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General Synthesis of Dinaphtho-[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (DNTT) Derivatives

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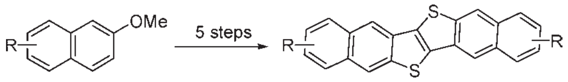
ABSTRACT



A new straightforward synthesis of dinaphtho[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (DNTT) derivatives from readily available 2-methoxynaphthalenes is described. Thus, newly developed derivatives of DNTT showed very high field effect mobility in the vapor-processed field-effect transistors up to 8 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$.

Organic thin-film transistors (OTFTs) have attracted great interest for their potential use in several electronic applications, including active-matrix displays, electronic paper, and chemical sensors.[1] The performances of OTFTs have been significantly improved in the past decade,[2] and in particular, the p-channel OTFT has now achieved many important milestones: high mobility ($>3.0\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$),[3] solution processability,[4] air-stability, flexibility, low-voltage operation,[5] and so on. For these achievements, the development of new superior materials, in particular, new organic semiconductors have contributed significantly.

Among the recently developed materials, dinaphtho[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (DNTT)[6] (Figure 1) and its derivatives[7] are particularly promising organic semiconductors for TFT applications because of high mobility ($\sim$3.0 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$ for DNTT,[6] $\sim$ 7.9 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$ for 2,9-$\mathrm{C_{10}}$-DNTTs[7b]) and good air stability. In addition, a recent investigation on derivatization of DNTT has revealed that

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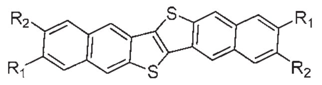
dimethyl derivatives (2,9- and 3,10-DMDNTT) can construct intriguing three-dimensional (3D) crystal structures.[7a]



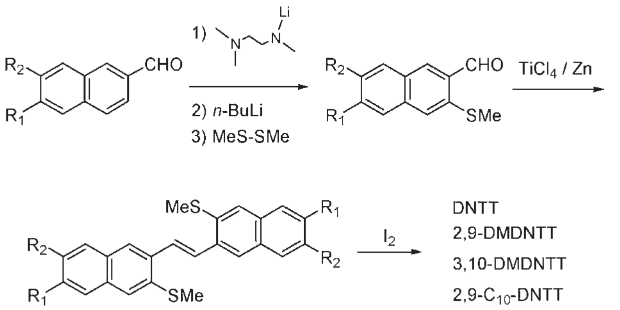
DNTT: R$_1$ = R$_2$ = H
2,9-DMDNTT: R$_1$ = CH$_3$, R$_2$ = H
3,10-DMDNTT: R$_1$ = H , R$_2$ = CH$_3$
2,9-C$_{10}$-DNTT: R$_1$ = n-C$_{10}$H$_{21}$, R$_2$ = H
2,9-DPhDNTT: R$_1$ = Ph, R$_2$ = H
3,10-DPhDNTT: R$_1$ = H , R$_2$ = Ph
3,10-C$_{10}$-DNTT: R$_1$ = H, R$_2$ = n-C$_{10}$H$_{21}$

Figure 1. Structure of DNTT and its derivatives.

For further development of organic semiconducting materials with the DNTT core, a general and efficient synthetic method is highly desirable. In the present contribution, we report a newly established synthetic route to DNTT from commercially available 2-methoxynaphthalene. Since various 2-methoxynaphthalene derivatives are readily available, the new method allows us to synthesize various DNTT derivatives. Here, straightforward syntheses of the parent DNTT, 2,9-C$_{10}$-DNTT,[7b] its 3,10-isomer, and two isomeric 2,9- and 3,10-diphenyl derivatives (DPhDNTTs) are demonstrated.

