Simple Transfer from Spin Coating to Blade Coating Through Processing Aggregated Solutions

Jeff L. Hernandez[‡], Nabankur Deb[‡], Rylan M.W. Wolfe[‡], Chi Kin Lo[‡], Sebastian Engmann[†], Lee J. Richter [†], and John R. Reynolds ^{*,‡}

‡ School of Chemistry and Biochemistry, School of Materials Science and Engineering, Center for Organic Photonics and Electronics, Georgia Tech Polymer Network, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

† Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

Supporting Information

Experimental

All starting materials were purchased from commercial suppliers and used without further purification. THF, DCM, Diethyl Ether, and Toluene were obtained from a Solvent Purification System (alumina columns) and contained less than 10 ppm of water by Karl Fischer titrations. All reactions were run under inert conditions (argon blanket) using standard Schlenk techniques. NMR spectra were recorded on a Varian Mercury Vx (300 MHz) spectrometer, and chemical shifts were referenced to the residual solvent signals (7.26 ppm/77.16 ppm for CDCl₃, 6.0 ppm for $C_2D_2Cl_4$). Elemental analysis was performed by Atlantic Microlab, Inc. (Norcross, GA). Molecular weights of the polymers were determined by gel permeation chromatography (GPC) analysis relative to a polystyrene standard with chloroform as an eluent using a Agilent 1100 system. Absorbance spectra were measured using a Varian Cary 5000 Scan UV-vis-NIR spectrophotometer. Electrochemistry experiments were performed using an EG&G Princeton Applied Research model 273A potentiostat-galvanostat. CV (scan rate 50 mV/s) and DPV differential pulse voltammetry (step size 2 mV, step time 50 ms, pulse amplitude 100 mV) of the polymers were measured using 0.02 cm² Pt disc electrodes in 0.5M TBAPF₆/acetonitrile, using a Ag/Ag⁺ reference electrode (0.01 M AgNO₃) and Pt flag counter electrode.

2-hexyldecan-1-amine¹, thiophene-3,4-dicarboxylic anhydride², 5-(2-hexyldecyl)thieno[3,4c]pyrrole-4,6-dione³,1,3-dibromo-5-(2-hexyldecyl)thieno[3,4-c]pyrrole-4,6-dione³, 3dodecylthiophene⁴, 2-bromo-3-dodecylthiophene⁵, 2-(trimethylstannyl)-3-dodecylthiophene⁴, and 2,5-bis(trimethylstannyl)thiophene⁶ were synthesized according to literature procedures.



Synthesis of 1,3-bis[3-(n-dodecyl)thien-2-yl]-5-(2-hexyldecyl)thieno[3,4-c]pyrrole-4,6-dione

The synthesis of the title compound follows a modified literature procedure.³ A flame-dried Schlenk flask was charged with 1,3-dibromo-5-(2-hexyldecyl)thieno[3,4-c]pyrrole-4,6-dione(6.53 mmol) and 2-(trimethylstannyl)-3-dodecylthiophene(20.9 mmol, 3.0 eq), Pd₂dba₃(0.17 mmol, 5mol% Pd), and tri(o-tolyl)phosphine (0.66 mmol, 10mol%). After holding under vacuum for one hour, followed by three evacuation-backfill cycles, toluene (70mL) was added. The reaction was stirred at 95 °C for 14 hours. The solvent was removed by rotary evaporation, and the crude orange material was passed through a silica pad (100% hexanes) to remove oligomers. The resulting yellow oil was purified by column chromatography (silica gel, 40-63 µm) with CH₂Cl₂/hexanes (15:85) as the eluent to obtain the title compound as a yellow oil which solidifies upon standing (1.5g, 26%).

¹H NMR (300 MHz, CDCl₃): δ 7.40 (d, J = 5.2 Hz, 2H), 7.01 (d, J = 5.2 Hz, 2H), 3.50 (d, J = 7.3 Hz, 2H), 2.83 – 2.74 (m, 4H), 1.92 – 1.77 (m, 1H), 1.71 – 1.56 (m, 4H), 1.42 – 1.16 (m, 60H), 0.95 – 0.79 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 162.72, 144.43, 137.11, 130.65, 129.95, 127.70, 125.07, 37.11, 32.08, 32.06, 31.99, 31.72, 30.69, 30.17, 29.85, 29.84, 29.81, 29.77, 29.71, 29.63, 29.52, 29.47, 26.51, 22.85, 22.84, 22.81, 14.28, 14.27. Note: some peaks in the 13C are overlapping and cannot be resolved.



