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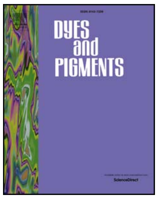

# Synthesis and electronic properties of 5,5″-diacceptor substituted terthiophenes

Natascha Breuer, Thomas J.J. Müller*

*Institut für Organische Chemie und Makromolekulare Chemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany*

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## ABSTRACT

Acceptor-substituted 5,5″-terthiophenes were synthesized by a consecutive pseudo-five-component Sonogashira alkynylation-Fiesselmann cyclocondensation synthesis generating diethyl terthiophene-5,5″-dicarboxylates and terthiophene-5,5″-dinitrile. The diethyl terthiophene-5,5″-dicarboxylates were directly reacted with a variety of amines to give 5,5″-biscarboxamide substituted terthiophenes in moderate to excellent yields (62-99%). The electrochemical and photophysical properties of these novel diacceptor-substituted terthiophenes were examined by cyclic voltammetry as well as by absorption and emission spectroscopy. All synthesized 5,5″-diacceptor-substituted terthiophenes possess reversible oxidation potentials between 300 und 1550 mV. The compounds are blue luminescent and the emission maxima appear between 461 and 476 nm with fluorescence quantum yields between 0.14 and 0.33.

## 1. Introduction

Organic solar cells are promising, economical electricity generators that are inexpensive and can be deposited on flexible substrates using low-cost materials and fabrication methods [1]. In this context a major challenge for synthetic chemistry lies in developing molecular materials with tailored properties for achieving optimal power efficiencies. Particularly interesting are conjugated oligomers with readily tunable electronic features by their length [2]. The electronic properties of oligothiophenes can be extensively controlled due to their structural diversity. They exhibit unique electronic, optical and redox characteristics and show unique self-assembly on solid surfaces or in bulk. The stability of the conjugated chain and favorable charge transport properties are warranted by the high polarizability of the thiophene rings. These traits are particularly favorable for application in organic and molecular electronics [3]. Acceptor-donor-acceptor type oligothiophenes have turned out to be efficient and well-investigated donor materials for organic solar cells [2b,4].

Terthiophenes can usually be accessed in two different ways. Either the central thiophene core is formed by cyclization of acyclic precursors or thiophene units are ligated by bond-forming reactions to furnish the terthiophene structure. Acyclic precursors can be for instance 1,4-diketones or butadiyne derivatives. 1,4-Diketones reacted with Lawesson's reagent as a thionation agent form the central thiophene core by Knorr-type cyclocondensation [5]. The cyclization of butadiynes by sodium sulfide or hydrogen sulfide also leads to the terthiophene system [6]. For ligating thiophene moieties, various cross coupling reactions can be efficiently used. For instance palladium-catalyzed coupling reactions, such as Stille [7] and Suzuki [8] couplings but also the nickel-catalyzed Kumada [9] coupling reaction can be employed.

Recently, we ~~have~~ disclosed a novel strategy for constructing terthiophenes in a one-pot fashion. Alkynones are reactive Michael systems generated by a preceding acid chloride alkynylation, which are most favorable for consecutive multicomponent syntheses of heterocycles [10]. They are known to undergo a Fiesselmann reaction with ethyl 2-mercaptoacetate furnishing the corresponding thiophene derivatives [11]. By employing 2,5-bisalkynone thiophene and ethyl 2-mercapto acetate, the desired terthiophene are directly accessed in good yields [12].

Starting from 2,5-diethynylthiophene diethyl terthiophene-5,5″-dicarboxylates are formed by a pseudo-five-component synthesis, where the diyne reacts with two equivalents of acid chlorides and two equivalents of ethyl 2-mercapto acetate [12a]. By variation of the acid chloride, differently 4,4″-disubstituted terthiophenes are readily accessible. Upon introducing electron withdrawing groups at the termini of terthiophenes their electron affinity can be increased. Furthermore, the choice of cyano groups enables close intermolecular contacts in the solid state by hydrogen-bonding (CN···H) [13].

As part of our program to develop diversity-oriented syntheses of blue emitters initiated by multicomponent reactions [14], we report herein the synthesis of 5,5″-diacceptor-substituted terthiophenes by a

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* Corresponding author.

*E-mail address:* ThomasJJ.Mueller@hhu.de (T.J.J. Müller).

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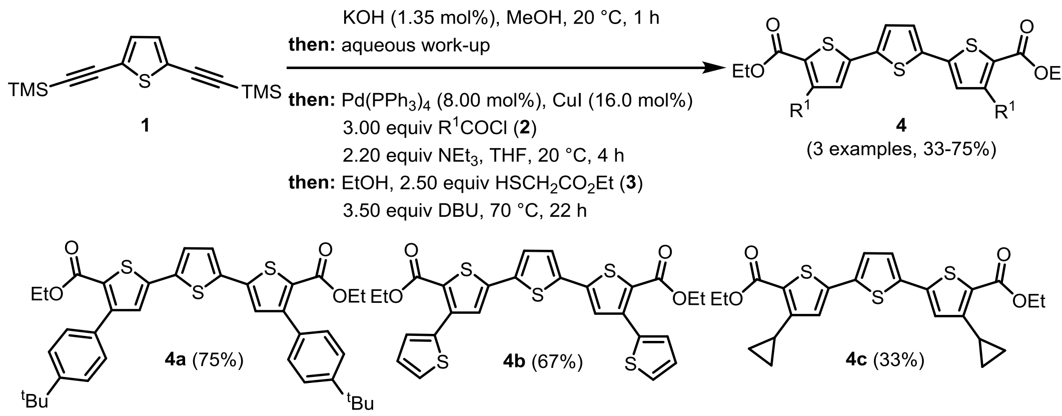


**Scheme 1.** Consecutive pseudo-five-component Sonogashira alkynylation-Fiesselmann cyclocondensation synthesis of diethyl terthiophene-5,5″-dicarboxylates **4**.

consecutive pseudo-five-component Sonogashira alkynylation-Fiesselmann cyclocondensation synthesis and by subsequent Lewis acid mediated conversion of 5,5″-diethylester-substituted terthiophenes into terthiophene-5,5″-diamides. The electronic and photophysical properties (redox potentials, absorption and emission) are reported and discussed.

