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Facile synthesis of naphthodithiophenediimide based small molecules and polymers via direct arylation coupling

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ABSTRACT

Naphthodithiophenediimide (NDTI) as a new electron-accepting building block has been used to synthesize narrow bandgap small molecules and polymers for ambi-polar organic field-effect transistors and organic solar cells. Herein, we report the first application of direct arylation coupling to synthesize a series of NDTI-based small molecules and polymers. The regioselectivity was examined in the direct arylation coupling of NDTI with 2-bromo-9,9-dihexylfluorene. Two NDTI-based narrow bandgap polymers, one with benzothiadiazole and the other with 9,9-dioctylfluorene, were synthesized via direct arylation polymerization. The chemical structures and optoelectronic properties of these molecules and polymers were characterized.

Introduction

Among the various π-conjugated building blocks utilized for organic optoelectronic devices, naphthalene diimide (NDI) is one of the most widely studied electron-accepting species in the rylene diimide family.[1] Core-extended NDI derivatives[2] have found great potential as building blocks for high electron mobility n-type[3–5] as well as ambi-polar thin film transistors (TFTs).[6] In particular, a new core-expanded NDI derivative called naphtho[2,3-*b*:6,7-*b*]-dithiophenediimide (NDTI) was recently reported by Takimiya and co-workers.[7] NDTI provides several advantages over other core-extended NDI derivatives: (i) the fused thiophene groups improve the planarity of the molecule as opposed to flanked thiophenes that form an out of plane angle with the NDI core,[8] (ii) the rigidity and overall long range ordering is conducive to extensive p-orbital overlap which consequently facilitates charge transport.

Most of the reported NDI-based small molecules and polymers have been synthesized through conventional coupling methods such as Suzuki coupling and Stille coupling, both of which involve tedious C–H pre-activation using organometallic reagents that suffer from high flammability (e.g., butyllithium), high toxicity (e.g., stannyl reagents) and poor stability. To that end, C–H direct arylation has emerged as a new efficient and green method that enables the facile synthesis of π-conjugated molecules and polymers in fewer steps, without the need for C–H bond pre-activation or involvement of toxic stannyl reagents. Although C–H direct arylation has been extensively studied in the organometallic community for the synthesis of a variety of organic small molecules for applications such as pharmaceutics,[9] its application to synthesis of π-conjugated systems (both small molecules and polymers) with tunable optoelectronic properties has until recently not attracted much attention.[10–12]

To date, a variety of π-conjugated small molecules,[13] homopolymers[14] and donor–acceptor copolymers[15] have been synthesized using C–H direct arylation coupling. For example, Sommer and co-workers recently reported the synthesis of donor–acceptor–donor (D–A–D) type NDI building blocks and polymers using highly efficient direct arylation routes.[16a,b] Moreover, core expansion on the lateral edges of NDI derivatives for fine tuning of electrical and optical properties can now be realized by the activation of the C–H bond of simple unsubstituted heteroaryls such as thiophene.[16c] More recently, a NDI-tetrafluorobenzene polymer (P(ThNDIThF4)) was synthesized by direct arylation polycondensation (DAP) and the polymer showed an electron mobility as high as 1.3 $cm^2 V^{-1} s^{-1}$ in top-gate, bottom-contact field effect transistors.[8] To the best of our knowledge, C–H direct arylation coupling has never been used in the synthesis of NDTI based polymers and small molecules.

Recently, we have reported the synthesis of donor–acceptor (D–A) type copolymers via direct-arylation cross-coupling polycondensation.[15d–f,18] We found that in the high-boiling-point, non-polar aromatic solvent 1,2-dimethylbenzene (*o*-xylene),

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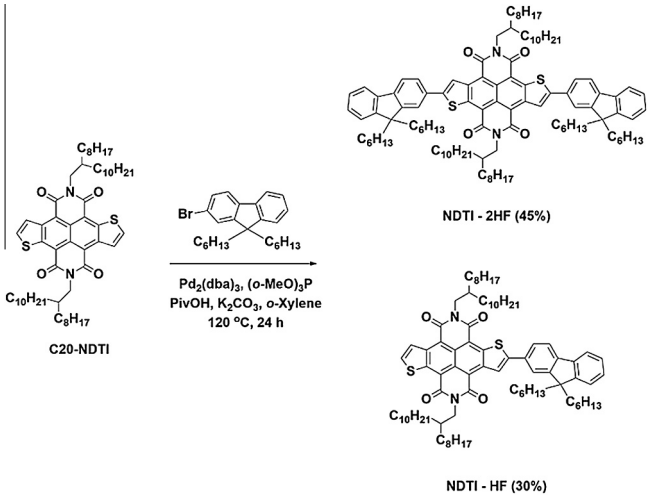
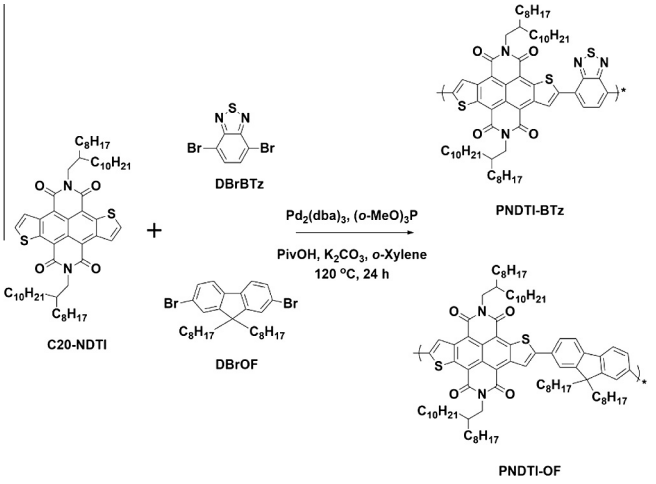


