

# Synthesis and Molecular Properties of Four Isomeric Dialkylated Angular-Shaped Naphthodithiophenes

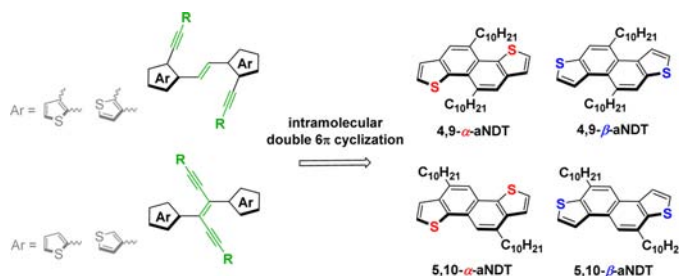
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## ABSTRACT



A new strategy to synthesize 4,9- and 5,10-dialkylated  $\alpha$ -aNDTs as well as 4,9- and 5,10-dialkylated  $\beta$ -aNDTs is described. Four isomeric precursors with different dithienyl-ene-diyne arrangements undergo base-induced double  $6\pi$ -cyclization to construct the central naphthalene cores, leading to the formation of the regiospecific products. These 2,7-distannylated dialkylated aNDT-based monomers can be used for Stille cross-coupling to produce promising conjugated materials for various optoelectronic applications.

The acenedithiophene (AcDT) family has been used as key building blocks to make superior organic semiconductors.<sup>1</sup> The regioselective functionalization at the  $\alpha$ -positions of the two outer thiophenes of AcDTs allows for versatile two-dimensional  $\pi$ -extension and polymerization. Because of the rigid and coplanar architecture of AcDTs to facilitate

$\pi$ -electron delocalization and  $\pi$ - $\pi$  stacking for efficient charge transport,<sup>2</sup> tricyclic benzodithiophene (BDT)<sup>3</sup> and pentacyclic anthradithiophene (ADT)<sup>2d,4</sup> derivatives have been extensively incorporated into a variety of conjugated polymers to produce high-performance organic field-effect transistors (OFETs) and polymer solar cells (PSCs). Very recently, another promising and attractive  $\pi$ -conjugated AcDT, tetracyclic naphthodithiophenes (NDTs), has received increasing attention. It has been demonstrated by Takimiya and co-workers that the molecular packing of NDT-based polymers is strongly influenced by the geometry of NDTs.<sup>5</sup> For instance, copolymers with the “zigzag” angular-fused NDT (aNDT) motif were reported to possess

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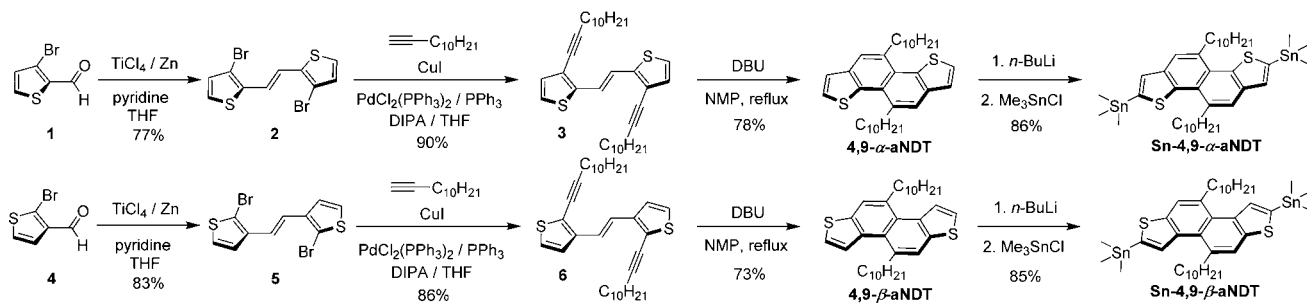
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# Scheme 1. Synthesis of Inner 4,9-Dialkylated $\alpha$ -aNDT and $\beta$ -aNDT



