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Supporting Information

Latent Pigment Strategy for Robust Active Layers in Solution-Processed, Complementary Organic Field-Effect Transistors

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Figure S1. TGA (black trace) and DSC (red trace) of a T3DPP-t-Boc sample.



Figure S2. TGA (black trace) and DSC (red trace) of a PDI-t-Boc sample.



Figure S3: Thermal gradient specular scan of a T3DPP-t-Boc drop-cast film from CHCl₃ in

Air



Figure S4: UV-Vis characterization of T3DPP-t-Boc thin films at different times of annealing at 200 °C. After 2 min the complete cleavage of the t-Boc group is achieved.



Figure S5: Fourier Transform Infrared transmission measurements of T3DPP-t-Boc thin films at different times of annealing at 200 °C. a) Region between 2000 and 1200 cm⁻¹ and b) region between 3300 and 2800 cm⁻¹



Figure S6: X-Ray Reflection measurement of a spin coated T3DPP-t-Boc film



Figure S7: X-Ray Reflection measurement after thermal cleavage of the t-Boc group of a spin coated T3DPP-t-Boc film

There is a significant decrease in film thickness upon thermal deprotection, from 40 to 29 nm, and an increase in surface roughness from 1.3 to 3 nm. The film thickness after thermal cleavage (72 % of its initial value) can be almost directly related to the loss of mass within the film as the tert-butyloxycarbonyl groups are removed:

 $\frac{797.17 \text{ g/mol}}{997.4 \text{g/mol}} x \frac{100}{1} = 79\% \text{ of mass remaining after deprotection}$ $\frac{29nm}{40nm} x \frac{100}{1} = 72\% \text{ of film thickness}$

 Table S1. Summary of the T3DPP-t-Boc film characteristics before and after the thermal

 cleavage of the t-Boc group extracted from the X-Ray Reflection measurements.

Characteristics	T3DPP-t-Boc	T3DPP-t-Boc annealed
SiO ₂ critical angle	0.225	0.2252
organic layer critical angle	0.17	0.18
Organic electron density (electrons per nm ³)	435	488
Roughness (nm)	1.3	3
Thickness (nm)	40	29
d-spacing (of Bragg peak) (nm)	1.14 (typical of edge on alignment)	No Bragg peak seen
Vertical crystal size (nm)	13	N/A



Figure S8: Electrical characterization of T3DPP-t-Boc FETs non deprotected. Transfer curves for hole (a) and electron (b) conduction of a T3DPP-t-Boc device. Output curves for hole (c) and electron (d) conduction. All the devices had $W = 10000 \ \mu m$ and $L = 20 \ \mu m$.



Figure S9: Electrical characterization of T3DPP FETs deprotected in air . Transfer curves for hole (a) and electron (b) conduction of a T3DPP device. Output curves for hole (c) and electron (d) conduction. All the devices had $W = 10000 \ \mu m$ and $L = 20 \ \mu m$.



Figure S10: Electrical characterization of T3DPP FETs deprotected under nitrogen atmosphere. Transfer curves for hole (a) and electron (b) conduction of a T3DPP device. Output curves for hole (c) and electron (d) conduction. All the devices had $W = 10000 \ \mu m$ and $L = 20 \ \mu m$.





Figure S11: T3DPP-t-Boc molecule synthesis scheme

1. In a Nitrogen Glove box, charge 3g (9.1mmol) 5-bromo-5'hexyl-2,2'bithiophene, 2.615g (23.96mmol) thiophene-2-carbonitrile, 2.483 (17.97mmol) K_2CO_3 , 53.79mg(0.24mmol) Palladium acetate, 195mg (0.529mmol) tricyclohexylphosphine tetrafluoroborate, 367mg(3.6mmol) Pivalic acid and 40ml dry toluene into a 100ml pressure tube with magnetic stirrer. Seal cap tightly. The solution has a light yellow colour. Heat to 150 °C for 24 hours. Allow to cool to room temperature before pouring solution into 100ml water. Dilute with 100ml toluene and separate. Wash organic phase with 2x100ml water and 100 ml brine. Dry organic phase on MgSO₄. Remove solvent with rotary Evaporator. A dark brown/yellow oil is

recovered. Purify with column chromatography 3:7 toluene: cyclohexane gradient to 1:1 toluene: cyclohexane. Recover a yellow solid. The final yield of this step is 40%. Characterization data are in agreement with those previously reported. ^[1]

2. In a 50ml tri-neck round bottom flask with Dean stark and dropping funnel dissolve 0.52g(4.7mmol) sodium-t-amylate in 5ml tert-amyl-alcohol under nitrogen atmosphere. In a separate flask under nitrogen dissolve 1.3g(3.6mmol) 5"hexyl-[2,2':5',2"-terthiophene]-5-carbonitrilein 5ml dry THF before transferring to the 50ml RBF. Heat this solution to 120°C to distill off the THF with magnetic stirring. Into the dropping funnel add dropwise over 90minutes a solution of tert-butyl-succinate 0.364g(1.58mmol) dissolved in 12ml THF. The solution should darken immediately upon addition. Stir for 3 hours at 120°C. Cool to 50°C add 1.5ml isopropyl alcohol and stir for a further 10minutes before adding 2ml distilled water. Take up solution in 10ml isopropyl alcohol and filter through fluted filter paper. Was extensively with 50:50 boiling iPrOH:H₂O. Stir the crude powder in boiling THF and Hot filter. Dry in Vacuum oven to afford 750mg of very dark powder. The final yield of this step is 52%. The product was not further purified and used directly in the next step. NMR was not taken due to lack of solubility.

3. In a 50ml round bottom flask with magnetic stirrer charge 0.75g (0.95mmol) of 3,6-bis(5"hexyl-[2,2':5',2"terthiophene]-5-yl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione and 0.29g(2.37mmol) of Dimethylaminopyridine under Nitrogen atmosphere. Dissolve in 10ml Dry THF. In a separate flask under Nitrogen dissolve 1.5g(6.8mmol) in 5ml Dry THF and transfer to the main reaction flask at room temperature. Stir vigorously for 18hrs.solution darkens with green particles dispersed. Filter and wash with 20ml THF followed by 20ml cold diethyl ether and 50ml 1:1 diethyl ether: Petroleum ether to afford dark green powder. The final yield of this step is about the 90%. 1H NMR (CDCl3) δ : 8.28 (2H, d, J=4.20 Hz), 7.20 (4H, dd, J=4.20, 3.86 Hz), 7.03 (4H, dd, J=3.75, 3.45 Hz), 6.70 (2H, d, J=3.55 Hz), 2.80 (4H, t, J=7.61 Hz), 1.68 (4H, quint, J=7.45 Hz), 1.42-1.28 (12 H, m), 0.9 (6H, t, J=7.01 Hz). 13C NMR (CDCl3) d: 159.97, 149.88, 147.42, 144.88, 140.16, 137.33, 136.34, 134.87, 134.84, 128.66, 127.17, 125.93, 125.09, 124.97, 124.77, 111.10, 86.88, 32.43, 32.41, 31.10, 29.62, 28.64, 23.44, 14.96. Anal Calcd for C₅₂H₅₆N₂O₆S₆: C, 62.62; H, 5.66; N, 2.81. Found: C, 62.65; H, 5.59; N, 2.78.

[1] H. Wada, T. Taguchi, M. Goto, T. Kambayashi, T. Mori, K. Ishikawa, H. Takezoe, Chem. Lett. 2006, 35, 280.