

## Upscaling and optimisation of the reaction conditions for direct arylation polymerisation

Martyn Jevric, Xun Pan, Mats R. Andersson

*Flinders Institute for Nanoscale Science and Technology, Flinders University, Sturt Road, Bedford Park, Adelaide, SA 5042, Australia*

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### Summary of Key Findings

To realise the fabrication of larger organic solar cells, we have upscaled polymer donors and polymer acceptors as well as a small molecule non-fullerene acceptor. The traditional polymerisation method used to synthesis high molecular weight conjugated polymers is transition-metal-catalyzed cross-couplings, especially Stille coupling that requires the use of toxic organotin compounds. To synthesis polymers in a more environmentally friendly way, we have explored the reaction conditions for direct arylation polymerisation, avoiding the use of organotin compounds. In addition, the optimised condition of the direct arylation method offered high yields and high molecular weights. Our results demonstrate a green way of upscaling the synthesis of conjugated polymers.

### Results

Totally we have synthesised more than 100 batches of polymers. To synthesise polymers, monomers first needs to be synthesised and this is a time demanding process. Most of the monomer synthesis were prepared through a multi-step process and sometime each step needs to be optimised. We have upscaled more than five polymers using direct arylation polymerisation and a small molecule non-fullerene acceptor ITIC-Br<sup>1</sup>. Direct arylation is a more environmentally friendly polymerisation method and suitable for upscaling of polymers.<sup>2</sup> The specific polymerisation reaction conditions need to be optimised for every specific synthesised polymer to optimise the resulting molecular weight. The optimised detailed synthetic conditions on a 1 g scale for six different materials are described below.

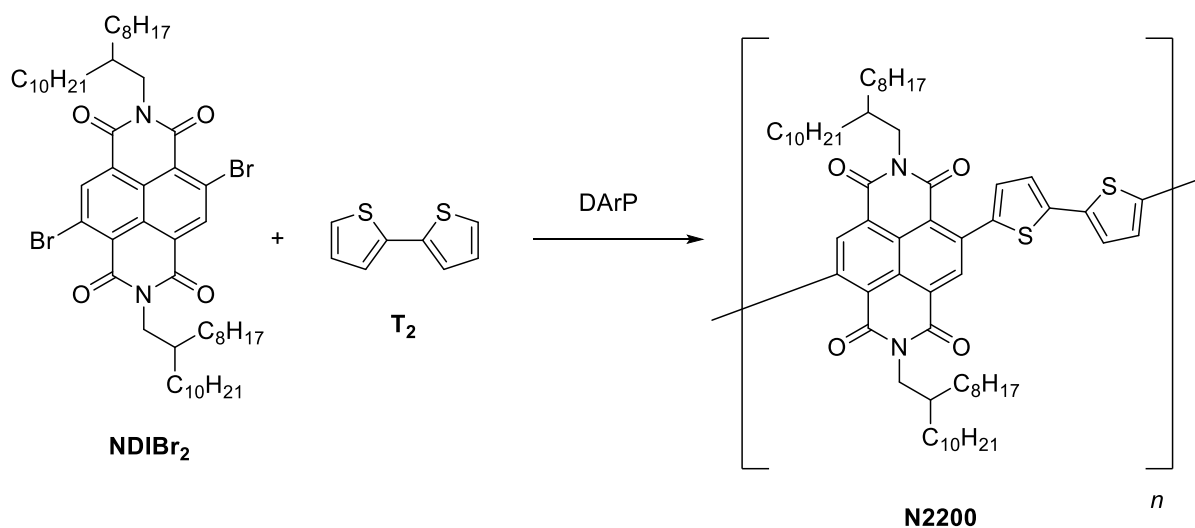
N2200 has been widely used as a polymer acceptor in organic solar cells, and upscaling and optimisation of the synthesis has been performed to facilitate studies of the polymer in all-polymer solar cells.<sup>3-4</sup> PNDI2OD-C8T2 is a derivative of N2200 but with octyl sidechain attached to the bithiophene unit. The addition of sidechains compared to N2200 improve the solubility of PNDI2OD-C8T2 making it soluble in a variety of greener solvents such as Me-THF. This made it possible to prepare solar cells from a larger variety of solvents.

