

## Adding irregularity to the N2200 structure using the direct arylation protocol

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### Summary of Key Findings

The direct arylation reaction provides a greener and scalable approach for the synthesis of  $\pi$ -conjugated polymers. It has been successfully employed in the synthesis of new variants based upon *n*-type polymer N2200, where additional irregularity was added to the structure by the use of an asymmetric mono substituted bithiophene monomer. In addition, random co-polymers were synthesised by doping the reaction mixture with small amounts of symmetric disubstituted bithiophenes. The optical and electrochemical properties of these novel materials were largely unaffected by these structural modifications.

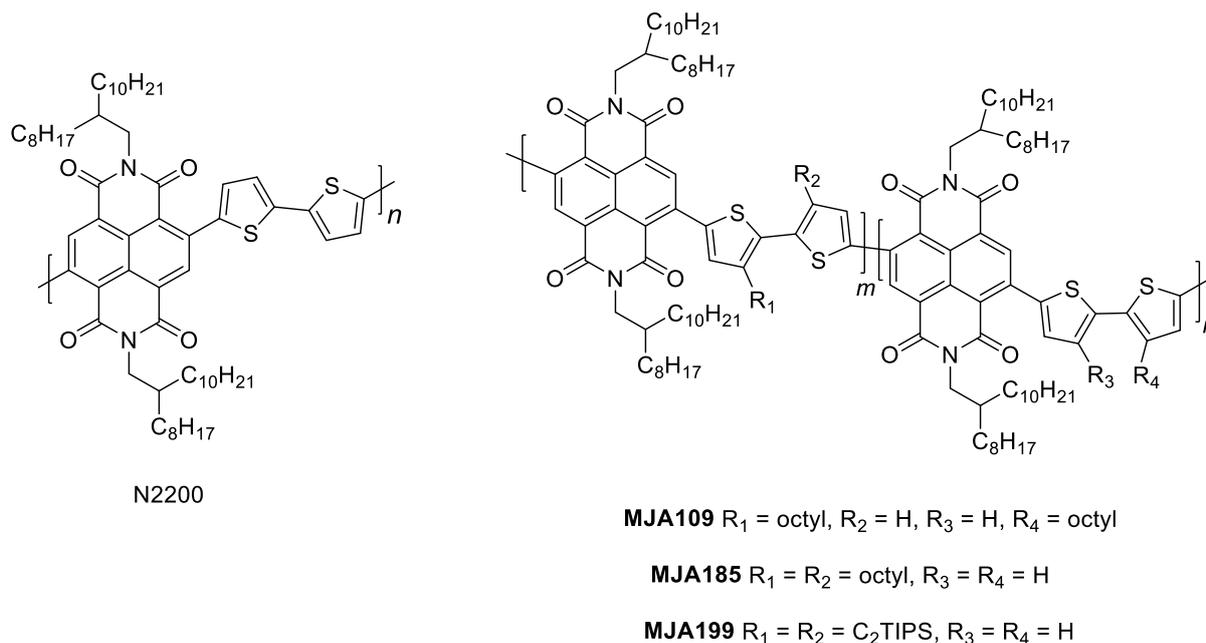
### Introduction

Stemming from an inherent potential for facile fabrication, flexible devices, roll-to-roll processing, and low costs, the area of polymer solar cells (PSCs) has experienced a rapid growth.<sup>1-4</sup> During the last decade power conversion efficiencies (PCEs) have increased from a few percent to current record devices exceeding 16%.<sup>5</sup> This can largely be attributed to an increasingly diverse material portfolio of donor and acceptor compounds. This portfolio includes acceptor materials such as PC<sub>71</sub>BM, ITIC, PTB7-Th, PM6 and N2200, which are some of the more noteworthy examples that have contributed to high PCE devices.<sup>6-9</sup> In the case of all-polymer solar cells, an acceptor polymer is used in conjunction with the donor polymer, instead of a fullerene or small molecule non-fullerene acceptor (NFA), for instance ITIC. This subclass of PSCs has indeed reached record PCEs of 11% for single layer devices.<sup>10</sup> With an active layer solely constituted by polymers, the device properties lead to a comparatively broad absorption, potentially inexpensive large scale production, a robust active layer morphology, as well as a greater long term stability.<sup>11</sup> For all-polymer solar cells the largest material contribution can undoubtedly be attributed to the naphthalenediimide (NDI)-bithiophene (BT) based acceptor polymer N2200, and its wide variety of high performing derivatives.<sup>12-13</sup> The N2200 polymer utilises octyldodecyl (OD) side-groups, anchored on the NDI monomer, for enhanced solution processability, which are bridged with bithiophene along the backbone. N2200 has pushed the efficiency boundaries of all-polymer solar cells with PCEs of over 10% achieved for devices incorporating this acceptor polymer.<sup>14</sup>

