



New fast synthesis route for symmetric and asymmetric phenyl-substituted photochromic dithienylethenes bearing functional groups such as alcohols, carboxylic acids, or amines

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ABSTRACT

This Letter describes an efficient three-step synthesis route of symmetric and asymmetric phenyl-substituted photochromic 1,2-dithienylethenes bearing unprotected functional groups (i.e., alcohols, carboxylic acids or amines). These products can be easily obtained by typical Suzuki cross-coupling between photochromic dichlorides and commercial available boronic acids or pinacol esters.

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During the last decade, photochromic compounds based on 1,2-dithienylethenes (DTEs) have been extensively studied^{1,2} for their possible application in optoelectronics,³ optical memories,^{4–9} waveguides,¹⁰ photo-switches,^{11,12} or even in astronomical devices.^{13,14} This is based on the fact that the reversible photoresponsive isomerization of these molecules turns into evident changes in the bulk material properties (UV–vis–NIR absorption, refractive index, and redox potential).² Moreover, DTEs offer excellent thermal stability of both isomers, fatigue resistant character, rapid response, and high reactivity in the solid state.^{2,15} By well considered molecular design these different properties can be tailored and optimized.

DTEs bearing phenyl groups have been of particular interest in the last years.^{16–18} The aromatic substituent increases the quantum yield of the ring closure reaction, and leads to very stable structures with extended delocalized π -systems. The phenyl group also increases the absorption coefficient of the photochromic molecule and the conversion at the photostationary state. The physical chemical properties of the phenyl-substituted DTEs can be further modified by suitable functionalization of the aromatic rings with electron-donating or electron-withdrawing groups.^{19,20} In this publication, we describe a fast synthesis route for symmetric and asymmetric functionalized phenyl-substituted dithienylethenes. The asymmetric photochromic molecules find potential application in different fields, for instance in biological systems^{21,22} or to

obtain donor–acceptor systems. Unfortunately, the synthesis of these asymmetric molecules is rather complex.

Another peculiarity of functionalized DTEs is the possibility of subsequent reactions to yield self-assembled monolayers (SAMs), polymers, or sol–gel materials, which are used to obtain devices for optoelectronic applications. As an example, organic photochromic molecules functionalized with thiols react with gold surfaces or nanoparticles, thus giving systems, which have been proposed as electro-optical molecular switches.^{23–26} Monolithic materials to be used as optical devices can also be produced by sol–gel technology, which has been already used to produce photochromic glasses.^{27–29} For both strategies, photochromic molecules with functional groups in the *para*-position of the phenyl ring are preferred. Appropriate groups can be alcohols, carboxylic acids, or amines. Except for the diamine derivative **3e**, synthesis routes for all molecules described in Figure 1 are already known in the literature.^{30,16,17,31} Although the development of new DTE derivatives is still a forefront research, until now just very time consuming and often low yielding reaction pathways are reported. To achieve the photochromic dicarboxylic acid **3d**, Irie et al. introduced a six-step synthesis route.³⁰ For the synthesis of dialcohol **3c**, first published by Kawai et al., protracted six-step procedures are known with typical protection and deprotection techniques.¹⁷ Furthermore, unsymmetrical DTEs with different functionalized phenyl rings are even more difficult to obtain.³²

In this Letter we describe a high yielding and fast three-step synthesis route³³ to achieve symmetric as well as asymmetric DTEs functionalized with phenyl derivatives such as phenyl alcohol, car-