PPDT2FBT is a polymer donor mainly used in fullerene based organic solar cells and has great potential to be used in large scale printed solar cells due to its relatively simple synthetic procedure.<sup>5-6</sup> However, PPDT2FBT has high crystallinity, and when used with polymer acceptor, the device performance turned out to be worse than fullerene-based cells. To suppress the crystallinity of PPDT2FBT, two copolymer derivatives, MJE29 and MJE51 were designed and synthesized. They both exhibit improved solubility compared to PPDT2FBT.

ITIC-Br was synthesized on a 3 gram scale and has been mainly used to pair with PTQ10 to fabricate high performing and scalable solar cells. This is a large molecule and not a polymer but it has shown promising device characteristic and we therefore also upscaled the synthesis of this material.

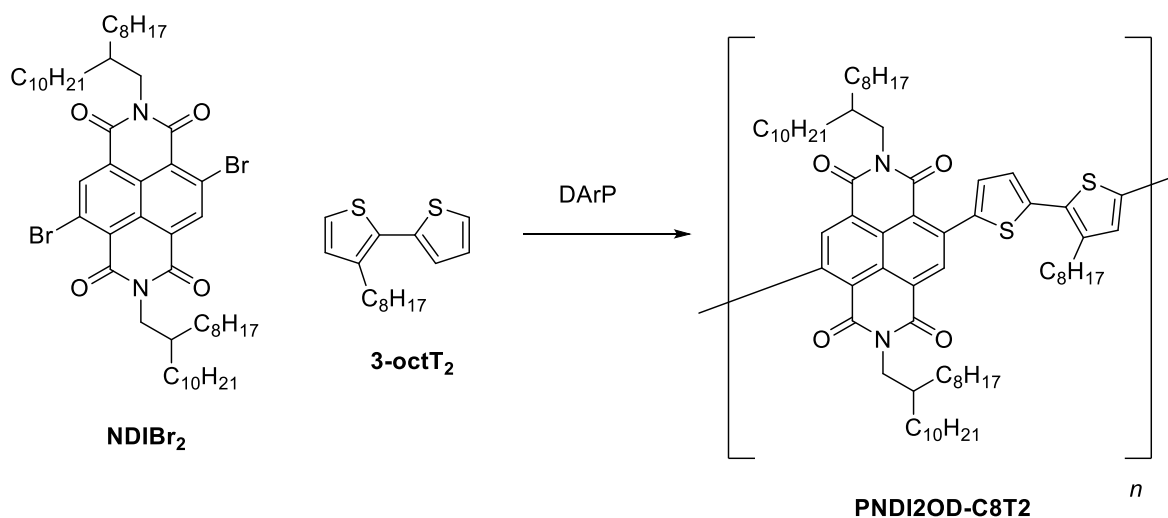
Detailed synthetic procedures of six upscaled materials

