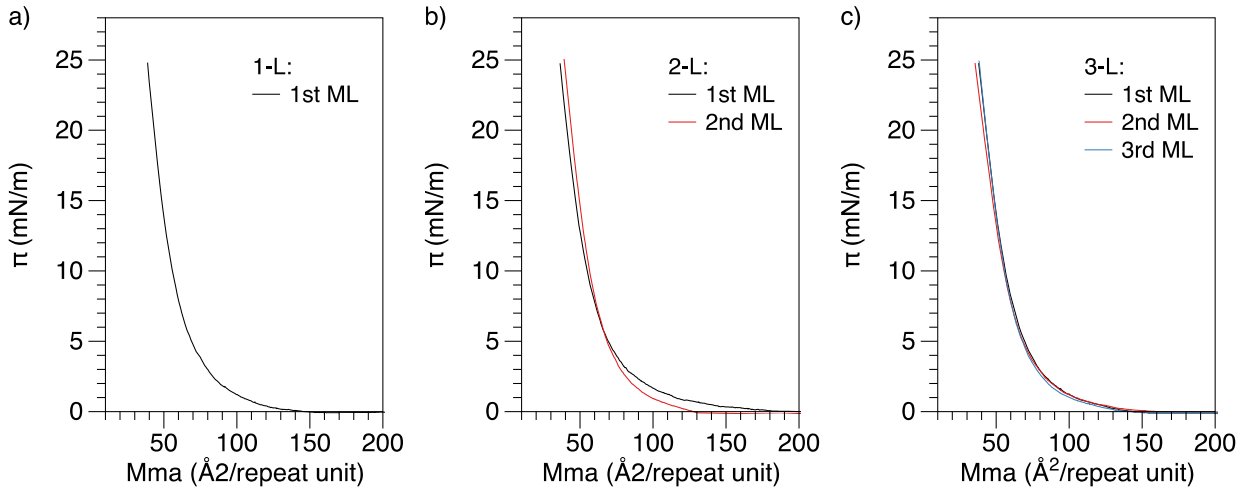
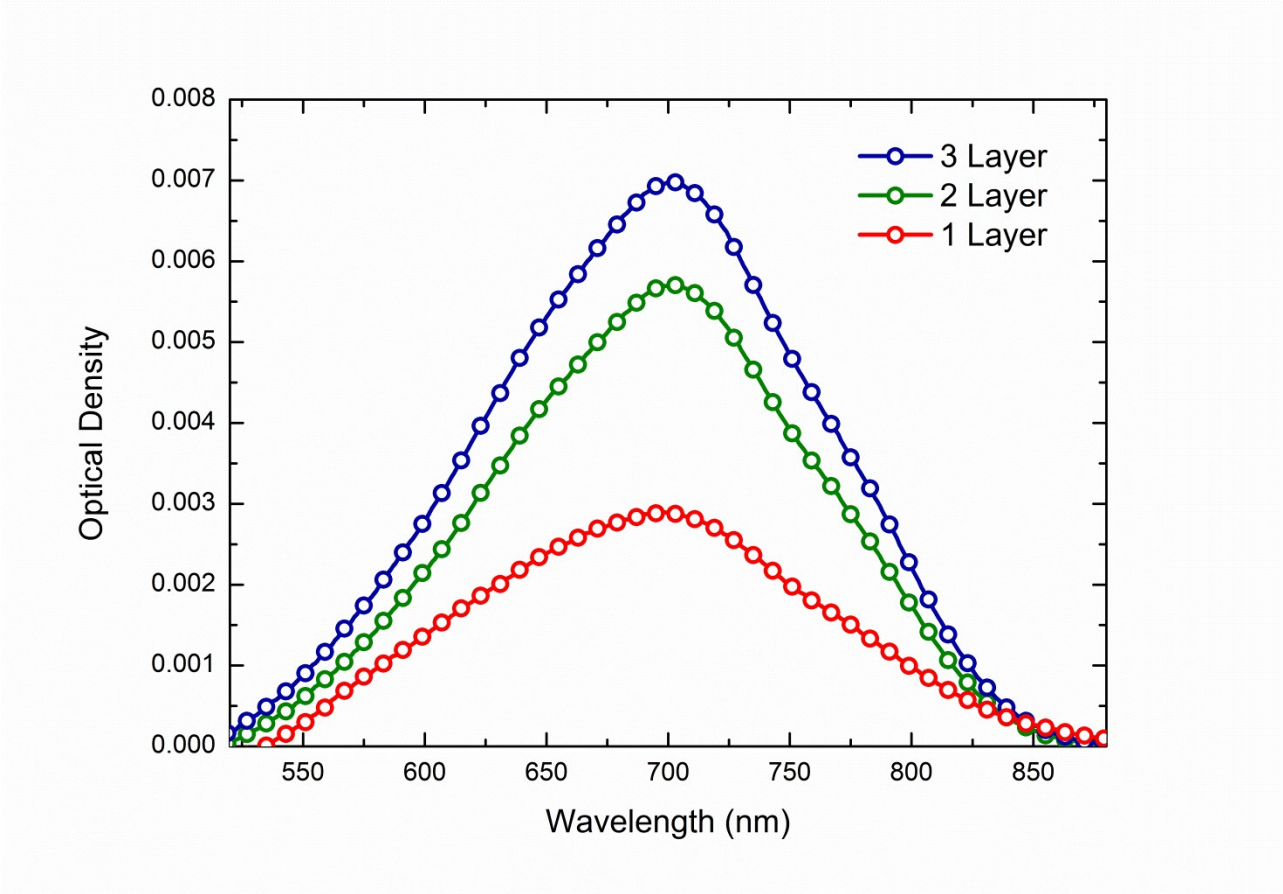


