

# Orthogonal Self Assembly and Selective Solvent Vapor Annealing: Simplified Processing of a Photovoltaic Blend

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ELECTRONIC SUPPORTING INFORMATION

## Experimental Details.

*Chemicals.* Chloroform and methanol (spectrophotometric grade) were purchased from Aldrich Chemical co. and used as received. Dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (DTBDT-C<sub>6</sub>) and N,N'-Di-[13-(2,5,8,11,15,18,21,24-octaoxapentacosanyl)]perylene-3,4:9,10-tetracarboxy diimide (PEG-PDI) have been synthesized according to previously reported literature protocols.<sup>1</sup>

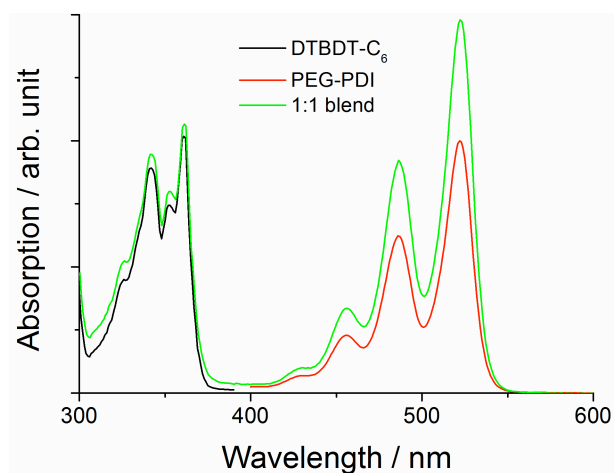
All the other chemicals and solvents were used without any purification.

*Methods.* PEG-PDI and DTBDT-C<sub>6</sub> stock solutions (200 μM) were prepared dissolving the solids in CHCl<sub>3</sub>. Solutions containing either the neat components or their 1:1 mixture were spin coated (1500 rpm, 60 s) on silicon substrates covered by a few nm thick native oxide layer (SiO<sub>x</sub>). The substrates were cleaned prior to use with standard RCA procedure. The solvent vapor annealing (SVA) procedure was carried out in methanol (30 min, room temperature) as described elsewhere.<sup>2</sup>

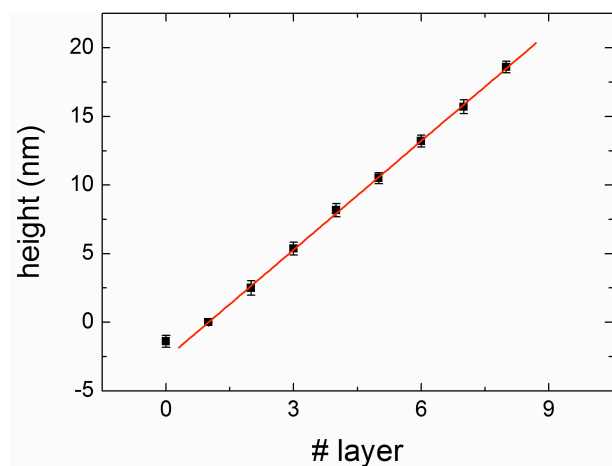
*Techniques.* UV-vis absorption spectra were recorded on a Jasco spectrophotometer (mod. V-560) using quartz cuvettes. Atomic force microscopy (AFM) and Kelvin Probe Force Microscopy (KPFM) images were recorded using a Multimode IIIA (Veeco) scanning probe microscope with Extender Electronics module. Imaging was done in tapping mode using a conductive SCM-PIT probe (Veeco, Pt/Ir coated Si with frequency  $f_0 = 75$  KHz and nominal tip radius  $\leq 20$  nm). All images were collected under ambient conditions at 10% relative humidity and RT with a scanning raster rate of 1 Hz. KPFM measurements were acquired in lift mode (lift height = 30 nm, V<sub>AC</sub>=500 mV).

## References

- 1 a) P. Gao, D. Beckmann, H. N. Tsao, X. Feng, V. Enkelmann, M. Baumgarten, W. Pisula and K. Müllen, *Adv. Mater.*, 2009, **21**, 213. b) M. R. Hansen, T. Schnitzler, W. Pisula, R. Graf, K. Müllen and H. W. Spiess, *Angew. Chem. Int. Ed.*, 2009, **48**, 4621.
- 2 G. De Luca, A. Liscio, P. Maccagnani, F. Nolde, V. Palermo, K. Müllen and P. Samorì, *Adv. Funct. Mater.*, 2007, **17**, 3791.



**Fig. S1.** UV-vis absorption spectra of the electron donor (black), acceptor (red), and their blend (green) dissolved in CHCl<sub>3</sub>. Concentrations:  $\sim 10^{-5}$  M; optical path length: 0.5 cm.



**Fig. S2.** Height of PEG-PDI layers after SVA in methanol vs. layer number, as determined through histogram analysis of AFM topographical images. First layer:  $(1.8 \pm 0.2)$  nm; overlayers  $(2.9 \pm 0.2)$  nm).