Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Tyrian Purple: An Ancient Natural Dye for Cross-Conjugated N-type Charge Transport

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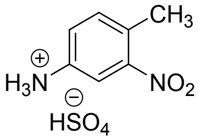
Supporting Information

1. Monomer Synthesis

3-Nitro-4-methylphenylammonium hydrosulfate

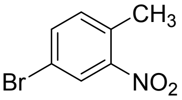


Under normal atmospheric conditions, *p*-toluidine (40.0 g, 0.37 mol) was cautiously dissolved in conc. H_2SO_4 (110 mL) and cooled to –10 °C. A solution of nitric acid (19 mL, 0.43 mol, 70%) in conc. H_2SO_4 (70 mL) was added dropwise insuring the internal temperature did not rise above – 5 °C. After 6 h the reaction was poured onto crushed ice (1 kg) precipitating a yellow solid which was collected by vacuum filtration and washed with cold water. The solid was dried thoroughly to give a pale-yellow solid (76.9 g, 83%).

A sample of solid was converted to 3-nitro-4-methylaniline for analysis.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.5 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.80 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.84 (s, 2H), 2.45 (s, 3H) **LRMS** (CI$^+$) *m/z* 153 [MH]$^+$

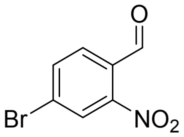
4-Bromo-2-nitromethylbenzene



Under normal atmospheric conditions, 3-nitro-4-methylphenylammonium hydrosulfate (29.5 g, 0.12 mol) was dissolved in water (129 mL) and hydrobromic acid (38.5 mL, 0.34 mol, 48%) and cooled to –5 °C. A cold solution of sodium nitrite (15.2 g, 0.22 mol) in water (40 mL) was added slowly, maintaining the temperature below 0 °C, and the reaction stirred for 30 min. Separately, copper(I) bromide (17.2 g, 0.12 mol) in hydrobromic acid (23.8 mL, 0.21 mol, 48%) was heated to reflux. The cold diazonium salt was added portionwise to the copper solution, liberating gaseous nitrogen dioxide. Following complete addition, the reaction was heated at reflux for 2 h, cooled and extracted with diethyl ether (3 × 100 mL). The combined organic extracts were successively washed with 5% ammonium hydroxide solution (2 × 100 mL), water (100 mL) and brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give a brown oil from which a brown solid separated. Recrystallisation from ethanol yielded 14.8 g (57%) of the title compound as a brown crystalline solid.

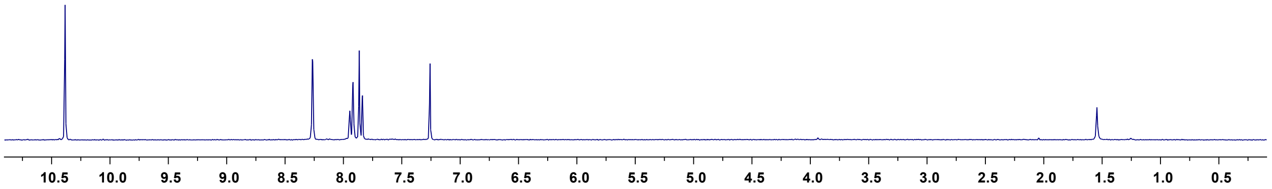
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.0 Hz, 1H), 7.62 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 2.55 (s, 3H) **LRMS** (CI+) *m/z* 217/215 [MH]$^+$