Synthesis of  $\pi$ -conjugated polymers are normally conducted via palladium catalysed cross coupling reactions. These include the Stille coupling, the Suzuki coupling, and more recently direct arylation polymerisation (DArP). Stille coupling polymerisations require the use of toxic organotin based monomers, whereas the Suzuki couplings solely require the additional preparation of comparatively less toxic boronic acid/ester reagents.<sup>15</sup> However, DArP, unlike the other two mentioned coupling reactions, has the advantage of not requiring additional functionalities to be introduced to the monomers and is thus the favoured method due its simplicity.<sup>16-17</sup>

Not only are the relative band gap energies between donor (*p*-type) polymers and acceptor (*n*-type) polymers important for the generation of a functional device but the morphology and mixing of

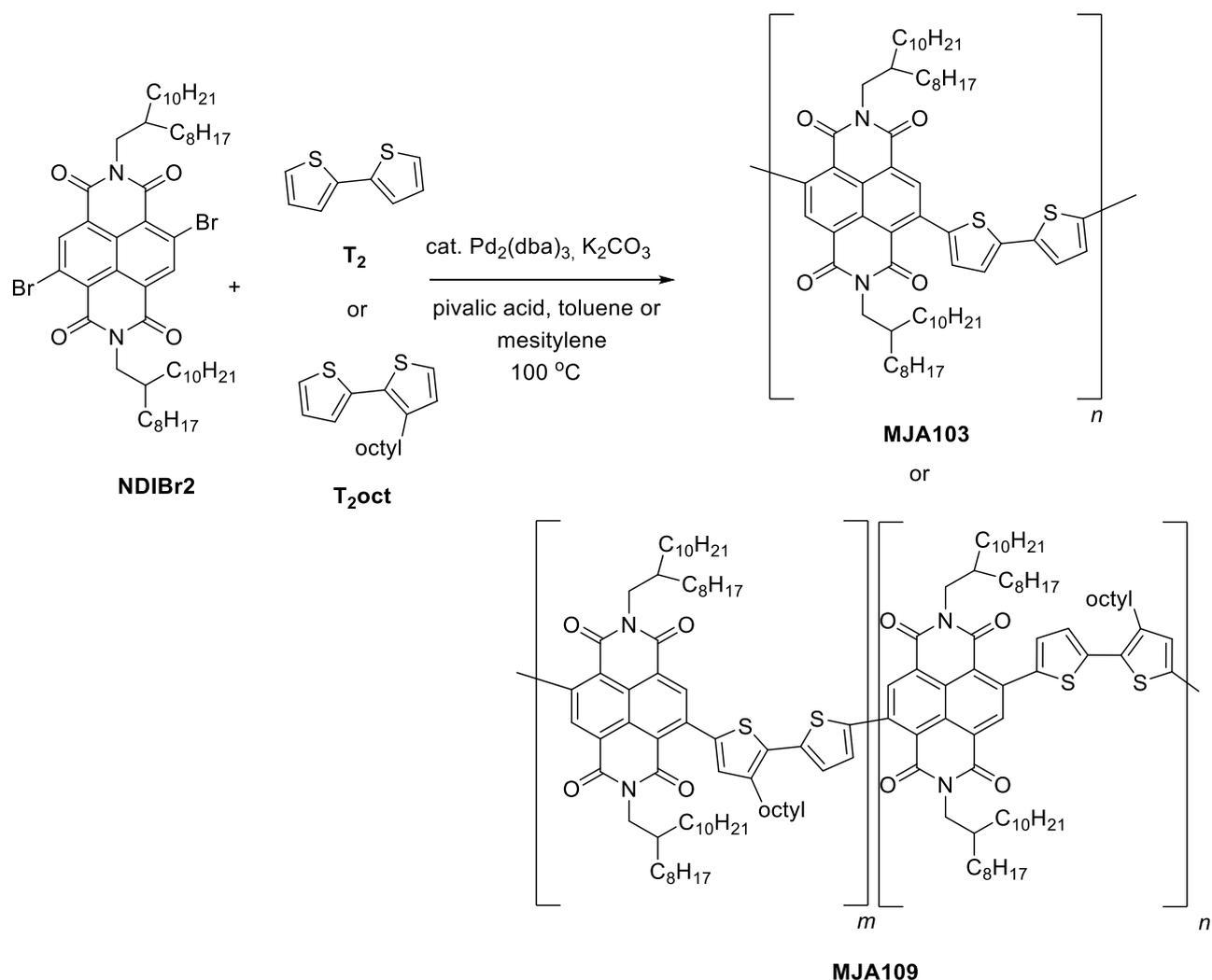
these polymers also influence device performance. From a simplistic point of view, adding an additional disorder to the N2200 structure could reduce its crystallinity and may afford more efficient mixing with the donor polymer. Additional advantages could also arise from more options for processing coming about from a higher solubility in organic solvents and possibly avoiding the use of chlorinated solvents. The aim of this project was to synthesise variants of N2200 using direct arylation where additional irregularity was introduced into the structure by modifying the bithiophene unit using two different reaction scenarios. Firstly, the use of an asymmetric bithiophene monomer to afford **MJA109** or by using a ternary mixture, where bithiophene was used in conjunction with a low loading of a symmetric disubstituted bithiophene bearing solubilising groups such as an octyl chain or triisopropylsilylacetylene groups giving co-polymers **MJA185** and **MJA199** (Figure 1).