Scheme 1. Synthesis of NDTI-2HF and NDTI-HF via direct arylation.



Scheme 2. Synthesis of PDNTI-OF and PNDTI-BTz via direct arylation.

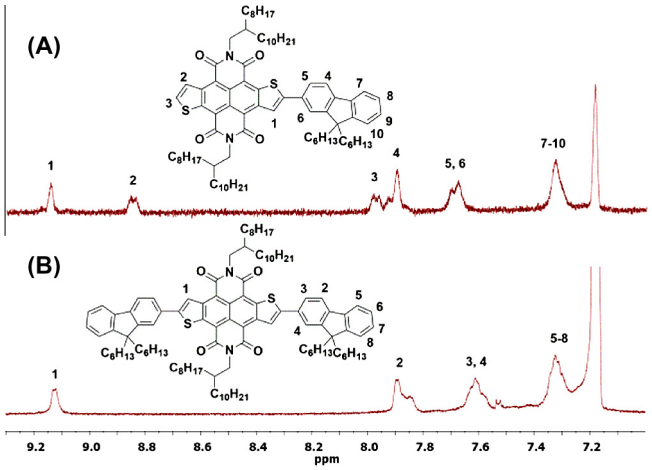


Figure 1. Aromatic range for ^{1}H NMR (300 MHz) spectra of (A) NDTI-HF and (B) NDTI-2HF.

Pd_2dba_3/(*o*-MeOPh)$_3$P, potassium carbonate and pivalic acid as an additive, serves as an efficient catalyst system to obtain high-quality polymers.[15d,e]

Herein, we report the synthesis and characterization of a novel NDTI polymer (PNDTI-OF) containing the electron-rich co-monomer unit 9,9-dioctylfluorene, and an analogous NDTI triad (denoted as NDTI-2HF) with 9,9-dihexylfluorene, by direct arylation. A narrow bandgap polymer—PNDTI-BTz, consisting of alternating NDTI and benzothiadiazole, which was synthesised by Stille coupling in an earlier report,[17] was also synthesized under the scheme of DAP.

Results and discussion

In contrast to previous reports of polymerization with NDTI where conventional coupling methods such as Suzuki coupling and Stille coupling were utilized to obtain high molecular weight polymers, we investigated the previously devised DAP route using the NDTI monomer to synthesize small molecular derivatives and polymers.[18] NDTI-based small molecules were obtained from a one-pot direct arylation of C20-NDTI (0.1 M) and 1-bromo-9,9-dihexylfluorene (molar ratio = 1:10). A mixture of mono-(denoted as NDTI-HF) and bi- (denoted as NDTI-2HF) substituted products was obtained with yields of 25% and 10%, respectively, which can be attributed to the relatively low reactivity of the NDTI molecule (Scheme 1).

Increasing the concentration of C20-NDTI to 0.2 M improved the yield of NDTI-2HF to 45% and NDTI-HF to 30%, while 10% of C20-NDTI remained unreacted. Although no significant formation of by-products was observed from the activation of the β-H in the NDTI monomer, the presence of unreacted monomers is an indication of the relatively low reactivity of the α-H under these reaction conditions. In addition, the homo-coupling of 1-bromo-9,9-dihexylfluorene (BrHF) is a possible side reaction that might also contribute to the relatively low yield of NDTI-2HF. The ^{1}H NMR spectra (Fig. 1) of both products (NDTI-HF and NDTI-2HF) show a clear peak at 9.15 ppm which could be assigned to the β-proton of the annulated thiophenes. All other peaks could be assigned to protons from the NDTI core and fluorene moieties. The broad peaks in the aromatic region of the ^{1}H NMR spectra

Table 1
Summary of the synthesis of NDTI-based small molecules and polymers

Species	Entry	Concentration (M)	Temperature (°C)	Time (h)	Yield (%)	M_n (kDa)	PDI
[a]NDTI-2HF	1	0.1	120	24	10	–	–
	2	0.2			45	–	
PNDTI-OF	3	0.1	120	24	[b]50	[b]3.56	1.53
	4	0.2			[b]50	[b]5.16	1.60
					[c]38	[c]7.21	2.16
PNDTI-BTz	5	0.1	120	24	[b]45	[b]3.34	1.54

[a] Molecular weight verified by mass spectroscopy (ESI).
[b] Results from the hexane fraction.
[c] Results from the chloroform fraction.