Synthesis of 1,3-bis[5-bromo-3-(*n*-dodecyl)thien-2-yl]-5-(2-hexyldecyl)thieno[3,4-*c*]pyrrole-4,6-dione

The synthesis of the title compound follows a modified literature procedure.³ 1,3-bis[3-(n-dodecyl)thien-2-yl]-5-(2-hexyldecyl)thieno[3,4-c]pyrrole-4,6-dione (0.5 mmol) was added to a flame-dried 250 ml round bottom flask containing 25 ml of chloroform and 5 ml of concentrated acetic acid. Bromine (1 mmol, 2.0 eq) was added into the mixture dropwise over 30 minutes. The

reaction was stirred at room temperature for 2 hours. 20 ml of water was added. The mixture was extracted with dichloromethane and washed with 20 ml of water, 20 ml of 10% potassium hydroxide, 20 ml of brine, and dried over magnesium sulfate. After solvent was removed by evaporation, the crude material was purified by column chromatography with hexane:dichloromethane (2:1) as the eluent. The pure product was obtained as a yellow solid (425 mg, 82%).

¹H NMR (300 MHz, CDCl₃): δ 6.97 (s, 2H), 3.51 (d, J = 7.2 Hz, 2H), 2.75 (t, J = 7.6 Hz, 4H), 1.95 - 1.80 (m, 1H), 1.79 - 1.48 (m, 4H), 1.40 - 1.17 (m, 60H), 0.95 - 0.83 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): 162.26, 144.84, 135.34, 132.52, 130.64, 126.37, 115.43, 42.81, 36.98, 34.65, 34.53, 31.95, 31.92, 31.85, 31.61, 31.59, 31.58, 31.57, 30.33, 30.02, 29.81, 29.72, 29.70, 29.69, 29.6, 29.50, 29.44, 29.39, 29.33, 26.3, 25.26, 22.67, 20.64, 14.08. Note: some peaks in the 13C are overlapping and cannot be resolved.



Synthesis of poly[(5-[2-hexyldecyl]thieno[3,4-c]pyrrole-4,6-dione)-1,3-diyl-*alt*-(3,3"-didodecyl-2,2":5",2"-terthiophene)-5,5"-diyl] (PT3TPD)

P(T3TPD) was synthesized according to according to the literature procedure with slight modifications.⁷ Both monomers were held under high vacuum overnight to remove any residual solvents. A flame dried 25mL Schlenk flask was cooled under vacuum and charged with monomers (0.50 mmol each), Pd₂dba₃ (0.0075 mmol, 3mol% Pd), and tri(o-tolyl)phosphine (0.06 mmol, 12mol%) (a 1:4 Pd:Ligand loading). The flask was subjected to three evacuationbackfill cycles using argon as the inert gas. Toluene (10mL), which was subjected to three freeze-pump-thaw cycles, was added to the flask. The reaction was heated to 110 °C, sealed, and allowed to react for 72 h. At 48 h, 1.5 mL of anhydrous, degassed toluene was added to replace lost volume and keep the polymer in solution. After 72 h, 2-(tributylstannyl)thiophene (0.25 mL) was added, and the reaction was stirred at 110 °C for 12h. Then, 2-bromothiophene (0.5mL) was added, and the reaction was stirred an additional 12 h. The reaction was allowed to cool to approx. 50 °C before being precipitated dropwise into 200 mL of methanol containing 5mL 12N HCl. The transfer was aided using hot chloroform. After stirring for 1 h, the precipitate was filtered directly into a cellulose thimble and subjected to Soxhlet extraction by methanol, acetone, hexanes, dichloromethane, and finally, chloroform. All solvents were run at least until the cycling solvent was colorless. The chloroform extraction, which removed all remaining polymer from the thimble, was concentrated and precipitated into 600 mL of methanol. The

precipitated polymer was collected on a 0.45 μ m nylon filter as a purple-blue solid (450 mg, 94%).