**Figure 1.** Chemical structure of N2200 (left) and variants for this study (right).

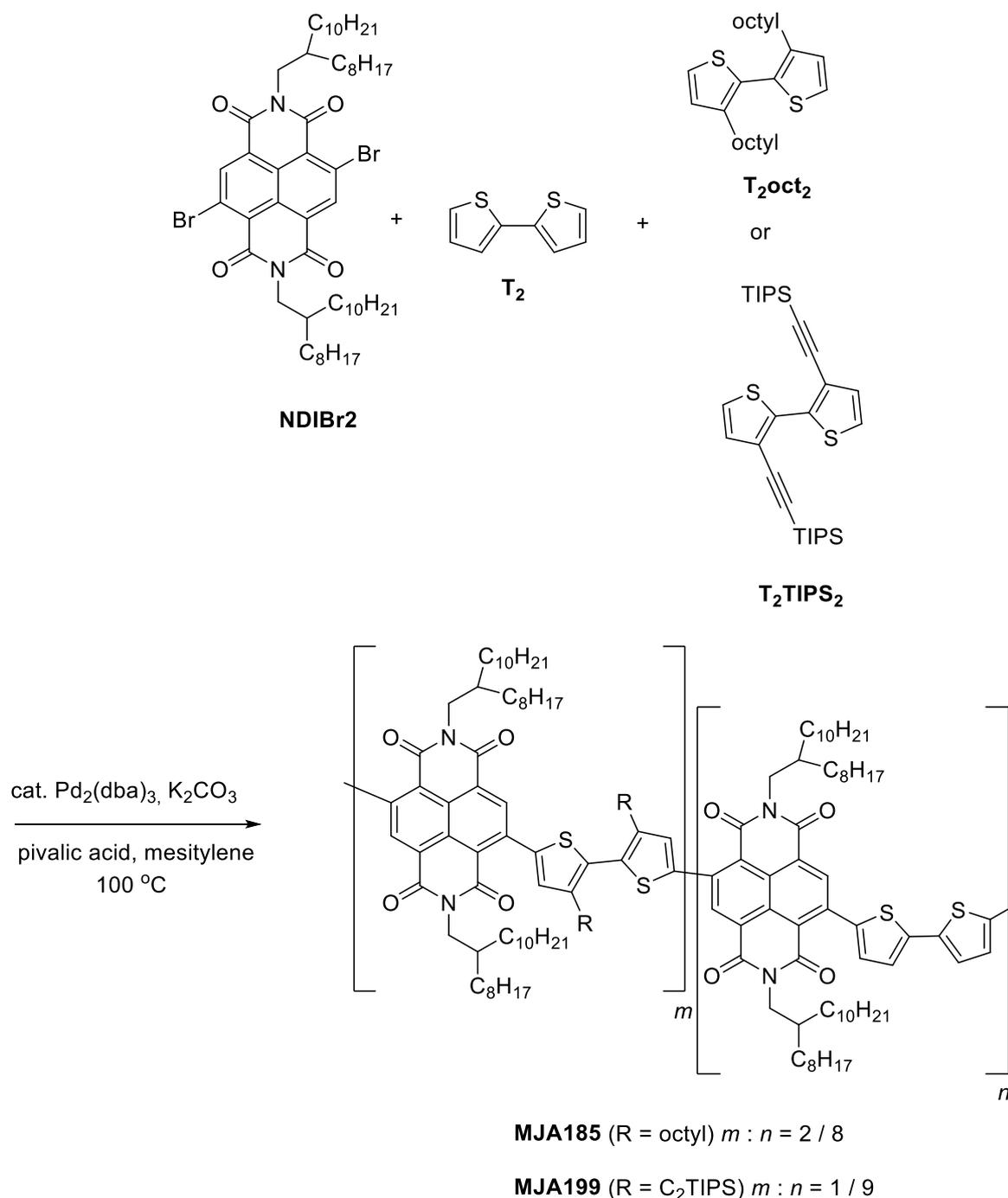
## Results and Discussion

**Synthesis.** Scheme 1 highlights the materials made in a two component polymerization using DARp, which included literature N2200 (**MJA103**) made from the coupling between **NDIBr2** with bithiophene (**T<sub>2</sub>**).<sup>18</sup> The purpose of making this polymer was to make direct data comparison with the new materials synthesized in this study. An asymmetric DARp reaction was also employed using 3-octylbithiophene (**T<sub>2</sub>oct**) with **NDIBr2** to afford a random co-polymer **MJA109**. In essence, this was a random co-polymer as the relative positioning of the octyl unit was not controllable along sequential units. For both these reactions, the standard conditions employing catalyst *tris*(dibenzylideneacetone)dipalladium ( $\text{Pd}_2\text{dba}_3$ ) in the presence of pivalic acid and potassium carbonate were capable of facilitating these polymerizations. The solvent used in the literature reaction forming **MJA103** was toluene, however, mesitylene was used for successive reactions owing to the convenience of handling of a higher boiling solvent. Both of these polymers were purified using standard procedures, where both polymers could be extracted into hot chloroform.



**Scheme 1.** Synthesis of **MJA103** (N2200) and **MJA109** using DARp.

Alternatively, three component reactions, using two symmetric bithiophene reactants, were also examined under identical conditions (Scheme 2). In these cases small amounts of 3,3'-disubstituted bithiophenes replaced some of the bithiophene in the reaction mixtures, which would otherwise give N2200, leading to random co-polymers. This third reaction component was either 3,3'-dioctylbithiophene (T<sub>2</sub>oct<sub>2</sub>) and 3,3'-bis[(triisopropylsilyl)ethynyl]-2,2'-bithiophene (T<sub>2</sub>TIPS<sub>2</sub>) which yielded **MJA185** and **MJA199**, respectively. In the case of the former, a loading of 20% T<sub>2</sub>oct<sub>2</sub> was used, where in the latter only 10% T<sub>2</sub>TIPS<sub>2</sub> was incorporated into the material.

