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Ambidextrous Catalytic Access to Dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT) Derivatives by Both Palladium-Catalyzed C−S and Oxidative Dehydro C−H Coupling

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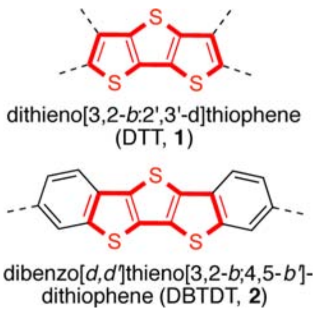
Ⓢ *Supporting Information*

ABSTRACT: A modular two-step synthesis of dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT) derivatives by C−S cross-coupling and oxidative dehydro C−H coupling is herein described. Dibenzo[*d*,*d*′]thieno[3,2-*b*;4,5-*b*′]dithiophene (DBTDT) and associated two donor (anisyl) and acceptor (acetyl) substituted DTT derivatives were synthesized by palladium-catalyzed cross-coupling sequences in 17% to 71% yield over two steps. The 5,5′-disubstituted DTT derivatives were characterized in terms of their photophysical (UV and fluorescence spectroscopy) and electrophysical (cyclovoltammography) properties.

Thiophene-based materials are widely used in organic electronics,[1] e.g. dye-sensitized solar cells[2] or semiconductors in organic field-effect transistors (OFET).[3] The fabrication of such electronic devices on flexible substrates is particularly interesting for displays[4] or sensors.[5] Thienoacenes have attracted considerable attention due to their increased optical transparency of visible light as well as thermal and atmospheric stability[6] in comparison to the most widely studied all-carbon-based semiconductor pentacene.[7] Fused sulfur-containing heteroacenes, e.g. dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT, **1**, Figure 1) derivatives, are useful as an active layer in thin film transistors,[8] and dibenzo[*d*,*d*′]thieno[3,2-*b*;4,5-*b*′]-dithiophene (DBTDT, **2**, Figure 1) has been found to be a promising candidate as a semiconductor in organic plastics.[9]

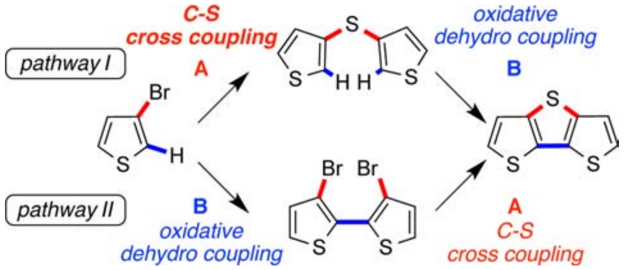
Notable efforts have been made for the efficient construction of dithieno[3,2-*b*:2′,3′-*d*]thiophene derivatives using condensation reactions[10] or reductive couplings.[6,9a,c,11] Despite the number of metal-catalyzed oxidative dehydro C−H couplings of thiophenes or benzothiophenes,[12] the application of this methodology has not been recognized for the synthesis of DTT or DBTDT derivatives or higher homologues until now. Herein we report the modular synthesis of DBTDT and two DTT derivatives by a two-step reaction sequence using C−S cross-coupling (**A**) followed by oxidative dehydro C−H coupling (**B**) methodologies (Scheme 1, pathway I). The order of the two


dithieno[3,2-*b*:2′,3′-d]thiophene (DTT, **1**)

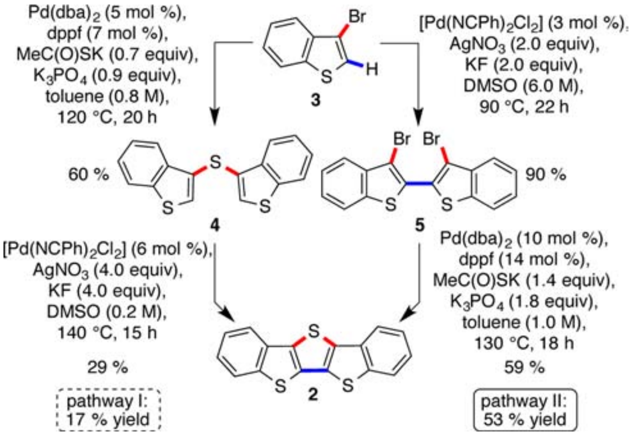
dibenzo[*d*,*d*′]thieno[3,2-*b*;4,5-*b*′]-dithiophene (DBTDT, **2**)

Figure 1. Dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT, **1**) dibenzo-[*d*,*d*′]thieno[3,2-*b*;4,5-*b*′]dithiophene (DBTDT, **2**).