¹H NMR (300 MHz, $C_2D_2Cl_4$, 80 °C, ppm): δ 7.25 (s, 2H), 7.18 (s, 2H), 3.59 (br, 2H), 2.96 – 2.74 (m, 4H), 1.96 (br, 1H), 1.86 – 1.64 (m, 4H), 1.50 – 1.25 (m, 60H), 1.02 – 0.85 (m, 12H). GPC (CHCl₃ vs polystyrene standards, RI): M_N =19.7 kDa, M_W =42.3 kDa, D=2.1. Anal. Calcd for $C_{58}H_{87}NO_2S_4$ (%): C, 72.67; H, 9.15; N, 1.46; S, 13.38. Found (%): C, 72.59; H, 9.16; N, 1.55; S, 13.49.





Figure S1. a) Solution/Film spectra of neat P(T3-TPD) in chloroform, b) P(T3-TDP):PC₇₁BM in CF [~0.12 mg/mL], c) P(T3-TPD):PC₇₁BM in CF:DIO [~0.1 mg/mL], d) solution UV vis absorbance of three heating and cooling cycles of P(T3-TPD) [~0.1 mg/mL] in CF at 50 °C and 20 °C. Overlapping spectra indicated no hysteresis effect. e) pictures of P(T3-TPD) in CF at varying temperatures.

| | J _{sc} Spin w/o DIO | J_{sc} Blade w/o | J_{sc} Spin DIO | J _{sc} Blade DIO |
|-------------------|------------------------------|--------------------|-------------------|---------------------------|
| | (mA/cm^2) | $DIO (mA/cm^2)$ | (mA/cm^2) | (mA/cm^2) |
| EQE | 2.5 | 2.6 | 12.5 | 12.3 |
| Measured | 2.7 | 2.7 | 11 | 11.5 |
| % difference | 7.7% | 3.4% | 12.8% | 6.7% |
| Table C1 Calaulat | ad I from EOE and | I hence a sum of I | | |

Table S1. Calculated J_{sc} from EQE and measured J_{sc} .







S7

0.0 Qxy ($Å^{-1}$) 0.00



Figure S2. 2D and 1D q_z/q_{xy} GIWAXS images of spin and blade coated samples.

| | Bla | ade | Sp | oin | Blac | de | Sp | oin | | |
|-----------------------|---------------------------------|----------|-------|-----------------------|-------|----------|---|-----------------|------|-------|
| | (100) lamellar d spacing (Å) | | | (010) π-π spacing (Å) | | | Crystal Coherence Length (100) (Å) | | | |
| | q_z | q_{xy} | q_z | q _{xy} | q_z | q_{xy} | q_z | q _{xy} | Spin | Blade |
| P(T3-TPD) | 25.0 | 27.1 | 26.3 | 26.8 | 3.6 | 3.7 | 3.7 | 3.7 | 107 | 82 |
| P(T3-TPD) DIO | 24.5 | 26.3 | 25.0 | 25.5 | 3.6 | 3.6 | 3.6 | 3.7 | 67 | 66 |
| P(T3-TPD) PCBM | 27.6 | 22.8 | 23.9 | 25.9 | 3.7 | 3.6 | 3.6 | 3.6 | 108 | 48 |
| P(T3-TPD) PCBM DIO | 24.5 | 25.7 | 23.7 | 25.6 | 3.6 | 3.6 | 3.6 | 3.6 | 77 | 45 |

Table S2. Blade/spin coated P(T3-TPD) neat polymer, and BHJ, processed with DIO and w/o DIO lamellar stacking distance, π - π stacking distance, and crystal coherence length (CCL) values taken from 1D line cuts.



Figure S3: SCLC of P(T3-TPD):PC₇₁BM processed w/o DIO and DIO. Fit was determined $J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V_{in}^2}{L^3} exp^{[10]} (\frac{0.89\beta}{\sqrt{L}} \sqrt{V})$ using , where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer which is assumed to be 3, μ is the mobility, β is field-

dielectric constant of the polymer which is assumed to be 3, μ is the mobility, β is field-activation factor, L is the active layer thickness, and V is the applied voltage (V_a) – the built in voltage (V_{bi}).