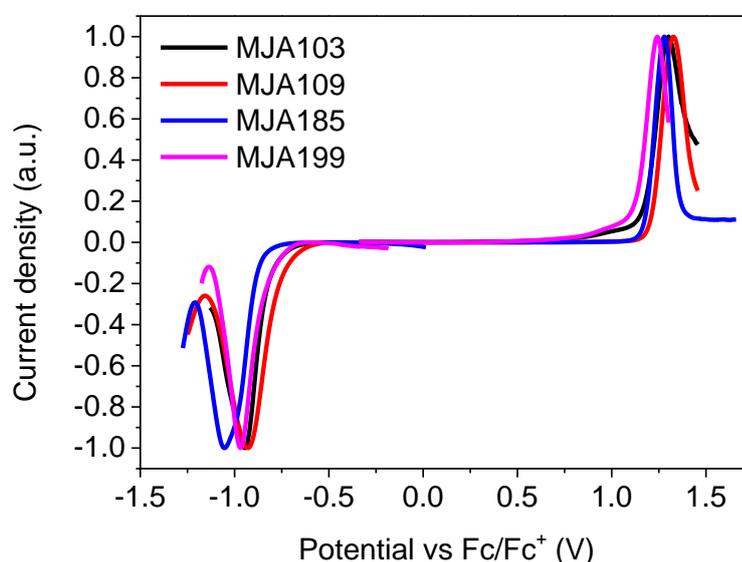


**Scheme 2.** Synthesis of random co-polymers **MJA185** and **MJA199** using DARp.

**Properties.** Spectroscopic and electrochemical properties of these new analogues were measured and are summarised in Table 1. Square wave voltammetry (SWV) was measured for all four polymers made in this study. This consisted of coating the polymer on to a working platinum electrode and measuring redox events through a medium of 0.1M tetrabutylammonium hexafluorophosphate in acetonitrile. A square wave voltammogram can be seen for all materials in Figure 2, showing both reduction and oxidation events. Nevertheless, these structural modifications to N2200 found in these novel materials did little to affect the band gap energies relative to **MJA103**.

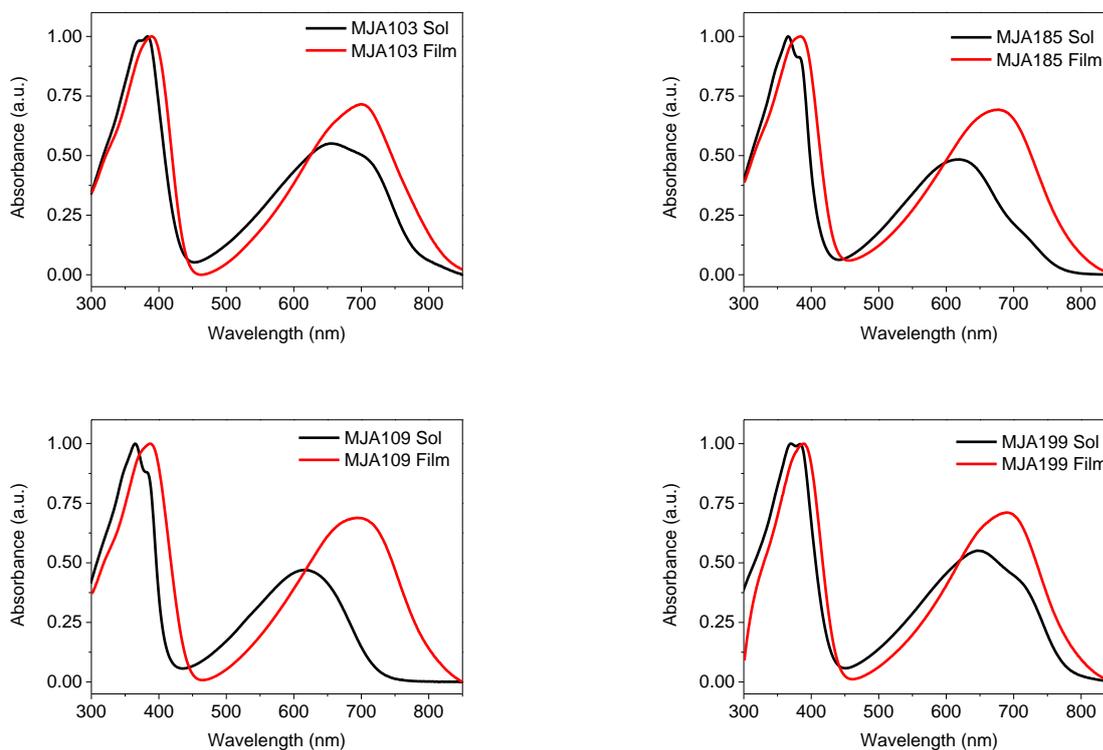
Compound	Optical						
	Electrochemistry (SWV)			Solution		Film	
	HOMO (eV)	LUMO (eV)	$E_g$ (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (nm)	$\lambda_{\text{onset}}$ (nm)	$E_g^{\text{opt}}$ (eV)
<b>MJA103</b>	-6.43	-4.19	2.24	656	700	838	1.48
<b>MJA109</b>	-6.46	-4.19	2.27	617	694	808	1.53
<b>MJA185</b>	-6.41	-4.07	2.34	619	675	792	1.57
<b>MJA199</b>	-6.37	-4.16	2.21	648	690	799	1.55