**N2200**



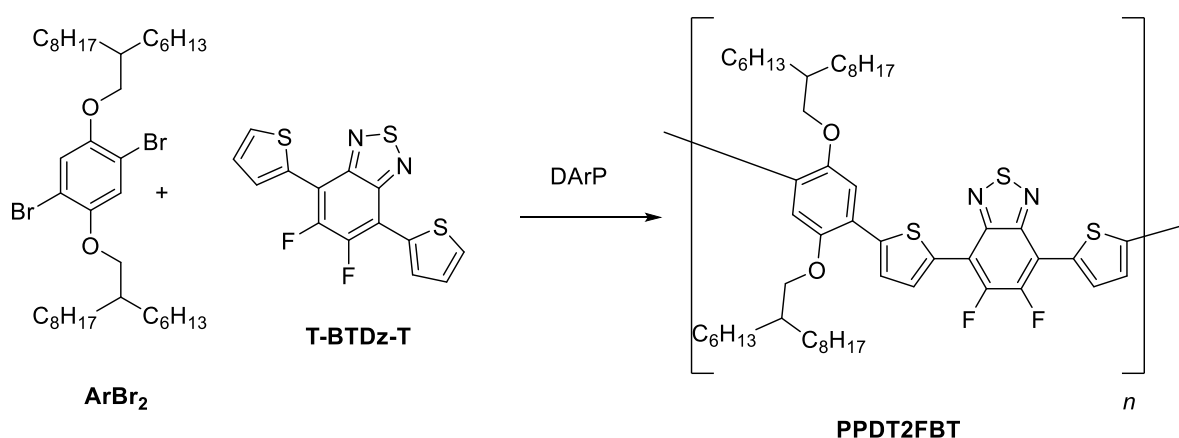
To a nitrogen degassed mixture consisting of **NDIBr<sub>2</sub>** (978.9 mg, 0.9937 mmol), **T<sub>2</sub>** (165.2 mg, 0.9936 mmol), pivalic acid (108 mg, 1.05 mmol) and K<sub>2</sub>CO<sub>3</sub> (457 mg, 3.31 mmol) in mesitylene (10 mL) was added Pd<sub>2</sub>dba<sub>3</sub> (10.8 mg, 11.8 μmol) and the stirring reaction mixture was immersed into a 100 °C preheated oil bath for 16 h. The cooled mixture was precipitated into stirring methanol and filtered. The solid mass was transferred to cellulose thimble and using a Soxhlet apparatus was extracted sequentially with acetone, Et<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub> and finally CHCl<sub>3</sub>. The CHCl<sub>3</sub> extract was passed through a pad of SiO<sub>2</sub>, concentrated and precipitated into stirring methanol. The solid was collected on a 0.45 μm PTFE membrane and dried under high vacuum affording **N2200** (936 mg, 95%) as a dark blue solid. SEC:  $\bar{M}_n = 44 \text{ kg mol}^{-1}$ ,  $\bar{D}_M = 2.8$ .