Scheme 1. Synthetic Strategy for the Modular Construction of the Dithieno[3,2-*b*:2′,3′-*d*]thiophene Core



Scheme 2. Modular Synthesis of DBTDT (2)



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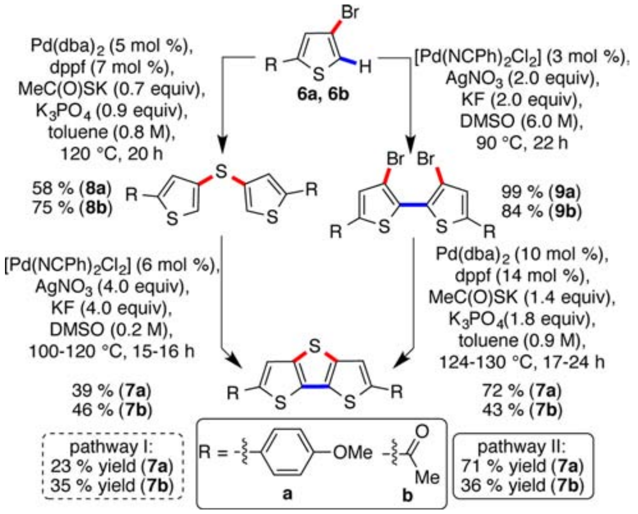
Scheme 3. Modular Synthesis of 2,6-Substituted DTT Derivatives



catalytic coupling reactions can be reversed (first **B** then **A**) permitting for the highest modularity while starting from the identical 3-bromothiophene as a precursor. This strategy both allows for choice of the sequence with the highest yield and also the ability to select the sequence with the most facile purification. Additionally, both reactions, the C−S and the oxidative dehydro C−H couplings, have well-documented functional group tolerance, which makes our strategy particularly attractive for acceptor-substituted DTT derivatives. Consequently this approach combines crucial synthetic aspects with multiple practical advantages. We selected C5-substituted 3-bromothiophene derivatives as substrates for the C−S/C−C cross-coupling sequence, since this position generally allows for electronic modification of DTT derivatives. 5-Substitued 3-bromothiophenes are readily accessible from commercial sources or by selective cross-coupling of 2,4-dibromothiophene.[13] To test our hypothesis we selected 3-bromobenzo[*b*]thiophene (**3**) as starting material for the two-step synthesis of DBTDT (**2**). First we investigated the palladium-catalyzed C−S coupling reaction[14] of **3** using different H_2S-surrogates, e.g. TIPS-SH,[15] Na_2S,[16] thiourea,[17] or thioacetate.[18] Generally these reactions were very efficient for the synthesis of the bis(3-benzothiophene)thioether (**4**), but only the thioacetate method[18b] gave synthetically useful yields for both of the C−S bond forming reactions according to pathways I and II (thioether and thiophene synthesis, Scheme 2). The palladium-catalyzed C−S cross-coupling was achieved in 60% yield starting from 3-bromobenzo[*b*]thiophene (**3**, Scheme 2, pathway 1). The final oxidative dehydro C−H coupling applying Moris conditions[12f] provided the product **2** in 29% yield (17% yield over two steps). However, reversal of the cross-coupling sequence improved the overall yield to 53% over two steps (pathway II). The oxidative dimerization of **3** to bis(3-bromobenzo[*b*]thiophene) (**5**) was achieved in excellent yield (90%). Subsequent reaction of **5** with potassium thioacetate in the presence of 10 mol % $Pd(dba)_2$/dppf furnished DBTDT (**2**) in 59% yield. Pathway II is attractive not only in light of the higher yields for both individual steps but also because the purification is facilitated. The bis-benzo[*b*]-thiophene derivative **5** and DBTDT (**2**) were both purified by extraction and crystallization. Our synthetic approach benefits from two catalytic transformations avoiding air or moisture sensitive reagents combining high yield with minimal synthetic effort, in comparison to literature-reported syntheses by Schroth (22% over two steps)[19] or Yamaguchi (56% over four steps).[20]

To demonstrate the feasibility of both pathways for the synthesis of 2,6-substituted DTT derivatives we conducted both reaction sequences with donor- and acceptor-substituted 3-bromo-5-(4-anisyl)thiophene (**6a**)[21] and commercially available 3-bromo-5- acetyl-thiophene (**6b**, Scheme 3). In general the unknown anisyl- and the acetyl-substituted DTT derivatives **7a** and **7b** were accessible by both pathways (yields over two steps: pathway I: 23% (**7a**); 35% (**7b**); pathway II: 71% (**7a**); 36% (**7b**)). Pathway II is very well suited for the synthesis of **7a** while the acetyl-substituted derivative **7b** was obtained in almost identical yields according to both reaction sequences. Such carbonyl-functionalized DTT derivatives are not accessible by the commonly applied reductive coupling since metalation of the 2-position by strong lithium bases is required.[6,9a,c,11a,b] Such reaction conditions are incompatible with carbonyl-containing functional groups. Our novel approach provides an efficient access to such acceptor-substituted DTT derivatives.