Figure S4. UV-vis spectroscopy of P(T3-TPD): $PC_{71}BM$ films with a rotating polarizer set to 0° (parallel to the coating direction) and 90° (perpendicular to the coating direction) for a) w/o DIO and b) DIO. No anisotropy was observed indicating that blade coating does not induce polymer alignment in this system.



Figure S5. 1D line profiles taken at specific wavelengths indicated on the y-axis from Figure 6 of a) in-situ absorbance/reflectance w/o DIO and b) in-situ absorbance/reflectance DIO. The timing for solvent removal is determined by the evolution of the reflectance spectra. Dashed lines indicate transition from solution to dry film.



Figure S6. Deconvoluted peak parameters from in-situ UV-vis sigma (σ), representing the FWHM, and height (H) representing the peak height as a function of time for a) w/o DIO and b) DIO. c) Example of how peaks were deconvoluted.

What is noticeable about the deconvoluted peaks as a function of time is that they are relatively constant in their σ and height. This alludes to there being very little change in polymer conformation during solidification. In **Figure S6** a) w/o DIO, peaks 1, the aggregate peak, show little change as the film solidifies. The evolution of Peak 2 shows a decrease in the height and σ during solidification due to the growth the Peak 3. Peak 3, the high energy peak, is the only peak that shows an increase in both its σ and height, however, this is likely caused by the fullerene rather than the polymer as it has been observed that fullerene aggregation is in the same wavelength region as peak 3, and the film is 1:2 weight ratio polymer to fullerene. When examining **Figure S6** b) DIO, peaks 1 and 2 again show little change in σ or height. Peak 3 shows a similar trend in both the w/o DIO and DIO case in which the FWHM (σ 3) slightly increases upon film solidification due to fullerene solidification. P(T3-TPD) processed with DIO and w/o DIO show little structural change upon solidification by in situ UV-vis absorbance.

Supplemental References:

- (1) Van Pruissen, G. W. P.; Gholamrezaie, F.; Wienk, M. M.; Janssen, R. A. J. Synthesis and Properties of Small Band Gap Thienoisoindigo Based Conjugated Polymers. *J. Mater. Chem.* **2012**, *22*, 20387.
- (2) Nielsen, C. B.; Bjørnholm, T. New Regiosymmetrical Dioxopyrrolo- and Dihydropyrrolo-Functionalized Polythiophenes. *Org. Lett.* **2004**, *6*, 3381–3384.
- (3) Guo, X.; Ortiz, R. P.; Zheng, Y.; Kim, M.; Zhang, S.; Hu, Y.; Lu, G.; Facchetti, A.; Marks, T. J. Thieno[3,4-C]pyrrole-4,6-Dione-Based Polymer Semiconductors: Toward High-Performance, Air-Stable Organic Thin-Film Transistors. *J. Am. Chem. Soc.* 2011, *133*, 13685–13697.
- (4) Biniek, L.; Chochos, C. L.; Leclerc, N.; Hadziioannou, G.; Kallitsis, J. K.; Bechara, R.; Lévêque, P.; Heiser, T. A [3,2-B]thienothiophene-Alt-Benzothiadiazole Copolymer for Photovoltaic Applications: Design, Synthesis, Material Characterization and Device Performances. J. Mater. Chem. 2009, 19, 4946.
- (5) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Deliomeroglu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. Design, Synthesis, and Characterization of Ladder-Type Molecules and Polymers. Air-Stable, Solution-Processable N-Channel and Ambipolar Semiconductors for Thin-Film Transistors via Experiment and Theory. J. Am. Chem. Soc.

2009, 131, 5586-5608.

- (6) Linshoeft, J.; Heinrich, A. C. J.; Segler, S. A. W.; Gates, P. J.; Staubitz, A. Chemoselective Cross-Coupling Reactions with Differentiation between Two Nucleophilic Sites on a Single Aromatic Substrate. *Org. Lett.* **2012**, *14*, 5644–5647.
- (7) Guo, X.; Zhou, N.; Lou, S. J.; Smith, J.; Tice, D. B.; Hennek, J. W.; Ortiz, R. P.; Navarrete, J. T. L.; Li, S.; Strzalka, J.; et al. Polymer Solar Cells with Enhanced Fill Factors. *Nat. Photonics* **2013**, *7*, 825–833.