**PNDI2OD-C8T2**

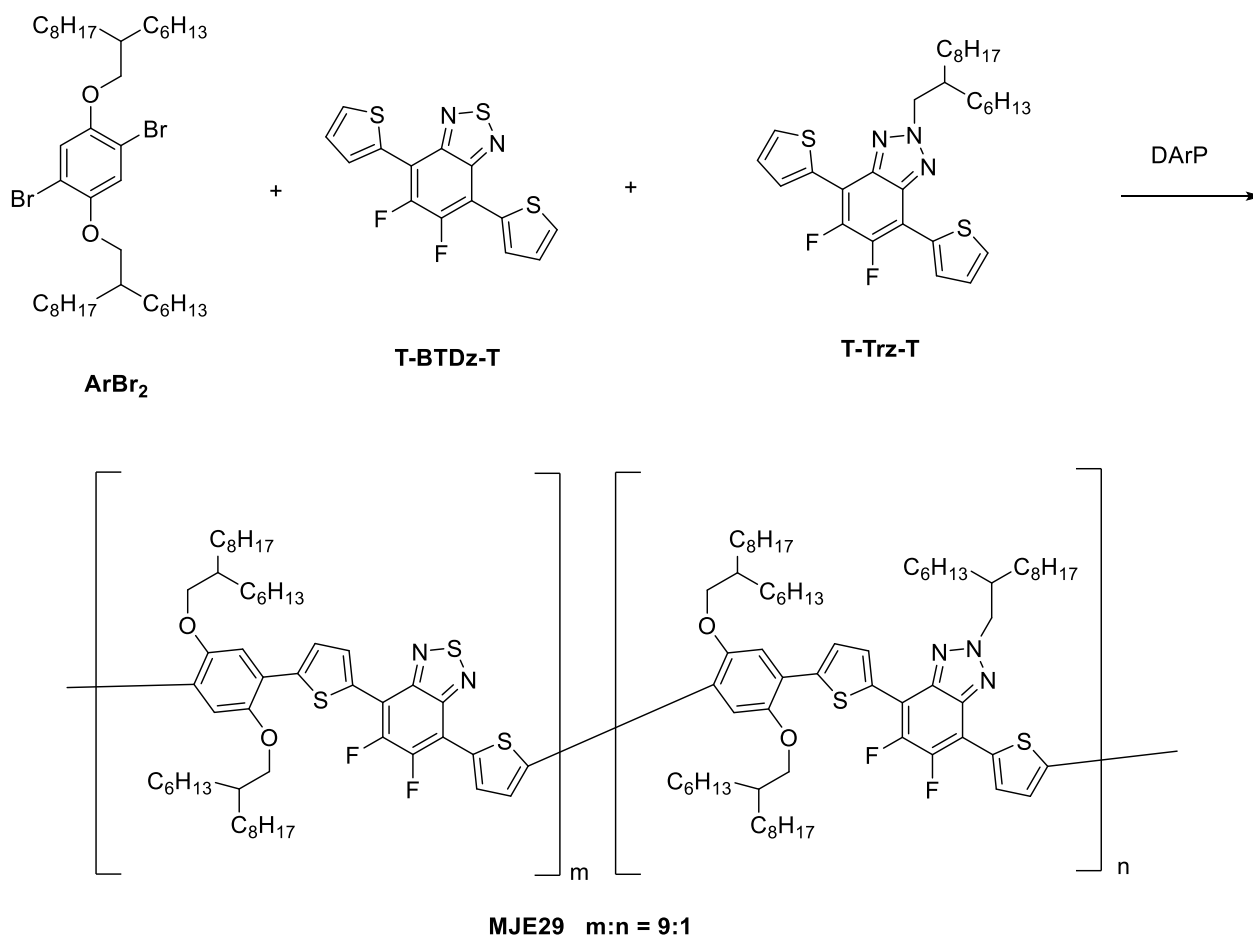


To a nitrogen degassed mixture consisting of **NDIBr<sub>2</sub>** (985.1 mg, 1.000 mmol), **3-octT<sub>2</sub>** (278.4 mg, 1.000 mmol), pivalic acid (105 mg, 1.03 mmol) and K<sub>2</sub>CO<sub>3</sub> (441 mg, 3.19 mmol) in mesitylene (12 mL) was added Pd<sub>2</sub>dba<sub>3</sub> (20.8 mg, 22.7 μmol) and the reaction mixture stirred at 100 °C using a preheated oil bath. The cooled mixture was precipitated into stirring methanol and filtered. The solid mass was transferred to cellulose thimble and using a Soxhlet apparatus was extracted with acetone, EtOAc, Et<sub>2</sub>O and finally CHCl<sub>3</sub>. The CHCl<sub>3</sub> extract was passed through a pad of SiO<sub>2</sub>, concentrated and precipitated into stirring methanol. The solid was collected on a 0.45 μm PTFE membrane and dried under high vacuum affording **PNDI2OD-C8T2** (1.079 g, 98%) as a dark blue solid. SEC:  $\bar{M}_n = 51 \text{ kg mol}^{-1}$ ,  $\bar{D}_M = 5.0$ .