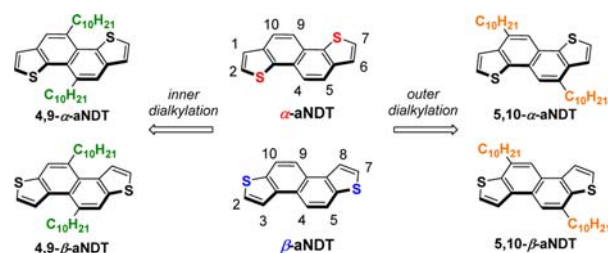
higher ordered solid-state structures and OFET mobilities than polymers incorporating the linear-fused NDT (INDT) component.<sup>2b,c,5,6</sup> Moreover, the aNDT units are expected to result in higher open-circuit voltage ( $V_{oc}$ ) and better oxidative stability for PSC applications than INDTs on account of the lower lying HOMO energy level of aNDTs.<sup>7,8</sup>

Depending on the geometry of the fused thiophenes, the sulfur atoms in aNDT can be functionalized on either the  $\alpha$ - or  $\beta$ -positions of the central naphthalene moiety, yielding two regioisomers denoted as  $\alpha$ -aNDT and  $\beta$ -aNDT, respectively (Figure 1). Although the synthesis of the  $\alpha$ -aNDT and  $\beta$ -aNDT small molecules has been reported,<sup>2-b,9</sup> the absence of aliphatic side chains as solubilizing groups greatly restricts their further application toward polymer synthesis.

To create a new class of aNDT-based polymers for widespread applications in solution-processable OFETs and PSCs, side-chain engineering and manipulation of the aNDT frameworks are highly desirable but synthetically challenging. The position of the aliphatic side chains can dramatically influence the solubility, crystallization, molecular packing and thus charge transportation of the polymers, resulting in variations of device performance.

Incorporation of two aliphatic side chains onto  $\alpha$ -aNDT and  $\beta$ -aNDT can be at the 4,9- or 5,10-positions of the central naphthalene core. The side-chain steric and electronic effects at 4,9- and 5,10-positions could play a crucial role in determining the photophysical, orbital, and bulk properties which are worthy of systematic investigation. Compared to dialkylation at outer 5,10-positions, substitution at inner 4,9-positions could in principle reduce their steric interference with other alkyl groups on the

neighboring aromatic rings, thereby maintaining coplanar backbone of the resulting oligomers or polymers. Very recently, Takimiya et al. first developed an approach to selectively functionalize two alkyl chains at the 5,10-positions of  $\alpha$ -aNDT.<sup>10</sup> A donor–acceptor copolymer incorporating 5,10-dodecyl  $\alpha$ -aNDT units successfully achieved a high OFET mobility of up to  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a high PSC efficiency of up to 8.2%.<sup>11</sup> Besides, although 4,9-dialkoxylated  $\alpha$ -aNDT and its corresponding oligomers<sup>12</sup> and polymers<sup>13</sup> were also reported to show moderate performance in PSCs, the electron-donating alkoxy groups might raise HOMO energy level of the corresponding polymers,<sup>10,11</sup> which could lower  $V_{oc}$ . Up to date, the synthesis of 4,9-dialkylated  $\alpha$ -aNDT, 5,10- and 4,9-dialkylated  $\beta$ -aNDT units has never been disclosed.



**Figure 1.** Molecular structures of  $\alpha$ -aNDT,  $\beta$ -aNDT, and four isomeric dialkylated aNDTs.

Herein, we present a novel and systematic strategy to implant lateral decyl substituents at inner 4,9- and outer 5,10-positions of  $\alpha$ -aNDT and  $\beta$ -aNDT units, leading to the successful construction of the four isomeric