The photophysical and electrophysical properties of **2**, **7a**, and **7b** were investigated by UV-absorption, fluorescence (Figure 2), and cyclovoltametric measurements (summarized in Table 1; see Supporting Information for details). The photophysical and electrochemical data for **2** are in excellent agreement with literature reported values. The PMP-substituted DTT derivative **7a** shows a red shift in the absorption and emission spectra compared to DTT (**10**) and DPDTT (**11**) and a relatively high lying HOMO with an energy gap of −5.64 eV. This can be attributed to the electron-donating nature of the PMP group and significant overlap of the aromatic systems. Its optical HOMO/LUMO gap of 2.83 eV is the smallest for all investigated DTT derivatives. The electron-withdrawing nature of the acyl group in **7b** results in a significant decrease of the HOMO and LUMO level with a separation of 3.19 eV.

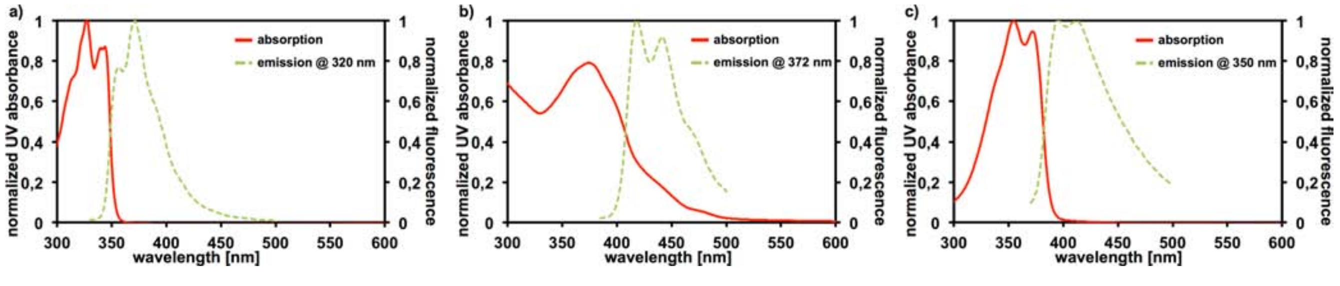


Figure 2. Normalized UV absorption and fluorescence spectra of (a) DBTDT (**2**), (b) **7a**, and (c) **7b** in tetrahydrofuran.

Table 1. Photophysical and Electrophysical Data for 2, 7a, and 7b

compound	λ_{max} [nm]	λ_{onset}[a] [nm]	λ_{em}[b] [nm]	ΔE_{opt}[c] [eV]	$eE_{1/2\ Fc/Fc+}$ [eV]	E_{HOMO}[d] [eV]	E_{LUMO}[e] [eV]
DBTDT	328	353	369	3.52	0.91	−6.01	−2.49
7a	274	439	416	2.83	0.54	−5.64	−2.81
7b	357	390	398	3.19	1.38[f]	−6.48	−3.29
data of literature reported compounds							
DBTDT	327[22]	359[9c]	368[22]	3.46[9c]	0.8[9c]	−6.08	−2.62
DTT (**10**)[g]	291[23]	319[23]	343[23]	3.88[23]	0.98[24]	−5.60	−1.72
DPDTT (**11**)	369[8a]	406[8a]	426[8a]	3.06	0.61[25]	−5.71	−2.65

[a] Calculated from the cross point of the absorption onset with baseline. [b] Maximum of emission. [c] Calculated from $E = h{\cdot}c/\lambda_{onset}$. [d] $E_{HOMO} = -(eE_{1/2(substrate)} + 5.1\ eV)$ referenced to Fc/Fc^+ couple. [e] $E_{LUMO} = E_{HOMO} + \Delta E_{opt}$. [f] Onset of oxidation peak. [g] Electronic spectra were reported for CH_2Cl_2; DPDTT = 2,6-diphenyldithieno[3,2-*b*:2′,3′-*d*]thiophene.

In summary, we exemplified the two-step synthesis of 2,6-donor- and acceptor-substituted dithieno[3,2-*b*:2′,3′-*d*]-thiophenes by two reaction sequences applying palladium-catalyzed C−S cross-coupling and oxidative dehydro C−H coupling. The new DTT derivatives were characterized by photophysical and electrophysical methods. The presented methodology generally allows the efficient synthesis of DTT derivatives by two alternative reaction sequences, which enable the optimization of the chemical yield and/or the purification (column chromatography vs crystallization).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, NMR spectroscopic data, UV absorption, fluorescence, cyclovoltammograms of **2**, **7a**, and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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