**Table 1.** Electrochemical and absorption properties for novel materials **MJA109**, **MJA185** and **MJA199** relative to literature N2200 (**MJA103**).



**Figure 2.** Square wave voltammograms (SWV) for all polymers made in this study.

UV-vis spectra were recorded for all novel materials in addition to **MJA103**, both as films upon glass slides and as chloroform solutions. In all these cases, absorption profiles consisted of two main bands, however, the low energy feature for both **MJA109** (seen in Figure 3) and **MJA185** were markedly blue shifted in solution relative to the  $\lambda_{\max}$  found in their corresponding films. This was thought to be attributed to twisting of the thiophene units out of the plane on the account of steric interaction between thiophenes bearing octyl substituents and neighbouring thiophene units. This was not evidenced to the same degree for **MJA199**, which only had 10% **T<sub>2</sub>TIPS<sub>2</sub>** incorporated into the polymer. It is possible that the additional conjugation from the acetylenic substituents to these bithiophene units may have been less disruptive to the conjugation despite their large steric bulk. In any case, the additional conjugation provided by the **T<sub>2</sub>TIPS<sub>2</sub>** in **MJA199** did not seem to significantly red shift the absorbance relative to **MJA103**. As found with the electrochemistry, the optical band gap energies were similar for all polymers.



**Figure 3.** UV-vis absorbance profiles for all polymers made in this study in both  $\text{CHCl}_3$  solution (black traces) and as a film (red traces).

## Conclusions.

It had been possible to use the direct arylation to afford variants of N2200, where additional degree of disorder had been introduced to the polymer backbone. The optical and electrochemical properties were not significantly affected for these materials. Future directions for this project involve device fabrication in conjunction with a suitable *p*-type donor material to investigate the influence of the additional disorder on the morphology and mixing.

## Experimental

**General Experimental.** Toluene and mesitylene used for direct arylation reactions were distilled from elemental sodium prior to use. Commercial 2,2'-bithiophene was purified by crystallisation from methanol and water. All other commercial solvents and reagents were used as received. 3-Octyl-2,2'-bithiophene,<sup>19</sup> 3,3'-dioctyl-2,2'-bithiophene,<sup>20</sup> 3,3'-bis[(triisopropylsilyl)ethynyl]-2,2'-bithiophene<sup>21</sup> and *N,N'*-bis(2-octyldodecyl)-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide)<sup>22</sup> were prepared by their respective literature procedures. <sup>1</sup>H NMR spectra were recorded on a Bruker 600 MHz instrument at ambient temperature, where spectra were referenced to the residual solvent peak ( $\delta$  7.26 ppm for  $\text{CDCl}_3$ ). UV-vis spectra were measured on a CARY 60 instrument as films prepared by spin-coating onto a glass slide or as solutions in chloroform. Square wave voltammetry (SWV) and cyclic voltammetry (CV) measurements were carried out for the determination of reduction/oxidation potentials, from which HOMO/LUMO energy levels were estimated. The SWV and CV traces were recorded on an