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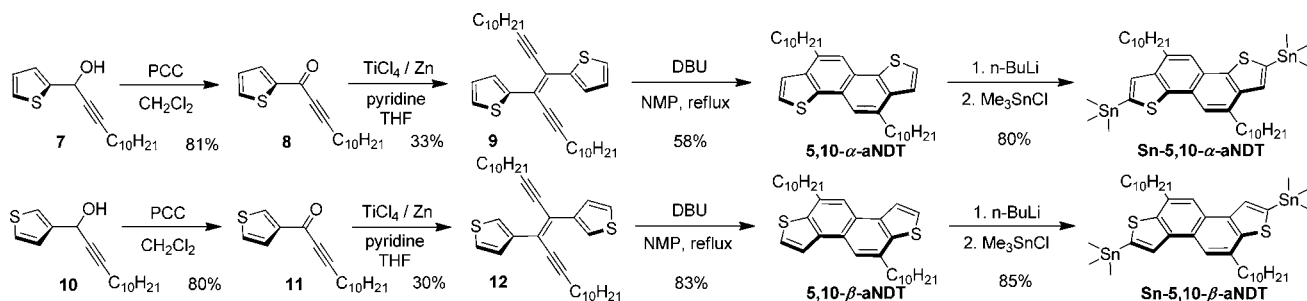
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**Scheme 2.** Synthesis of Outer 5,10-Dialkylated  $\alpha$ -aNDT and  $\beta$ -aNDT



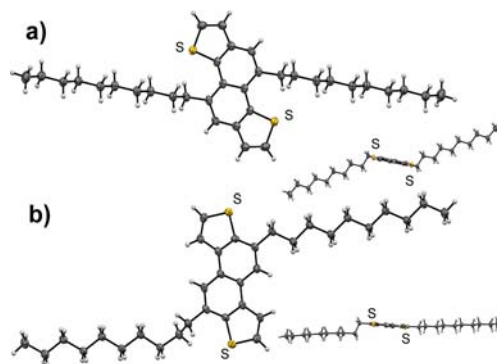
aNDT-based structures including 5,10-didecyl  $\alpha$ -aNDT and 4,9-didecyl  $\alpha$ -aNDT (simplified as 5,10- $\alpha$ -aNDT and 4,9- $\alpha$ -aNDT) as well as 5,10-didecyl  $\beta$ -aNDT and 4,9-didecyl  $\beta$ -aNDT (simplified as 5,10- $\beta$ -aNDT and 4,9- $\beta$ -aNDT). The regiospecific synthesis of inner and outer dialkylated aNDTs was accomplished through two key steps, McMurry coupling<sup>14</sup> and base-catalyzed  $6\pi$ -cyclization<sup>16</sup> of diene-yne moieties.

The synthetic route toward 4,9- $\alpha$ -aNDT and 4,9- $\beta$ -aNDT is depicted in Scheme 1. In the presence of titanium tetrachloride and a reducing agent of Zn, the starting materials, 3-bromothiophene-2-carbaldehyde (**1**) and 2-bromothiophene-3-carbaldehyde (**4**), underwent McMurry coupling reactions to furnish dimerized alkenes 1,2-bis-(3-bromothiophen-2-yl)ethene (**2**) and 1,2-bis(2-bromothiophene-3-yl)ethene (**5**), respectively, with almost *E*-form olefinic configuration in moderate yields. Sonogashira coupling reactions of **2** and **5** with 1-dodecyne afforded the dithiophenyl enediynes **3** and **6**, respectively, in high yields. The key step to construct the inner 4,9- $\alpha$ -aNDT and 4,9- $\beta$ -aNDT involves tandem base-induced  $6\pi$ -cyclizations in the presence of diazabicycloundecene (DBU) in refluxing *N*-methylpyrrolidone (NMP), forming the central naphthalene cores with the alkyl chains specifically at the 4,9-positions. Finally, the 4,9- $\alpha$ -aNDT and 4,9- $\beta$ -aNDT were doubly lithiated by *n*-butyllithium followed by treatment with trimethyltin chloride, yielding 2,7-distannyl-4,9-didecyl  $\alpha$ -aNDT (Sn-4,9- $\alpha$ -aNDT) and 2,7-distannyl-4,9-didecyl  $\beta$ -aNDT (Sn-4,9- $\beta$ -aNDT), respectively, in good yields.