4-Bromo-2-nitrobenzaldehyde

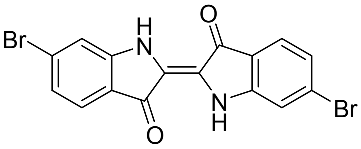


To a solution of 4-bromo-2-nitromethylbenzene (27.5 g, 0.13 mol) in anhydrous DMF (130 mL) under argon was added *N*,*N*-dimethylformamide dimethyl acetal (50.6 mL, 0.38 mol). The reaction was heated at 135 °C for 24 h. Separately, sodium periodate (81.5 g, 0.38 mol) was dissolved in a 2:1 mixture of H_2O:DMF (380 mL). The cooled red enamine intermediate added dropwise to the vigorously stirring periodate solution at RT. If stirring became prevented due to viscosity, H_2O/DMF (2:1) was added until stirring resumed. The reaction was stirred for 3 h at RT and then filtered. The filter cake was washed thoroughly with toluene (300 mL). From the filtrate, the organic layer was separated and washed with water (2 × 200 mL) then brine (2 × 200 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give an oil to which hexane was added to crystallise the aldehyde (19.6 g, 67%). If the reader obtained a solid following concentration, the crude residue is best purified by dry-flash chromatography eluting with 10% ethyl acetate in hexane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 8.27 (d, *J* = 1.8 Hz, 1H), 7.93 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H) **LRMS** (CI+) *m/z* 232/230 $[M]^+$



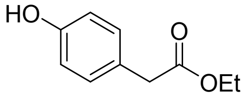
(E)-6,6'-dibromo-[2,2'-biindolinylidene]-3,3'-dione (6,6’-dibromoindigo)



Under normal atmospheric conditions, 4-bromo-2-nitrobenzaldehyde (20 g) was dissolved in acetone (200 mL) and water (200 mL) was added dropwise with vigorous stirring to create a fine suspension. A 1M sodium hydroxide solution (100 mL) was added dropwise, precipitating the purple indigoid. Once addition was complete the reaction was stirred overnight then filtered and washed with acetone. The purple solid was dried thoroughly to give 10.4 g of the title compound (58%).

^{1}H NMR (600 MHz, DMSO) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.55 (s, *J* = 1.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H) **HRMS** Found (EI): $[M]^+$ 417.8957, $C_{16}H_8Br_2N_2O_2$ requires 417.8953

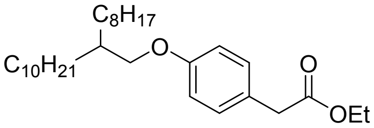
Ethyl 2-(4-hydroxyphenyl)acetate



Under normal atmospheric conditions, a solution of 2-(4-hydroxyphenyl)acetic acid (10 g, 65.7 mmol) in ethanol (120 mL) and conc. H_2SO_4 (1 mL) was heated to reflux for 4 h then cooled and diluted with water (240 mL). The solution was extracted with diethyl ether (3 × 50 mL) and the combined organic extracts were washed with brine (2 × 50 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give the title compound as a light-yellow oil (11.7 g, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6, 2H), 6.74 (d, *J* = 8.6, 2H), 4.15 (q, *J* = 7.1, 2H), 3.54 (s, 2H), 1.25 (t, *J* = 7.1, 3H) **LRMS** (EI+) *m/z* 180 $[M]^+$

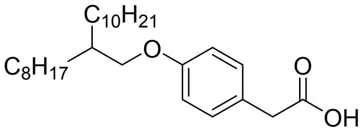
Ethyl 2-(4-((2-octyldodecyl)oxy)phenyl)acetate



To a solution of ethyl 2-(4-hydroxyphenyl)acetate (11.6 g, 64 mmol) and 2-octyldodecyl bromide (29.7 g, 82 mmol) in anhydrous DMF (330 mL) under argon was added potassium carbonate (27.6 g, 0.2 mol). The reaction was heated at 80 °C for 12 h, then neutralised by the addition of 6M hydrochloric acid (20 mL). The suspension was filtered, and the filtrate was extracted with diethyl ether (3 × 100 mL). The combined organic extracts were washed with water (2 × 100 mL) then brine (2 × 100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified by dry-flash chromatography eluting initially with hexane to remove excess 2-octyldodecyl bromide, then with 10% ethyl acetate in hexane to give the title compound as a pale-yellow oil (19.3 g, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.7, 2H), 6.85 (d, *J* = 8.7, 2H), 4.14 (q, *J* = 7.1, 2H), 3.80 (d, *J* = 5.7, 2H), 3.54 (s, 2H), 1.82 – 1.68 (m, 1H), 1.48 – 1.38 (m, 2H), 1.38 – 1.18 (m, 33H), 0.93 – 0.82 (m, 6H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 158.6, 130.2, 125.9, 114.6, 70.9, 60.9, 40.6, 38.0, 32.0, 31.4, 30.1, 29.8, 29.7, 29.4, 26.9, 22.8, 22.7, 14.3, 14.2 **HRMS** Found (CI+): $[M]^+$ 460.3912, $C_{30}H_{52}O_3$ requires 460.3911