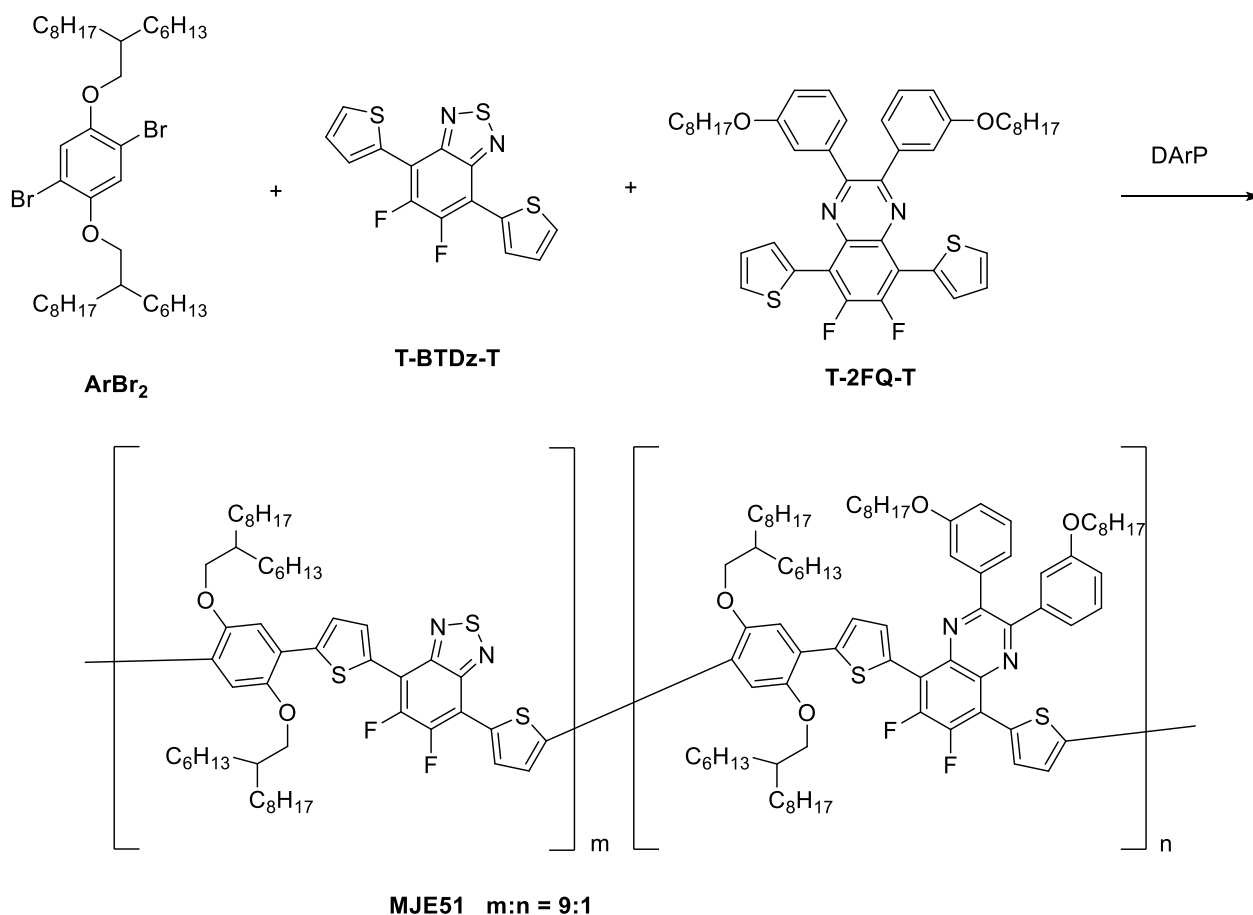
### PPDT2FBT



To an argon degassed solution consisting of **ArBr<sub>2</sub>** (831.9 mg, 1.161 mmol) and **T-BTDz-T** (390.4 mg, 1.161 mmol) in dry THF (12 mL) was added pivalic acid (119 mg, 1.17 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.21 g, 3.71 mmol), Pd<sub>2</sub>dba<sub>3</sub> (19.3 mg, 21.1 μmol) and tris(*o*-methoxyphenyl)phosphine (63.5 mg, 0.180 mmol). The vessel was sealed and immersed directly into a preheated oil bath (120 °C) and stirred for 13 h. The gel was diluted into hot *o*-DCB and precipitated into stirring MeOH/10% aqueous HCl (10:1). The suspension was filtered and the solid was subjected to a series of Soxhlet extractions, consisting of acetone, Et<sub>2</sub>O, hexane, CHCl<sub>3</sub> and the material collected in *o*-xylene. To the latter extract was added a solution of sodium diethyldithiocarbamate (2 g in 50 mL) and the biphasic mixture was stirred 16 h at 60 °C. The phases were separated, and the organic phase washed thrice with hot H<sub>2</sub>O. The volume of the *o*-xylene phase was reduced *in vacuo* and poured into stirring methanol. The solid was collected by suction filtration on a 0.45 μm PTFE membrane and dried under high vacuum yielding **PPDT2FBT** (894.4 mg, 86%) as a dark blue solid. SEC:  $\bar{M}_n = 50 \text{ kg mol}^{-1}$ ,  $\bar{D}_M = 2.6$ .