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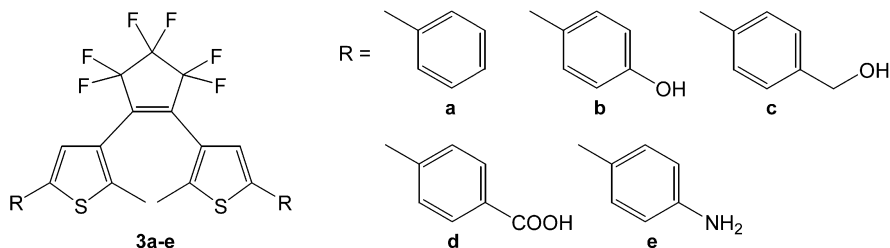
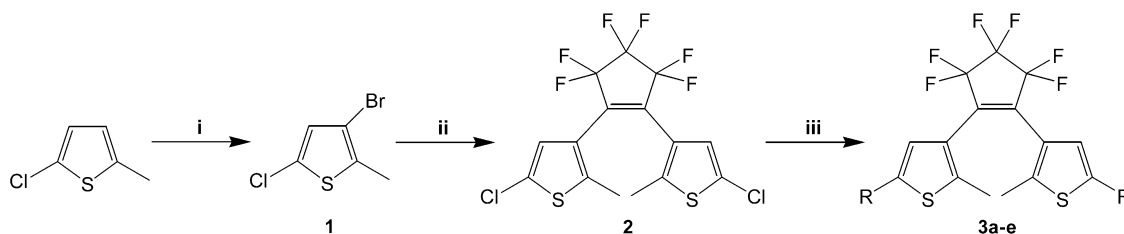


Figure 1. Photochromic DTEs bearing functionalized phenyl rings.



Scheme 1. Reagents and conditions: (i) Br_2 , CHCl_3 , 93% (ii) $n\text{-BuLi}$, -78°C , C_5F_8 , THF (iii) $\text{Pd}(\text{PPh}_3)_4$, Na_2CO_3 , Phenylboronic acid (a), 4-hydroxyphenylboronic acid pinacol ester (b), 4-(hydroxymethyl)phenylboronic acid (c), 4-aminophenylboronic acid pinacol ester (d), 4-carboxyphenylboronic acid (e), $\text{DME-H}_2\text{O}$ (4:1), reflux.

boxylic acids, or amines. The general reaction (Scheme 1) consists in (i) the bromination³⁴ of the commercially available 2-chloro-5-methylthiophene, (ii) the Dixon reaction³⁵ with the octafluorocyclopentene, and (iii) a Suzuki coupling with different boronic acids or pinacol esters.

Following this procedure, **2** is used as the key intermediate;³⁶ indeed the photochromic dichloride is a known source material for the preparation of photochromic derivatives.^{37,19} Consequently, well established recipes based on a McMurry coupling have been already reported.^{38,39} However, to obtain this molecule we followed a fast reaction pathway previously not mentioned concretely in the literature.⁴⁰ As only the bromine atom of 3-bromo-5-chloro-2-methylthiophene **1** is reactive against n -butyllithium at -78°C , **1** can be selectively lithiated and subsequently treated with octafluorocyclopentene to yield the desired photochromic dichloride in a quite good yield (55%) via a twofold addition–elimination sequence (Scheme 1). Without exception, the subsequent reactions of **2**, which have been so far described in the literature, are based on lithiation followed by the treatment with different reactive reagents to yield the corresponding carboxylic acids,³⁷ aldehydes,³⁷ thioethers,³⁷ boronic acids,¹⁹ phosphines,⁴¹ or other halogenides.³⁷ A following Suzuki coupling of the boronic acid with a bromobenzene derivative provided phenyl-substituted 1,2-dithienylethenes.

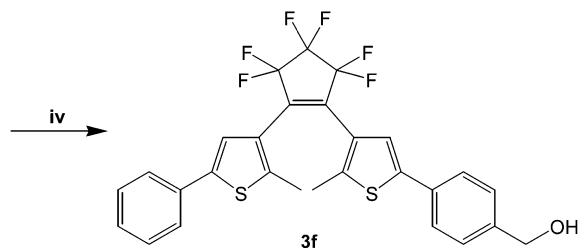
In the route herewith presented, the phenyl-substituted 1,2-dithienylethenes **3a–e** (Fig. 1) are directly synthesized via typical Suzuki cross-coupling reactions⁴² using commercially available boronic acids or pinacol esters.^{43–47} In practice, this is a powerful methodology for the incorporation of acidic, neutral, and weakly basic functional groups such as acids, alcohols, or even amines attached to the phenyl substituents without further protection. In this case, we used $\text{Pd}(\text{PPh}_3)_4$ as the catalyst, which is known to couple activated heteroaryl chlorides such as **2** with phenylboronic acids and especially with derivatives bearing unprotected functional groups.⁴⁸ Thus, a variety of photochromic molecules with the desired functionalized phenyl substituents are accessible in remarkably high isolated yield (among 85–95%). For instance, **2** couples with 4-(hydroxymethyl)phenylboronic acid in the presence of 5 mol % $\text{Pd}(\text{PPh}_3)_4$ ($\text{DME-H}_2\text{O}$ (4:1), reflux) to give 1,2-bis-[2-methyl-5-(p -(hydroxymethyl)phenyl)-3-thienyl] hexafluorocyclopentene **3c**⁴⁴ in high yield (86%). Although only a few