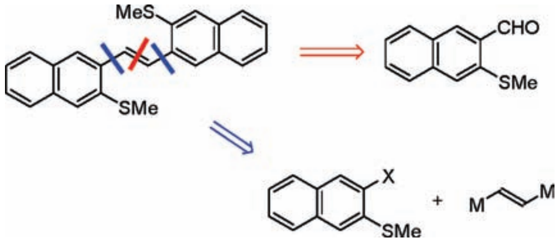
The reported synthesis of DNTT and its derivatives is shown in Scheme 1, which features the double-ring-closing reaction at the final step to construct the central thieno[3,2-*b*]thiophene moiety from the *trans*-1,2-bis(3-methylthionaphthalen-2-yl)ethenes.[6,7] For the synthesis of the precursors from 2-naphthaldehydes, the first methylthiolation at the 3-position is the critical step. However, this reaction is often problematic owing to tedious purification and moderate yields of the desired 3-functionalized naphthalenes (45–70% isolated yield depending on substituents on the 6- or 7-position). This is due to a concomitant competing reaction at the naphthalene α-position (1-functionalization) to form isomeric byproducts (15–30% yield), which should be removed by column chromatography and careful recrystallization processes. Thus, for the large-scale synthesis and further derivatization of DNTT, a new synthetic approach that enables highly selective synthesis from a readily available starting material should be developed.

Scheme 1. Reported Syntheses of DNTT and Its Derivatives



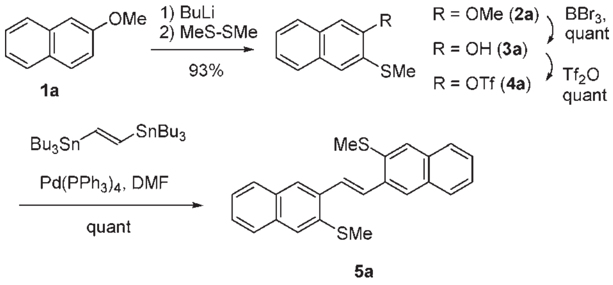
For this reason, we have examined another synthetic strategy for the precursor of DNTT, 1,2-bis(3-methylthionaphthalen-2-yl)ethenes (Scheme 2); different from the original DNTT syntheses, where the precursors were synthesized via the reductive dimerization of the corresponding 3-methylthio-2-naphthaldehydes (red arrow in Scheme 2), the new strategy involves a cross coupling reaction between two 3-methylthionaphthalene moieties and a bis-metalated ethene reagent (blue arrow in Scheme 2).

Scheme 2. Retrosynthetic Analysis of 1,2-Bis(3-methylthionaphthalen-2-yl)ethene



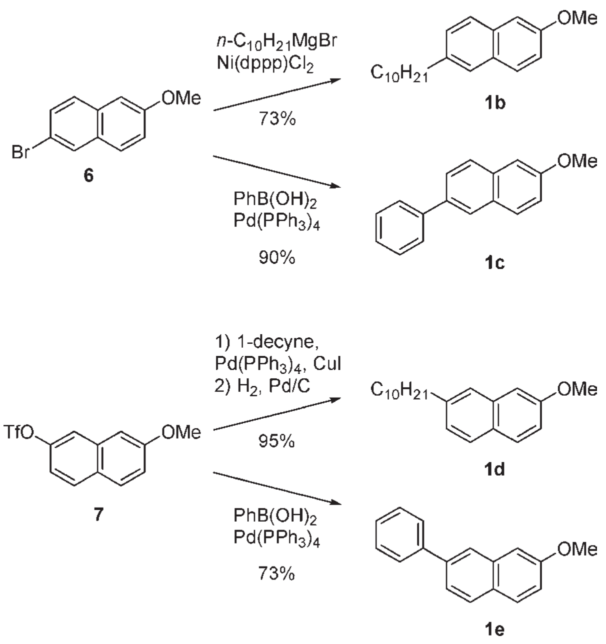
After several trials using different combinations of the X group on the naphthalene moiety and the metal (M) on the ethene moiety, we have finally found that the combination of X = OTf (i.e., 3-methylthio-2-naphthyl trifluoromethanesulfonate, **4a**) and M = SnBu$_3$ (i.e., *trans*-1,2-bis(tributylstannyl)ethene)[8] provides 1,2-bis(3-methylthionaphthalen-2-yl)ethene (**5a**) in a quantitative yield. More importantly, the synthesis of **4a** was demonstrated to be very easy as shown in Scheme 3. Starting from commercially available 2-methoxynaphthalene (**1a**), selective thiomethylation at the 3-position via a lithiation with butyllithium followed by a reaction with dimethyl disulfide gave 2-methoxy-3-methylthionaphthalene (**2a**) in 93% isolated yield after recrystallization.[10] Subsequent selective demethylation on the methoxy group followed by triflation of the resulting 3-methylthio-2-naphthol (**3a**)[9] proceeded quantitatively to give **4a**.