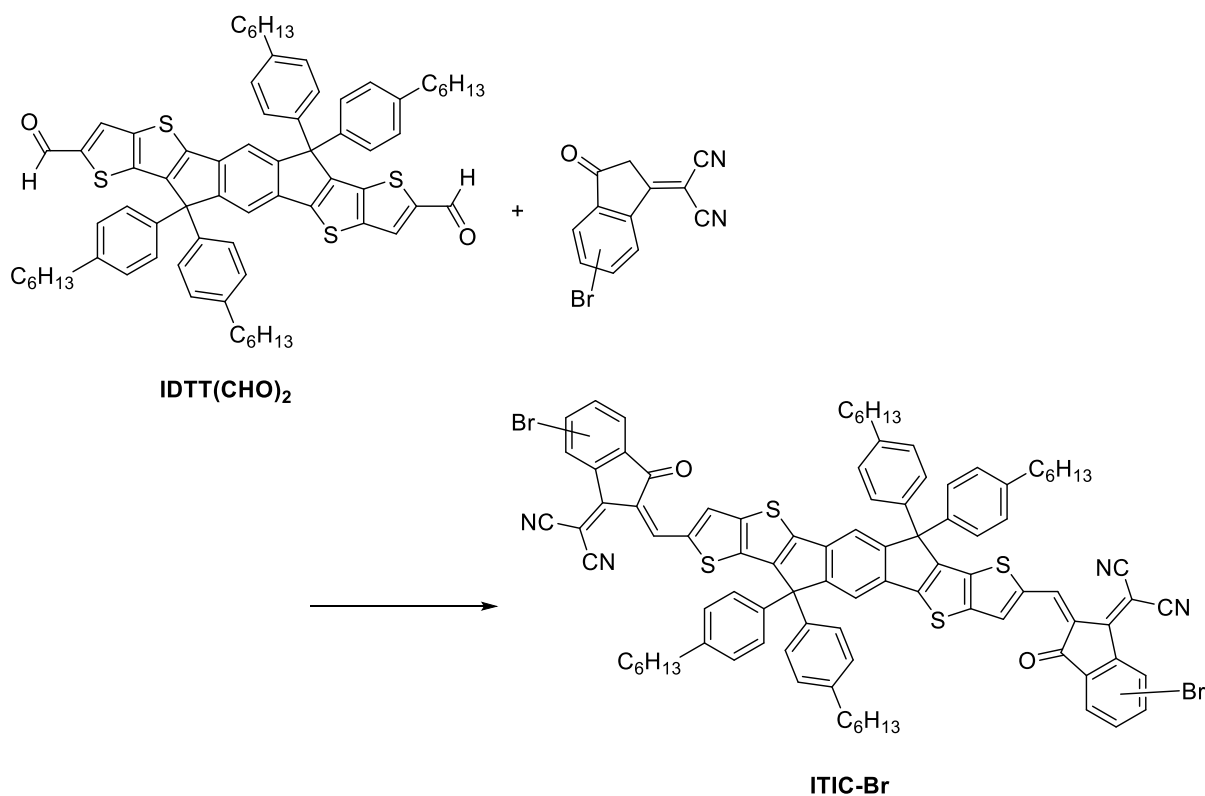
**MJE29**


To an argon degassed solution consisting of **ArBr<sub>2</sub>** (851.8 mg, 1.189 mmol), **T-BTDz-T** (359.6 mg, 1.069 mmol) and **T-Trz-T** (64.6 mg, 0.119 mmol) in dry THF (12 mL) was added pivalic acid (136 mg, 1.33 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.20 g, 3.68 mmol), Pd<sub>2</sub>dba<sub>3</sub> (24.7 mg, 27.0 μmol) and tris(*o*-methoxyphenyl)phosphine (76.8 mg, 0.217 mmol). The vessel was sealed and immersed directly into a preheated oil bath (120 °C) and stirred for 2 h. The gel was diluted into hot chlorobenzene and precipitated into stirring MeOH/10% aqueous HCl (10:1). The suspension was filtered and the solid was subjected to a series of Soxhlet extractions, consisting of acetone, Et<sub>2</sub>O, hexane, CHCl<sub>3</sub> and the material collected in CHCl<sub>3</sub>. The CHCl<sub>3</sub> extract was passed through a pad of SiO<sub>2</sub>, concentrated under reduced pressure and precipitated into stirring methanol. The solid was collected by suction filtration on a 0.45 μm PTFE membrane and dried under high vacuum yielding **MJE29** (1.00 g, 92%) as a dark blue solid. SEC:  $\bar{M}_n = 29 \text{ kg mol}^{-1}$ ,  $\bar{D}_M = 3.2$ .

**MJE51**


To an argon degassed solution consisting of **ArBr<sub>2</sub>** (833.4 mg, 1.163 mmol), **T-BTDz-T** (352.1 mg, 1.047 mmol) and **T-2FQ-T** (86.0 mg, 0.116 mmol) in dry THF (12 mL) was added pivalic acid (122 mg, 1.20 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.22 g, 3.74 mmol), Pd<sub>2</sub>dba<sub>3</sub> (18.8 mg, 20.5 μmol) and tris(*o*-methoxyphenyl)phosphine (65.7 mg, 0.186 mmol). The vessel