reports can be found on the successful Suzuki coupling of arylchlorides with reactants possessing unprotected amino groups⁴⁹ also the previously unknown diamine **3e** is achievable in a 84% yield⁴³.

The same reaction pathway can be conveniently applied to obtain not only symmetric-substituted dithienylethenes, but also asymmetric photochromic units. In this case, a phenylboronic acid derivative is initially added in a molar ratio of 1:1 to dichloride **2** following the same procedure adopted for the symmetrical 1,2-diarylethenes **3a–e**. After a certain reaction time which is determined monitoring the reaction by TLC, the second derivative is introduced. For example, by using phenylboronic acid as the first derivative (iv) (Scheme 2), and 4-(hydroxymethyl)-phenylboronic acid as the second (v), we were able to obtain **3f**.⁵⁰ If compared to **3a–e** the yield is slightly decreased to 60% because of symmetric by-products we were not able to prevent completely. The stoichiometric ratio between reactants was varied to determine its effect on reaction yield. An excess of 30 mol % of dichloride **2** results in an increase of 5% of yield, thus indicating that changes in the stoichiometry slightly affect the conversion.

This concept should be easily transferred to numerous different phenyl-substituted photochromic molecules with mixed functionalization, and it offers a fast possibility to tune the optical properties of DTEs or to introduce single groups for further reactions.

In conclusion, we have accomplished an efficient three-step synthesis route of symmetric and asymmetric phenyl-substituted photochromic 1,2-dithienylethenes bearing unprotected functional groups such as alcohols, carboxylic acids, or amines. Starting from the versatile intermediate **2**, these products can be easily obtained



Scheme 2. (iv) $\text{Pd}(\text{PPh}_3)_4$, Na_2CO_3 , phenylboronic acid, 4-(hydroxymethyl)phenylboronic acid, $\text{DME-H}_2\text{O}$ (4:1), reflux.

by typical Suzuki cross-coupling. The results presented here offer the possibility to obtain a number of different 1,2-diarylethenes compounds in a very fast and high yielding process.