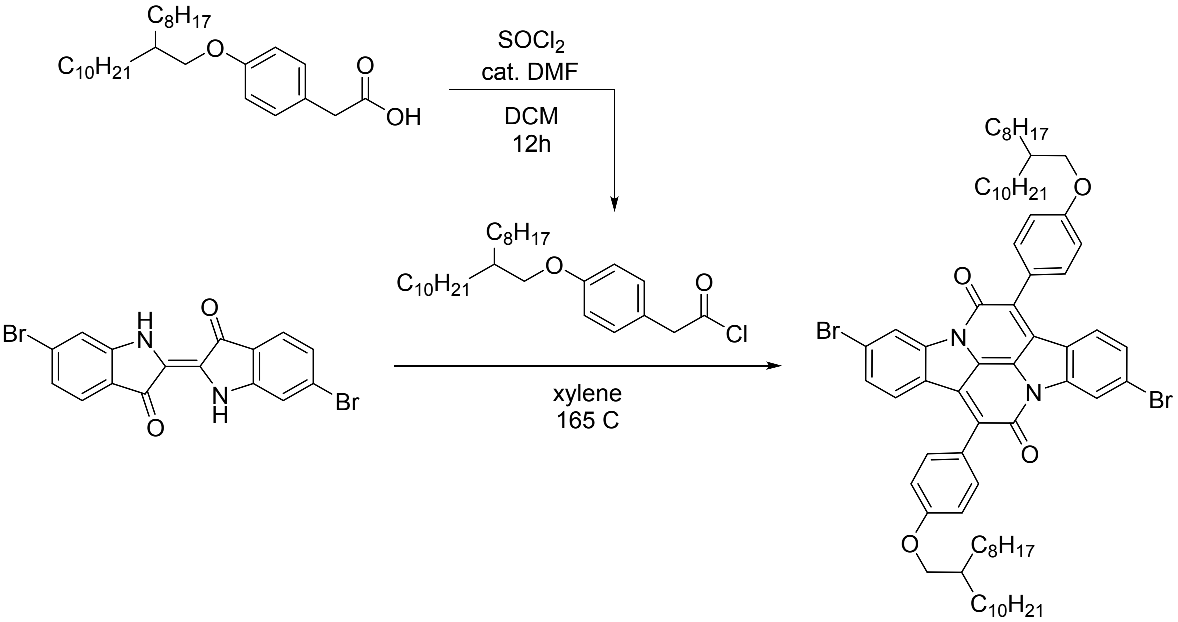
2-(4-((2-Octyldodecyl)oxy)phenyl)acetic acid