Scheme 2 shows the synthetic route toward 5,10- $\alpha$ -aNDT and 5,10- $\beta$ -aNDT. Nucleophilic addition of 2-formylthiophene and 3-formylthiophene with dodecynyllithium led to the formation of the corresponding 1-(thiophene-2-yl)tridec-2-yn-1-ol (**7**) and 1-(thiophene-3-yl)tridec-2-yn-1-ol (**10**), which were oxidized by pyridinium chlorochromate (PCC) to generate the respective thiophenyl decynyl

ketones (**8** and **11**). The McMurry coupling reactions of **8** and **11** by using  $\text{TiCl}_4/\text{Zn}$  conditions afforded the olefinic products **9** and **12**, respectively, with a dominating *E*-form configuration.

In a similar manner, double annulations of the diene-yne moieties in **9** and **12** in the presence of DBU in heating NMP successfully formed the central naphthalene units of the desired 5,10- $\alpha$ -aNDT and 5,10- $\beta$ -aNDT products, which were further converted to 2,7-distannyl-5,10-didecyl  $\alpha$ -aNDT (Sn-5,10- $\alpha$ -aNDT) and 2,7-distannyl-5,10-didecyl  $\beta$ -aNDT (Sn-5,10- $\beta$ -aNDT), respectively, in good yields. The bis-stannylated aNDT-based monomers are ready for a variety of end-capping cross-coupling reactions or polymerization. By installation of aliphatic substituents, the resultant aNDT molecules all show good solubility in common organic solvents. All of the compounds were fully characterized by using  $^1\text{H}$  and  $^{13}\text{C}$  NMR and mass spectrometry (see the Supporting Information). The X-ray crystallographic structures of 4,9- $\alpha$ -aNDT and 5,10- $\beta$ -aNDT are shown in Figure 2. Indeed, the side-chain arrangement and the geometry of conjugated frameworks dramatically influence the intermolecular packing. The decyl groups of 4,9- $\alpha$ -aNDT are situated outside of the two  $\pi$ - $\pi$  stacking channels (Figure S3, Supporting Information), whereas the decyl groups of 5,10- $\beta$ -aNDT are intercalated within the  $\pi$ - $\pi$  stacking channels (Figure S4, Supporting Information).



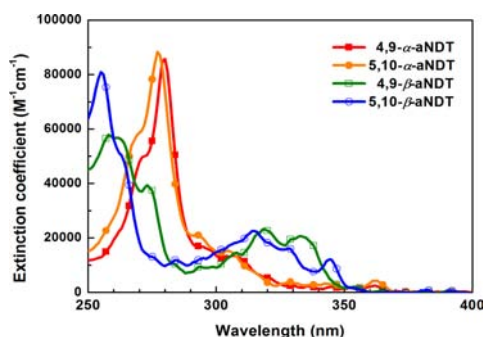
**Figure 2.** Top and side view of ORTEP: (a) 4,9- $\alpha$ -aNDT and (b) 5,10- $\beta$ -aNDT (80% probability for thermal ellipsoids).