Scheme 3. New Synthetic Route to DNTT from 2-Methoxynaphthalene



Although the number of steps are increased, the new synthetic route to DNTT is superior to the original one in terms of easy experimental operation (no chromatographic separation of the isomer is necessary), cheap starting material, scalability, and total yield (79% for the present vs 39% yield for the previous one). As a result, a very effective synthetic route to DNTT is now established.

Scheme 4. Synthesis of 6- and 7-Substituted 2-Methoxynaphthalene Derivatives



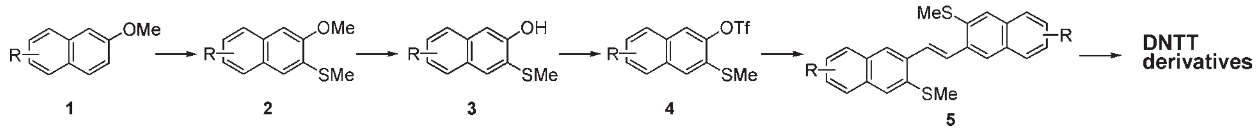
Another merit of the new method is that various derivatives of 2-methoxynaphthalene are readily available. For example, commercially available 6-bromo-2-methoxynaphthalene (**6**) can be easily converted into the 6-alkyl (**1b**) or 6-phenyl derivative (**1c**) via the Kumada[11] or Suzuki coupling[12] as shown in Scheme 4. Although it is not easy to prepare 7-halo-2-methoxynaphthalene derivatives, 7-methoxy-2-naphthyl trifluoromethanesulfonate (**7**) has been conveniently used for the synthesis of various 7-substituted 2-methoxynaphthalene derivatives.[13] Thus, **7** was employed either in the Sonogashira coupling with 1-decyne followed by hydrogenation to give the 7-decyl derivative (**1d**) or in the Suzuki coupling with phenylboronic acid to give the 7-phenyl derivative (**1e**).

Using these 2-methoxynaphthalene derivatives, the same synthetic method as in Scheme 3 was applied to synthesize the corresponding di-*n*-decyl and diphenyl derivatives of DNTT. The isolated yield in each step summarized in Table 1 is somewhat varied, since the reaction conditions for each transformation were not fully optimized. However, efficient syntheses of all the derivatives regardless of either the substituents or the substituted positions are achieved. Compared to the previous synthesis of 2,9-C_{10}-DNTT, not only the numbers of steps are reduced (from 7 to 6 steps)[14] but also the total yield is fairly improved (from 28% to 41%). Furthermore, it should be again emphasized that the present method does not require chromatographic separation of the isomeric byproduct, enabling a scalable synthesis.

Since DNTT and 2,9-C_{10}-DNTT give high-performance OTFTs, newly synthesized DNTT derivatives were also examined as the active semiconducting materials in the vapor processed OTFTs with the top-contact configuration on ODTS-treated Si/SiO_2 (200 nm) substrates. Preliminary measurements revealed unoptimized field-effect mobilities of ~8.0 $cm^2\ V^{-1}\ s^{-1}$ for 3,10-C_{10}-DNTT, ~3.4 cm^2 $cm^2\ V^{-1}\ s^{-1}$ for 2,9-DPh-DNTT, and ~3.8 $cm^2\ V^{-1}\ s^{-1}$ for 3,10-DPh-DNTT (Figure 2, Table 1). These high mobilities are quite promising, and further optimizations of the device processing conditions are now underway. In addition, the isomeric pairs of DNTT derivatives are suitable for investigating the structure-properties relationship in terms of the molecular ordering in the solid state.