Under normal atmospheric conditions, aqueous sodium hydroxide (4M, 80 mL) was added to ethyl 2-(4-((2-octyldodecyl)oxy)phenyl)acetate (19.2 g, 42 mmol) in ethanol (80 mL) at RT. After 4 h the reaction was acidified, and the solution extracted with diethyl ether (3 × 100 mL). The combined organic extracts were washed with brine (2 × 50 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give the title compound as a pale-yellow oil that solidified partially on standing (17.9 g, 99%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 (d, *J* = 8.7, 2H), 6.85 (d, *J* = 8.7, 2H), 3.80 (d, *J* = 5.7, 2H), 3.58 (s, 2H), 1.81 – 1.70 (m, 1H), 1.48 – 1.38 (m, 2H), 1.38 – 1.19 (m, 31H), 0.88 (t, *J* = 6.8, 6H) **^{13}C NMR** (100 MHz, CDCl$_3$) δ 177.3, 158.8, 130.4, 125.0, 114.7, 70.9, 40.1, 38.0, 32.0, 31.4, 30.1, 29.8, 29.7, 29.4, 26.9, 22.8, 22.8, 14.2 **HRMS** Found (EI+): [M]$^+$ 432.3599, $C_{28}H_{48}O_3$ requires 432.3598

3,10-Dibromo-7,14-bis(4-((2-octyldodecyl)oxy)phenyl)diindolo[3,2,1-*de*:3',2',1'-*ij*][1,5]naphthyridine-6,13-dione (3)

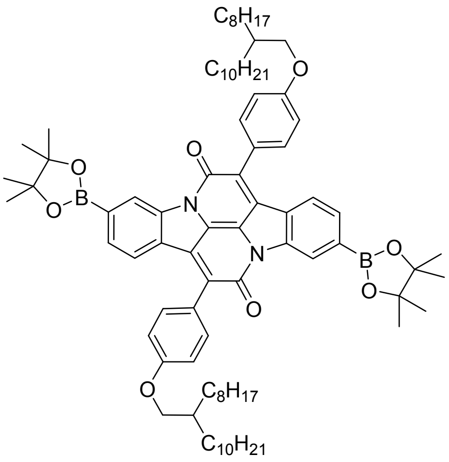


To a solution of 2-(4-((2-octyldodecyl)oxy)phenyl)acetic acid (24 g, 55.5 mmol) in anhydrous DCM (55 mL) was added catalytic anhydrous DMF (0.1 mL) and thionyl chloride (12.2 mL, 0.167 mol). The reaction was heated at reflux for 2 h and total conversion confirmed by NMR. All volatiles were carefully removed *in vacuo* to give the corresponding acyl chloride (**2**) quantitively which was used immediately without further purification.

To a suspension of 6,6'-dibromoindigo (5.8 g, 14 mmol) in xylenes (185 mL) was heated to 165 °C. Acyl chloride **2** (55.5 mmol) was added in one portion and the reaction heated for 24 h. Xylenes were removed *in vacuo* and the resulting crude residue purified by dry-flash chromatography eluting with 40% chloroform in hexanes. Fractions containing the product (R_F = 0.2, pink) were combined and concentrated *in vacuo* to give a residue which was then washed with ethyl acetate and the insoluble red solid collected by vacuum filtration (0.95 g, 6%).

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.72 (d, *J* = 1.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 4H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.37 (dd, *J* = 8.5, 1.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 4H), 3.96 (d, *J* = 5.6 Hz, 4H), 1.90 – 1.78 (m, 2H), 1.50 – 1.21 (m, 64H), 0.89 (td, *J* = 7.0, 5.3 Hz, 12H) **^{13}C NMR** (150 MHz, CDCl$_3$) δ 160.6, 159.6, 145.1, 131.7, 131.0, 130.6, 129.3, 126.3, 126.2, 125.1, 124.5, 122.1, 121.1, 114.7, 71.2, 38.1, 32.1, 31.5, 30.2, 29.8, 29.5, 27.0, 22.8, 14.3 **HRMS** Found (EI): [MH]$^+$ 1211.5818, $C_{72}H_{97}Br_2N_2O_4$ requires 1211.5815

7,14-Bis(4-((2-octyldodecyl)oxy)phenyl)-3,10-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)diindolo[3,2,1-*de*:3',2',1'-*ij*][1,5]naphthyridine-6,13-dione (XINDB, 4)