## 2. Results and discussion

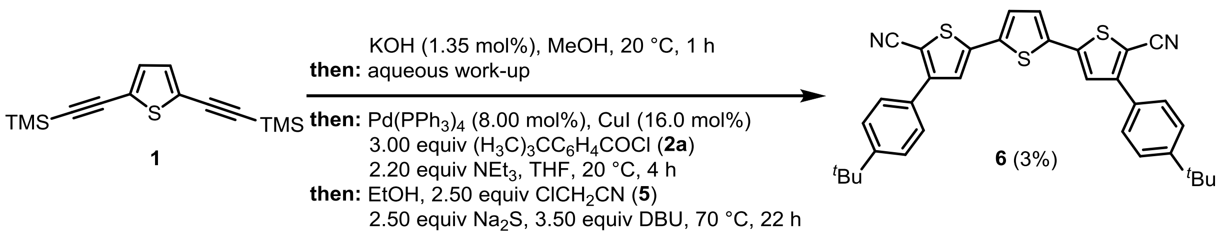
### *2.1. Synthesis*

The consecutive pseudo-five-component synthesis of diethyl terthiophene-5,5″-dicarboxylates begins from 2,5-bis(trimethylsilylethynyl) thiophene [15] (**1**) as a stable storage form of the sensitive 2,5-diethynyl thiophene. In situ desilylation and quick aqueous work-up furnished the diyne, which underwent Sonogashira coupling acid chlorides **2** forming dialkynones that were transformed in the same reaction vessel by a Fiesselmann reaction with ethyl 2-mercaptoacetate (**3**) to give three terthiophene diesters **4** in moderate to good yield (Scheme 1).

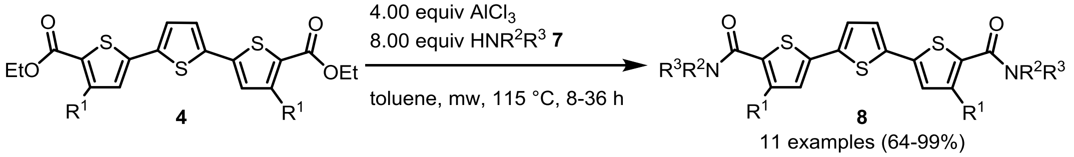
For introducing cyano groups in the 5,5″-positions of the terthiophene mercapto acetonitrile was used as condensation agent. Due to the instability and pronounced reactivity of mercapto acetonitrile, it was *in situ* generated by addition of chloroacetonitrile (**5**) and sodium sulfide in the second step of the one-pot synthesis. The terthiophene-5,5″-dicarbonitrile **6** was isolated in only 3% yield due to poor solubility and difficult separation upon purification by column chromatography (Scheme 2).

For preparing 5,5″-biscarboxamide substituted terthiophenes the transformation of an ester moiety to an amide could be considered in a three step reaction via carboxylic acid and acyl chloride [16]. However, we considered the direct conversion of an ester into the corresponding amide. Employing diethyl terthiophene-5,5″-dicarboxylates **4**, amines **7**, and different bases, such as potassium *tert*-butoxide, sodium ethoxide or potassium phosphate, only gave trace amounts of the desired 5,5″-biscarboxamide substituted terthiophenes. Upon using aluminum chloride as an activating Lewis acid instead of base addition gave rise to moderate yields. Further optimization led to an increase of yield with toluene as a solvent at 115 °C for 45 h. Finally, the reaction time was reduced from 45 to 16 h by performing the reaction under microwave irradiation. With these optimized reaction conditions in hand, a variety of primary and secondary amines **7** were employed in the synthesis and 11 examples of 5,5″-biscarboxamide substituted terthiophenes **8** were obtained in moderate to excellent yields (Scheme 3, Table 1). Besides heterocyclic secondary amines, such as morpholine (**7a**), piperidine (**7b**), and pyrrolidene (**7c**), aliphatic primary amines are equally well transformed (Table 1, entries 5-11).

Interestingly, the synthesis of compound **8a** can also be performed in a one-pot fashion as a pseudo-seven component reaction starting from bis(trimethylsilyl)ethynyl thiophene (**1**) upon increasing the loading of AlCl$_3$ and morpholine (**7a**) as well as the reaction time of the amidation step give the bisamide **8a** in 54% yield compared to 60% for the two-step process (calculated as combined yields for the formation of compounds **4a** and **8a**), however, with a single purification operation for the one-pot process (Scheme 4).



**Scheme 2.** Consecutive pseudo-five-component Sonogashira alkynylation-Fiesselmann cyclocondensation synthesis of 4,4″-bis[4-(*tert*-butyl)phenyl]-(2,2′:5′,2″-terthiophene)-5,5″-dicarbonitrile (**6**).



**Scheme 3.** Synthesis of 5,5″-biscarboxamide substituted terthiophenes **8**.