AUTOLAB PGSTAT potentiostat (Metrohm AG) using a three-electrode setup with platinum wires, both for working electrode (WE) and counter electrode (CE) and a Ag/Ag<sup>+</sup> reference electrode. The peak maxima and the peak onset positions were determined from the recorded square wave voltammograms and cyclic voltammograms, respectively. These were then referred to ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) by analyzing the Fc/Fc<sup>+</sup> couple after each measurement. In each experiment, polymers were coated onto a platinum working electrode for square wave voltammetry in conjunction with an electrolyte of 0.1M tetrabutylammonium hexafluorophosphate in acetonitrile. Size exclusion chromatography (SEC) was performed on an Agilent PL-GPC 220 Integrated HT-GPC System including Refractive Index Detector, PL-GPC 220 Viscometer, and a PL-GPC 220 Dual Angle LSD columns: 3x PL gel 10 μm MIXED-B LS. The eluent was 1,2,4-trichlorobenzene and was heated to 150 °C. The molecular weights were calculated according relative calibration with polystyrene standards and with a universal calibration.

#### Polymer **MJA103** (literature compound N2200 made using direct arylation reaction protocol)<sup>18</sup>

To a nitrogen degassed mixture consisting of **NDIBr2** (303.5 mg, 0.308 mmol), 2,2'-bithiophene (51.2 mg, 0.308 mmol), K<sub>2</sub>CO<sub>3</sub> (125 mg, 0.904 mmol) and pivalic acid (31 mg, 0.304 mmol) in dry distilled toluene (0.8 mL) was added Pd<sub>2</sub>(dba)<sub>3</sub> (5.0 mg, 0.00546 mmol). The vessel was immediately placed into a preheated oil bath (100 °C) and stirred under a nitrogen atmosphere for 3 h, after which time dry toluene (1.5 mL) was added to the vessel. After a total of 24 h of stirring at 100 °C, the resulting blue gel was allowed to cool to rT, diluted with CHCl<sub>3</sub> (80 mL) and precipitated into stirring methanol (200 mL). A blue solid was collected by filtration and this material subjected to Soxhlett extraction consecutively with acetone, EtOAc, Et<sub>2</sub>O and CHCl<sub>3</sub>. The last extract, containing **MJA103** was passed through a silica gel plug and concentrated to ca. 50 mL. This solution was again precipitated into stirring methanol (200 mL) and collected on a 0.43 μm PTFE membrane and dried under high vacuum to afford **MJA103** (294 mg) as a dark blue solid. SEC (relative vs polystyrene standards): Mn = 20 kDa, Mw = 71 kDa, PDI = 3.584. SEC (universal calibration): Mn = 16 kDa, Mw = 67 kDa, PDI = 4.243.

#### Polymer **MJA109**

To a nitrogen degassed mixture consisting of **NDIBr2** (432.3 mg, 0.439 mmol), 3-octyl-2,2'-bithiophene (122.2 mg, 0.439 mmol), K<sub>2</sub>CO<sub>3</sub> (189 mg, 1.37 mmol) and pivalic acid (47 mg, 0.46 mmol) in dry distilled mesitylene (1.0 mL) was added Pd<sub>2</sub>(dba)<sub>3</sub> (6.4 mg, 0.00698 mmol). The vessel was immediately placed into a preheated oil bath (100 °C) and stirred under a nitrogen atmosphere for 2 d. The contents of the flask were allowed to cool to rT, diluted with CHCl<sub>3</sub> (70 mL) and precipitated into stirring methanol (300 mL). A blue solid was collected by filtration and this material subjected to Soxhlett extraction consecutively with acetone, EtOAc, Et<sub>2</sub>O and CHCl<sub>3</sub>. The last extract, containing **MJA109** was passed through a silica gel plug and concentrated to ca. 70 mL. This solution was again precipitated into stirring methanol (300 mL) and collected on a 0.43 μm PTFE membrane and dried under high vacuum to afford **MJA109** (460 mg) as a dark blue solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.85 (apparent t, 2H), 7.37 (s, 1H), 7.32 (s, 1H), 7.27 (s, 1H), 4.14 (s, 4H), 2.95 (s, 2H), 2.02 (s, 2H), 1.80 (2H), 1.49 (s, 2H), 1.44-1.16 (m, 72H), 0.90-0.82 (m, 15H) ppm. SEC (relative vs polystyrene standards): Mn = 32 kDa, Mw = 195 kDa, PDI = 6.109. SEC (universal calibration): Mn = 27 kDa, Mw = 187 kDa, PDI = 6.944.