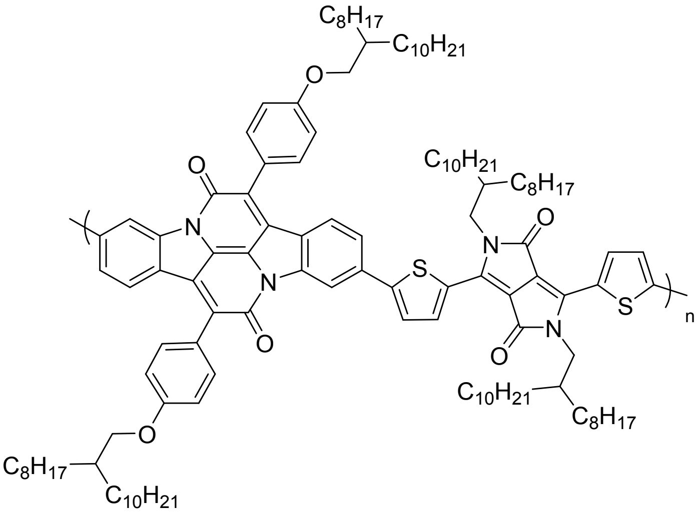


In a dry microwave vial degassed with argon, a solution of indolonaphthyridine **3** (300 mg, 0.25 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (11 mg, 6 mol%), fused potassium acetate (145 mg, 1.5 mmol) and bis(pinacolato)diboron (151 mg, 0.6 mmol) in anhydrous dioxane (10 mL) was heated to 80 °C for 12 h. The reaction was cooled, and methanol (20 mL) added. The resulting precipitate was collected by vacuum filtration to give the pure title compound (282 mg, 87%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.98 (s, 2H), 7.74 – 7.69 (m, 6H), 7.66 – 7.64 (m, 2H), 7.11 – 7.07 (m, 4H), 3.96 (d, *J* = 5.7 Hz, 4H), 1.90 – 1.81 (m, 2H), 1.54 – 1.47 (m, 4H), 1.47 – 1.20 (m, 84H), 0.91 – 0.86 (m, 12H) **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.4, 159.7, 144.1, 132.3, 131.9, 131.3, 131.0, 128.3, 125.7, 124.6, 123.7, 122.2, 114.5, 84.4, 71.2, 51.1, 38.1, 32.1, 31.5, 30.2, 29.8, 29.5, 27.0, 25.0, 22.8, 14.3 **HRMS** Found (EI): $[MH]^+$ 1307.9308, $C_{84}H_{121}B_2N_2O_8$ requires 1307.9309

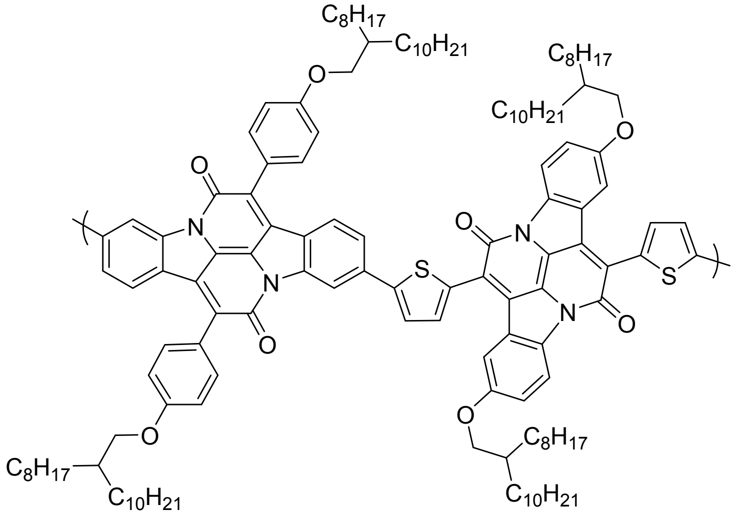
2. Polymer Synthesis

XINDP-DPP (*P1*)