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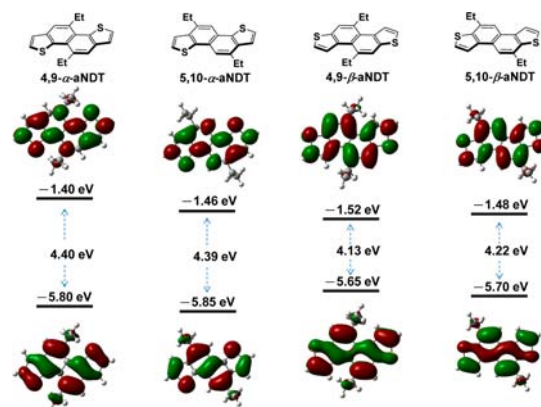
The normalized absorption spectra of the four isomeric aNDTs structures are shown in Figure 3. The absorption is highly dependent on the isomeric geometry of the aNDT frameworks. Although the absorption edges of the four isomeric aNDT molecules all reach up to around 350 nm, their absorption profiles are strikingly different. In comparison to  $\alpha$ -aNDTs-based molecules, the  $\beta$ -aNDT-based molecules not only showed a hypsochromic  $\lambda_{\text{max}}$  band at around 260–270 nm but also exhibited much intense peaks from 300 to 350 nm. The position of alkyl chains on  $\alpha$ -aNDT and  $\beta$ -aNDT also exerts notable effects on the optical properties. Inner 4,9- $\alpha$ -aNDT and 4,9- $\beta$ -aNDT showed slightly more red-shifted absorption  $\lambda_{\text{max}}$  than their corresponding outer 5,10-alkylated ones.



**Figure 3.** Absorption spectra of 4,9- $\alpha$ -aNDT, 5,10- $\alpha$ -aNDT, 4,9- $\beta$ -aNDT, and 5,10- $\beta$ -aNDT in dichloromethane.

By means of cyclic voltammetry (CV), the HOMO energy level was estimated to be  $-5.66$ ,  $-5.70$ ,  $-5.60$ , and  $-5.63$  eV for 4,9- $\alpha$ -aNDT, 5,10- $\alpha$ -aNDT, 4,9- $\beta$ -aNDT, and 5,10- $\beta$ -aNDT (Supporting Information). It is expected that the aNDT-based materials with low-lying HOMO energy levels will be advantageous for enhancing air stability and  $V_{\text{oc}}$  values for photovoltaic applications.

To gain more insight into the molecular orbital properties of four-isomeric aNDT structures, quantum-chemical calculations were performed. The decyl substituents are replaced with the ethyl groups for simplicity. The calculated data are summarized in Table S3 (Supporting Information) and HOMO/LUMO orbitals of the model compounds are shown in Figure 4.  $\beta$ -aNDT-based molecules have smaller theoretical optical band-gaps and higher lying HOMO energy levels compared to their corresponding  $\alpha$ -aNDT-based counterparts. Notably, the oscillator strengths of the HOMO–LUMO transitions of  $\alpha$ -aNDT units are much weaker than those of  $\beta$ -aNDT units, suggesting that the HOMO and LUMO orbitals of the  $\beta$ -aNDT units have better symmetry transition. This result can also rationally



**Figure 4.** Calculated HOMOs and LUMOs of 4,9- $\alpha$ -aNDT, 5,10- $\alpha$ -aNDT, 4,9- $\beta$ -aNDT, and 5,10- $\beta$ -aNDT with the DFT B3LYP/6-311G (d,p) level.

explain why  $\alpha$ -aNDT units showed much small absorption signals between 300 and 360 nm.

In conclusion, we developed a useful synthetic strategy to successfully prepare four isomeric aNDT molecules where the angular geometry of the fused thiophenes and the position of the side chain on the central naphthalene cores can be regiospecifically controlled. Dialkylated  $\alpha$ -aNDT and  $\beta$ -aNDT exhibited interesting and different optical and orbital properties which allow for fine-tuning the optoelectronic performance of the resultant aNDT-based materials. These dialkyl  $\alpha$ -aNDT and  $\beta$ -aNDT molecules have been further stannylated for future Stille cross-coupling. Incorporation of these dialkylated  $\alpha$ -aNDT and  $\beta$ -aNDT frameworks into donor–acceptor conjugated polymers with sufficient solubility are highly promising for PSCs and currently underway in our laboratory. We envision that this synthetic concept can also be applied to prepare a variety of coplanar acenes/heteroacenes substituted with solubilizing side chains.

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**Supporting Information Available.** Detailed synthesis, emission spectra, theoretical calculations, CV and DSC measurements, NMR spectra, and X-ray crystallographic data of 4,9- $\alpha$ -aNDT and 5,10- $\beta$ -aNDT. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.