### Polymer **MJA185**

To a nitrogen degassed mixture consisting of **NDIBr2** (299.9 mg, 0.304 mmol), 3,3'-dioctyl-2,2'-bithiophene (23.9 mg, 0.0612 mmol), bithiophene (40.5 mg, 0.244 mmol),  $K_2CO_3$  (130 mg, 0.941 mmol) and pivalic acid (34 mg, 0.333 mmol) in dry distilled mesitylene (3 mL) was added  $Pd_2(dba)_3$  (6.6 mg, 0.00721 mmol). The vessel was immediately placed into a preheated oil bath (100 °C) and stirred under a nitrogen atmosphere for 24 h. The contents of the flask were allowed to cool to rT, diluted with  $CHCl_3$  (120 mL) and precipitated into stirring methanol (300 mL). A blue solid was collected by filtration and this material subjected to Soxhlett extraction consecutively with acetone, EtOAc,  $Et_2O$  and  $CHCl_3$ . The last extract, containing **MJA185** was passed through a silica gel plug, eluting with  $CHCl_3$  and concentrated to ca. 50 mL. This solution was again precipitated into stirring methanol (300 mL) and collected on a 0.43  $\mu m$  PTFE membrane and dried under high vacuum to afford **MJA185** (116 mg) as a dark blue solid. The remaining material in the thimble was heated in chlorobenzene (80 mL) under  $N_2$  for 1h and allowed to stir overnight at ambient temperature. The extract was passed through a pad of silica gel, eluting firstly with hot chlorobenzene (25 mL), followed by  $CHCl_3$  (300 mL). The volume of this dark blue solution was reduced to ca. 100 mL and added to stirring ethanol (400 mL). Filtration onto a 0.43  $\mu m$  PTFE membrane and drying under high vacuum afforded **MJA185CB** (154 mg) as a dark blue solid. **MJA185**:  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  = 8.86-8.84 (m, 2H), 7.34-7.29 (m, 3.6H), 4.13 (s, 4H), 2.75 (s, 0.8H), 2.01 (s, 2H), 1.71 (s, 0.8H), 1.41-1.23 (m, 52H), 0.83 (s, 13.2H) ppm. SEC (relative vs polystyrene standards):  $M_n$  = 32 kDa,  $M_w$  = 438 kDa, PDI = 13.86. SEC (universal calibration):  $M_n$  = 24 kDa,  $M_w$  = 414 kDa, PDI = 17.42.

### Polymer **MJA199**

To a nitrogen degassed mixture consisting of **NDIBr2** (301.9 mg, 0.306 mmol), **T<sub>2</sub>TIPS<sub>2</sub>** (15.5 mg, 0.0294 mmol), 2,2'-bithiophene (46.1 mg, 0.277 mmol),  $K_2CO_3$  (129 mg, 0.933 mmol) and pivalic acid (32 mg, 0.313 mmol) in dry distilled mesitylene (3 mL) was added  $Pd_2(dba)_3$  (6.2 mg, 0.00677 mmol). The vessel was immediately placed into a preheated oil bath (100 °C) and stirred under a nitrogen atmosphere for 24 h. The contents of the flask were allowed to cool to rT, diluted with  $CHCl_3$  (60 mL) and precipitated into stirring methanol (250 mL). A blue solid was collected by filtration and this material subjected to Soxhlett extraction consecutively with acetone, EtOAc,  $Et_2O$  and  $CHCl_3$ . The last extract, containing **MJA199** was passed through a silica gel plug, eluting with  $CHCl_3$  and concentrated to ca. 100 mL. This solution was precipitated into stirring acetone (400 mL) and filtered. The dark blue solid was redissolved in  $CHCl_3$  (100 mL) and re-precipitated into stirring methanol (300 mL), collected on a 0.43  $\mu m$  PTFE membrane and dried under high vacuum to afford **MJA199** (303 mg) as a dark blue solid.  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  = 8.84 (s, 1H), 8.53 (s, 1H), 7.34 (br s, 3.8H), 4.13 (s, 4H), 2.06 (s, 2H), 1.43-1.15 (m, 56.2H), 0.90-0.85 (m, 12H) ppm.

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