3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (109 mg, 0.11 mmol), tetrakis(triphenylphosphine)palladium(0) (12.4 mg, 10 mol%) and monomer **XINDB** (140 mg, 0.11 mmol) were added to a degassed 10 mL microwave vial equipped with a stirrer bar and sealed. A degassed solution of aliquot 336 (2 drops) in toluene (3 mL) was added via syringe and the solution further degassed with argon for 30 min. A degassed solution of 1M K_2CO_3 (0.6 mL) was then added and the reaction was heated at 125 °C for 3 days. The reaction mixture was cooled and added into rapidly stirring methanol (100 mL) and allowed to stir for 30 min. The polymeric material was filtered under reduced pressure into a cellulose thimble and washed with methanol then acetone. The polymer was purified by soxhlet extraction as follows: acetone for 12 h, hexane for 12 h and chloroform for 12 h. The chloroform was then concentrated and the plastic film dissolved in a minimum volume of hot chlorobenzene and precipitated into methanol. After stirring for 30 min the polymer was collected by vacuum filtration, and air dried for 1 h. Finally, the polymer was dried under vacuum for 12 h (169 mg, 83%).

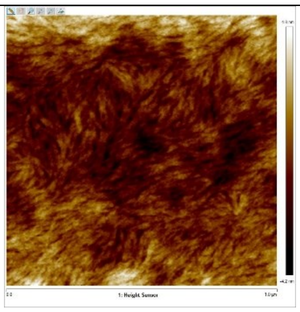
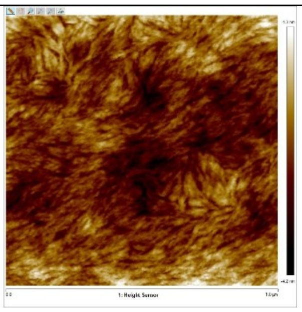
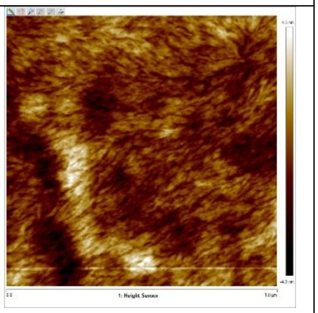
XINDP-INDT (*P2*)



Tetrakis(triphenylphosphine)palladium(0) (6.8 mg, 10 mol%), monomer **XINDB** (76.4 mg, 58.4 µmol) and INDT-Br_2[†] (71.6 mg, 58.4 µmol) were added to a degassed 10 mL microwave vial equipped with a stirrer bar and sealed. A degassed solution of aliquot 336 (2 drops) in toluene (1.7 mL) was added via syringe and the solution further degassed with argon for 30 min. A degassed solution of 1M K_2CO_3 (0.35 mL) was then added and the reaction was heated at 125 °C for 3 days. The reaction mixture was cooled and added into rapidly stirring methanol (100 mL) and allowed to stir for 30 min. The polymeric material was filtered under reduced pressure into a cellulose thimble and washed with methanol then acetone. The polymer was purified by soxhlet extraction as follows: acetone for 12 h, hexane for 12 h and chloroform for 12 h. The chloroform was then concentrated and the plastic film was dissolved in a minimum volume of hot chlorobenzene and precipitated into methanol. After stirring for 30 min the polymer was collected by vacuum filtration, and air dried for 1 h. Finally, the polymer was dried under vacuum for 12 h (107 mg, 86%).

[†] K. J. Fallon, N. Wijeyasinghe, E. F. Manley, S. D. Dimitrov, S. A. Yousaf, R. S. Ashraf, W. Duffy, A. A. Y. Guilbert, D. M. E. Freeman, M. Al-Hashimi, J. Nelson, J. R. Durrant, L. X. Chen, I. McCulloch, T. J. Marks, T. M. Clarke, T. D. Anthopoulos and H. Bronstein, *Chem. Mater.*, 2016, **28**, 8366–8378.

3. AFM

	Picture 1	Picure 2	Picture 3
P1			

	Picture 1	Picure 2	Picture 3
P2