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- Procedure for the synthesis of 1,2-bis-[2-methyl-5-(p-hydroxyphenyl)-3-thienyl]hexafluorocyclopentene (3b)*: Following the procedure as described for **3a**, the title compound was prepared from **2** (0.5 g, 1.14 mmol) and 4-hydroxyphenylboronic acid pinacol ester (0.554 g, 2.52 mmol). After purification by column chromatography on silica gel (diethyl ether), a slightly blue solid is obtained (0.54 g, 85%). ¹H NMR (400 MHz, CDCl₃): δ 1.94 (s, 6H), 6.86 (d, J = 8.7 Hz, 4H), 7.15 (s, 2H), 7.42 (d, J = 8.7 Hz, 4H); ESI-MS: m/z 570.9 [M+Na]⁺. Calcd for C₂₇H₁₈F₆O₂S₂: C, 58.69; H, 3.28. Found: C, 58.49; H, 3.49.
- Procedure for the synthesis of 1,2-bis-[2-methyl-5-(p-(hydroxymethyl)phenyl)-3-thienyl]hexafluorocyclopentene (3c)*: Following the procedure as described for **3a**, the title compound was prepared from **2** (0.5 g, 1.14 mmol) and 4-(hydroxymethyl)phenylboronic acid (0.383, 2.52 mmol). After purification by column chromatography on silica gel (diethyl ether), a slightly blue solid is obtained (0.57 g, 86%). ¹H NMR (400 MHz, CDCl₃): δ 1.97 (s, 6H), 4.71 (s, 4H), 7.28 (s, 2H), 7.38 (d, J = 8.2 Hz, 4H), 7.54 (d, J = 8.2 Hz, 4H); ESI-MS: m/z 603.0 [M+Na]⁺. Calcd for C₂₉H₂₂F₆O₂S₂: C, 59.99; H, 3.82. Found: C, 61.11; H, 3.91.
- Procedure for the synthesis of 1,2-bis-[2-methyl-5-(p-carboxyphenyl)-3-thienyl]hexafluorocyclopentene (3d)*: Following the procedure as described for **3a**, the title compound was prepared from **2** (0.5 g, 1.14 mmol) and 4-carboxyphenylboronic acid (0.418, 2.52 mmol). In contrast to **3a** the reaction mixture had to be quenched with aqueous HCl to protonate the product. After purification by column chromatography on silica gel (diethyl ether) a slightly blue solid is obtained (0.65 g, 94%). ¹H NMR (400 MHz, acetone-d₆): δ 2.10 (s, 6H), 7.70 (s, 2H), 7.81 (d, J = 8.5 Hz, 4H), 8.08 (d, J = 8.5 Hz, 4H); ESI-MS: m/z 606.9 [M-H][−]. Calcd for C₂₉H₁₈F₆O₄S₂: C, 57.24; H, 2.98; found: C, 57.60; H, 3.19.
- Procedure for the synthesis of 1,2-bis-[2-methyl-5-(p-aminophenyl)-3-thienyl]hexafluorocyclopentene (3e)*: Following the procedure as described for **3a**, the title compound was prepared from **2** (0.5 g, 1.14 mmol) and 4-aminophenylboronic acid pinacol ester (0.552, 2.52 mmol). After purification by column chromatography on silica gel (diethyl ether), a green-blue solid is obtained (0.53 g, 84%). ¹H NMR (400 MHz, CDCl₃): δ 1.95 (s, 6H), 3.76 (s, 4H), 6.67 (d, J = 8.5 Hz, 4H), 7.10 (s, 2H), 7.34 (d, J = 8.5 Hz, 4H); ESI-MS: m/z 551.0 [M+H]⁺. Calcd for C₂₇H₂₀F₆N₂S₂: C, 58.90; H, 3.66; N, 5.09. Found: C, 58.79; H, 3.81; N, 5.30.

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50. Procedure for the synthesis of 1-[2-methyl-5-phenyl-3-thienyl]-2-[2-methyl-5-(p-(hydroxymethyl)phenyl)-3-thienyl]hexafluorocyclopentene (**3f**): Phenylboronic acid (0.139 g, 1.14 mmol), **2** (0.5 g, 1.14 mmol), Na₂CO₃·10H₂O (1.31 g, 4.58 mmol), and Pd(PPh₃)₄ (0.132 g, 0.11 mmol) were placed in a reaction flask under inert atmosphere. DME (20 ml, degassed) and water (5 ml, degassed) were subsequently added, and the solution was refluxed under Argon. After 24 h 4-(hydroxymethyl)phenylboronic acid (0.190, 1.25 mmol) and Pd(PPh₃)₄ (13 mg, 0.01 mmol), were added and heating was continued for ca. 15 h. Now the mixture was quenched with water (20 ml) and ether (50 ml). The organic layer was separated and the water phase was extracted further times with ether (3 × 50 ml). The combined organic phases were dried (Na₂SO₄), filtered, and the solvent was evaporated in vacuo. A blue solid (0.38 g, 60%) was obtained after purification by twofold column chromatography on silica gel (preliminary purification: diethyl ether, final purification: chloroform). ¹H NMR (400 MHz, CDCl₃): δ 1.97 (s, 6H), 4.72 (s, 2H), 7.28 (s, 2H), 7.32–7.56 (m, 9H); ESI-MS: *m/z* 572.9 [M+Na]⁺. Calcd for C₂₈H₂₀F₆OS₂: C, 61.08; H, 3.66. Found: C, 60.89; H, 3.94.