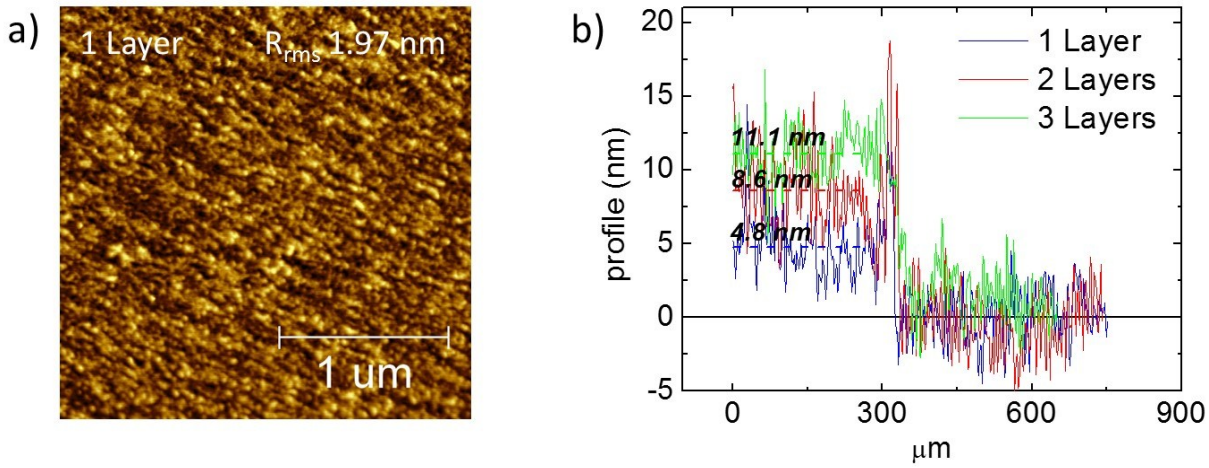
Figure S1 shows the surface pressure (π) as a function of the mean monomeric area (Mma) for P(NDI2OD-T2) 1-L (a), 2-L (b) and 3-L (c). The isotherms show a transition from an expanded state to a condensed state with abrupt slopes. In the condensed phase, the strong π–π interactions between the aromatic backbones and the van der Waals interactions between the branched alkyl side chains promote self-assembly in ordered close-packed films at the air/water interface upon compression. The limit molecular area is of about 63 $Å^2$, in agreement with a previous report [1]. This value is consistent with the area per repeat unit (~55 $Å^2$) calculated for a Langmuir close-packed monolayer having out-of-plane molecular order, by considering a π–π distance of about 3.9 Å and a chain backbone repeat distance of 13.9 Å.[2]