was sealed and immersed directly into a preheated oil bath (120 °C) and stirred for 3 h. The gel was diluted into hot chlorobenzene and precipitated into stirring MeOH/10% aqueous HCl (10:1). The suspension was filtered and the solid was subjected to a series of Soxhlet extractions, consisting of acetone, Et<sub>2</sub>O, hexane, CHCl<sub>3</sub> and the material collected in CHCl<sub>3</sub>. The CHCl<sub>3</sub> extract was passed through a pad of SiO<sub>2</sub>, concentrated under reduced pressure and precipitated into stirring methanol. The solid was collected by suction filtration on a 0.45 μm PTFE membrane and dried under high vacuum yielding **MJE51** (1.01 g, 93%) as a dark blue solid. SEC:  $\overline{M}_n = 24 \text{ kg mol}^{-1}$ ,  $\overline{D}_M = 3.1$ .

**ITIC-Br**



To a stirring solution of **IDTT(CHO)<sub>2</sub>** (2.11 g, 1.96 mmol) and malononitrile derivative (1.30 g, 4.76 mmol) in CHCl<sub>3</sub> (250 mL) was added pyridine (5 mL) and the resulting reaction mixture heated to 60 °C for 16 h. Volatiles were removed under reduced pressure and the crude residue taken up in CHCl<sub>3</sub> (ca. 50 mL) and passed through a SiO<sub>2</sub> column (CHCl<sub>3</sub>) to give the **ITIC-Br** (3.00 g, 97%) as a dark blue solid.

**Conclusion**

An environmentally friendly polymerisation method, direct arylation, was investigated and the reaction condition was optimised to upscale both polymer donors and acceptors. High yield was achieved with minimised toxic waste due to the absence of toxic organotin compound in the polymerisation reaction.

**Acknowledgements**

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