In summary, we have successfully established a general and improved synthetic route to DNTTs from 2-methoxynaphthalene derivatives. Compared to the previous synthesis of DNTTs, the new method has many advantages including high yield, good selectivity, easy experimental operations, and versatility in derivatization. Using the new method, facile syntheses of isomeric C_{10}-DNTT and DPh-DNTT are demonstrated, and these new DNTT derivatives turn out to be very promising as high performance organic semiconductors. Thus, further device

Table 1. Isolated Yields (%) in the Synthesis of a Series of DNTT Derivatives and Mobilities (μ_{FET}s)[a] of Their Vapor-Processed Devices



R	2	3	4	5	DNTT derivatives	product	μ_{FET}[a]/$cm^2\ V^{-1}\ s^{-1}$
6-*n*-$C_{10}H_{21}$ (**1b**)	quant	72	quant	quant	85	2,9-C_{10}-DNTT	7.9[b]
7-*n*-$C_{10}H_{21}$ (**1d**)	93	85	94	quant	71	3,10-C_{10}-DNTT	8.0
6-Ph (**1c**)	quant	73	quant	57	89	2,9-DPh-DNTT	3.4
7-Ph (**1e**)	77	94	quant	63	85	3,10-DPh-DNTT	3.8

[a] Extracted from the saturation regime. [b] Reference 7b.

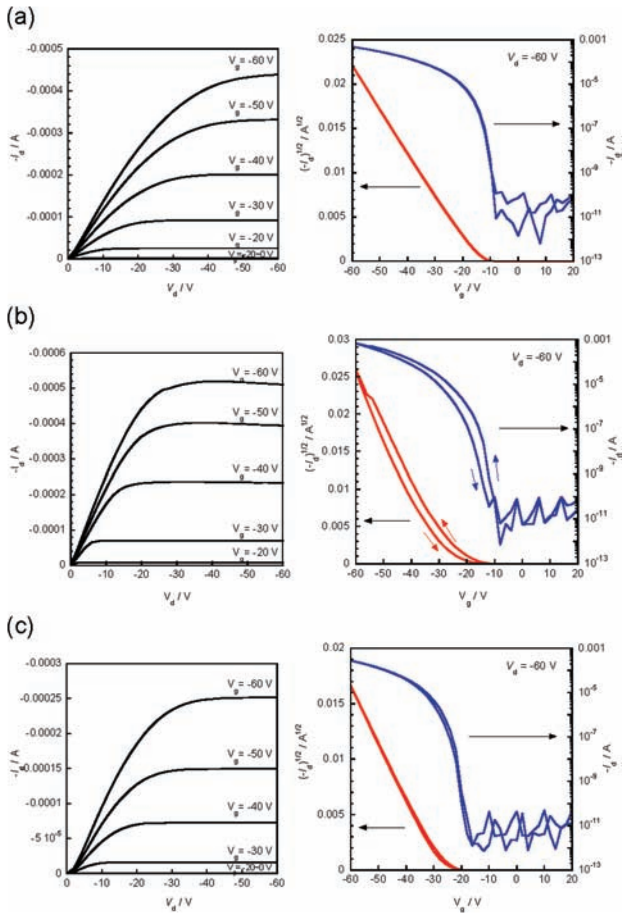


Figure 2. Transfer and output curves of (a) 2,9-DPhDNTT-, (b) 3,10-C_{10}-DNTT-, and (c) 3,10-DPhDNTT-based devices.

optimizations as well as structural investigation are now underway for the new DNTT materials.

From the viewpoint of synthetic chemistry, the essential point in the new synthetic method is the selective *o*-functionalization of methoxy-substituted aromatic rings. Thus, the present synthetic method may open the door to the synthesis of DNTT-related materials possessing the benzo-fused thieno[3,2-*b*]thiopehene substructure. Further explorations to various π-extend materials using the present synthetic method are also conducted in our group.

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Supporting Information Available. Experimental procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The previous synthesis of 2,9-C_{10}-DNTT started with methyl 6-bromo-2-naphthalate, which was first reduced to the corresponding hydroxymethyl compound and then oxidized to 6-bromo-2-naphthalaldehyde. Introduction of the *n*-decyl group on the aldehyde was done via the palladium-catalyzed Sonogashira coupling followed by dehydrogenation. As a result, the previous method consists of seven synthetic reactions from commercially available starting compound.