Figure S2



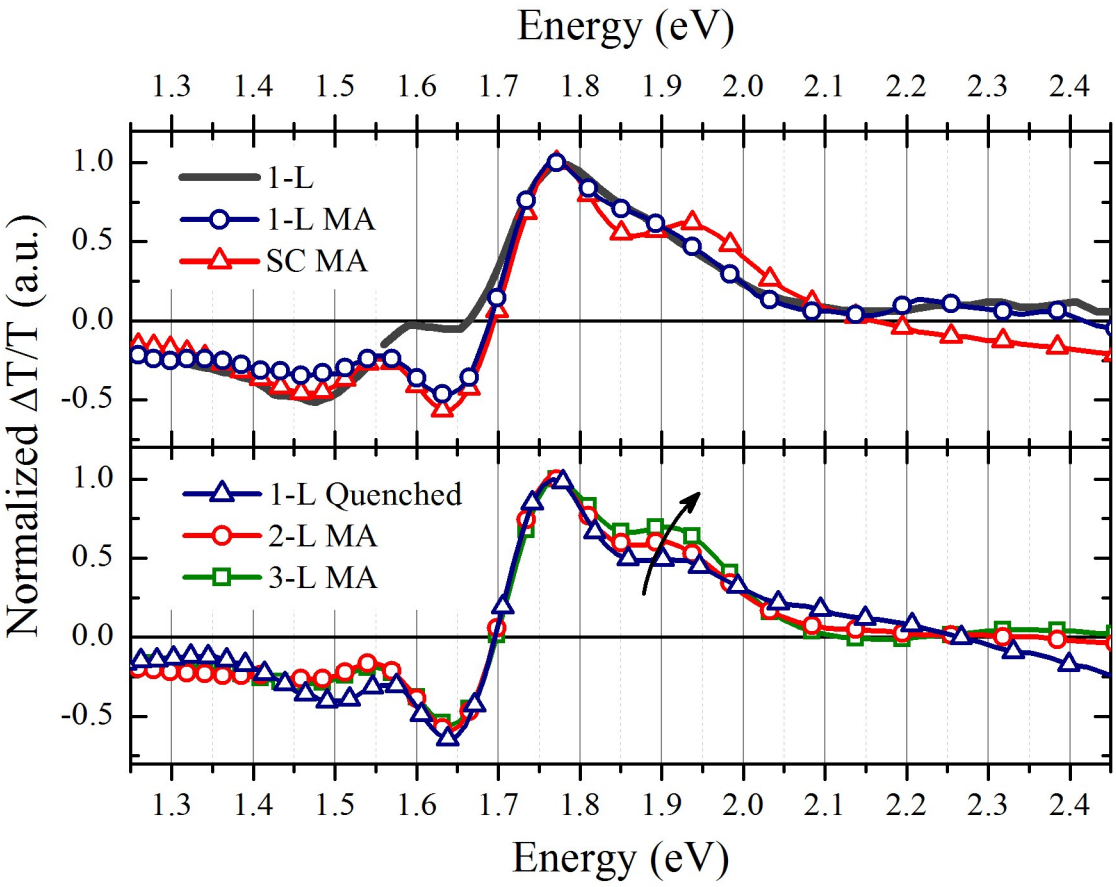
Optical Density measurements of the P(NDI2OD-T2) one (1-L), two (2-L) and three (3-L) layers samples. The measurements were performed on a contacts free area of the samples which included the FET devices measured and reported in the manuscript, where the CYTOP dielectric layer, and the semi-transparent top gate electrode had been peeled-off.

Figure S3



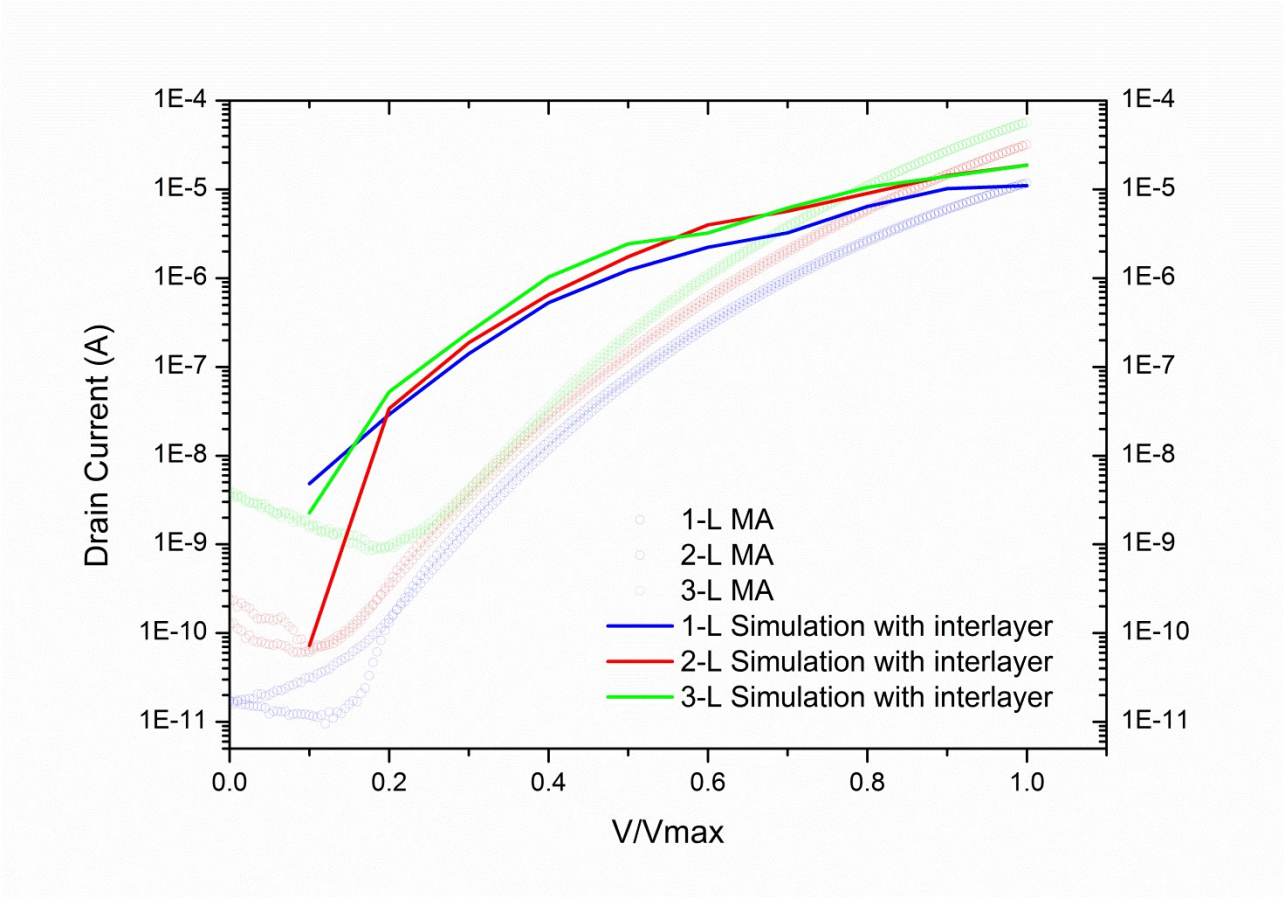
a) Atomic force microscopy image of a LS deposited single layer after dielectric delamination; a film corrugation can be observed after dielectric delamination, leading to a root mean square roughness (Rrms) of about 2 nm. b) profile analysis (with Digital Holographic Microscopy LynceeTec) of LS deposited 1 layer, 2 layer and 3 layers after dielectric delamination. An average thickness of 4.8 nm is measured on the 1 Layer sample, in agreement with the thickness of a corrugated monomolecular layer of P(NDIT2-OD) (edge on monomolecular spacing ~3 nm plus corrugation); 2 Layers and 3 Layers samples display average thicknesses of 8.6 nm and 11.1 nm, respectively, corresponding to the addition of 1 and 2 monomolecular distances (edge on) with respect to the 1 layer sample.

Figure S4



Top: CMS spectrum of 1-L (grey solid line) sample, compared to a spectrum of the same device after MA process and to a spectrum of a SC film. Bottom: comparison of CMS spectra of MA samples, where the 1-L sample, differently from the other two samples and from what reported in the text, is immediately quenched after thermal treatment.

Figure S5



To mimic the loss of the LS structure and the resulting possibility of hops between molecules within an individual monolayer, we changed the rectangular unit cell of size (1x1x3) to contain two smaller rectangular unit cells of size (1x1x1.5), i.e. what used to be one monolayer now consists of two thinner (in z-direction) monolayers. Figure S2 accordingly reports the simulated transfer characteristic curves of 1-L (blue line), 2-L (red line), 3-L (green line) based OFETs where each monolayer includes an interlayer in the center. Experimental data for MA samples (circles) are reported for comparison.

References

[1] S, Fabiano, C. Musumeci, Z, Chen, A. Scandurra, H, Wang, Y.-L. Loo, A. Facchetti, B. Pignataro, *Adv. Mater.* **2012**, 24, 951.

[2] J. Rivnay, M. F. Toney, Y. Zheng, I. V. Kauvar, Z. Chen, V. Wagner, A. Facchetti, A. Salleo, *Adv. Mater.* **2010**, *22*, 4359.