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Synthesis of Spiro[cyclopenta[1,2-*b*:5,4-*b'*]DiThiophene-4,9'-Fluorenes] SDTF dissymmetrically functionalized

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ABSTRACT

Recently, spiro compounds and more precisely spirobifluorene (SBF) based organic semiconductors have attracted considerable attention. In this context, the development of heterocyclic analogues of the SBF appears interesting. In this Letter, we report a strategy to prepare two selectively brominated Spiro[cyclopenta[1,2-*b*:5,4-*b'*]DiThiophene-4,9'-Fluorene] SDTF derivatives. Moreover, it is worth noting that our investigations also allowed the synthesis of an original and scantily described dispiro-oxepine motif. In order to probe the potential and the difference of properties of prepared compounds, the later have been functionalized by ethylenedioxythiophene moieties. Electrochemical and spectroscopic properties of the corresponding compounds are described herein.

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Introduction

Spiro-annulated compounds represent an important and promising class of materials for optoelectronic applications. The spiro concept consists in connecting two or more π -conjugating systems via a common sp^3 hybridized atom.¹ The 3D-steric hindrance brought by these cross-shaped derivatives typically conducts to improved solubilities in comparison with parent compounds, high glass transition temperatures associated with isotropic optoelectronic properties for molecular materials. Among numerous examples reported in the literature (such as e.g., spiroopyran, spirooxazine,² spirobisindane³ or spirozilabifluorene⁴) spirobifluorene (SBF) derivatives are certainly the most studied.⁴ Indeed, applications involving the latter span various domains including organic light emitting devices (OLED), hybrid and organic solar cells as well as electrode materials.⁵

In order to design new materials, some synthetic efforts have been dedicated to the substitution of one or more benzene cycle(s) by heterocycle(s) especially thiophene ring(s). In this context, Sinige and co-workers in 1970 have reported the preparation of Spiro[cyclopenta[1,2-*b*:5,4-*b'*]DiThiophene-4,9'-Fluorene] SDTF.⁶ Alternative syntheses were also independently described by Bauerle et al. and then by Kobayashi et al.⁷ In both cases, the synthesis consists in preparing in first place a carbinol intermediate from a diarylfluorenone derivative and a nucleophilic lithiated or organo-

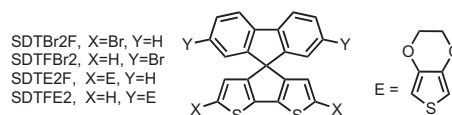


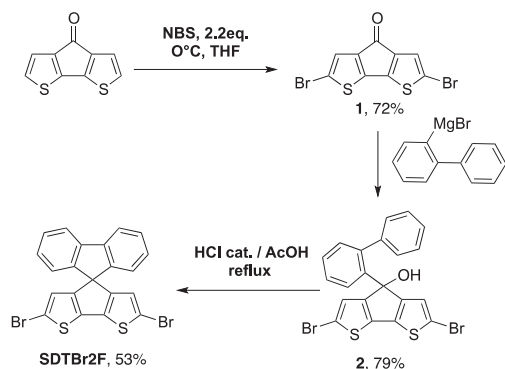
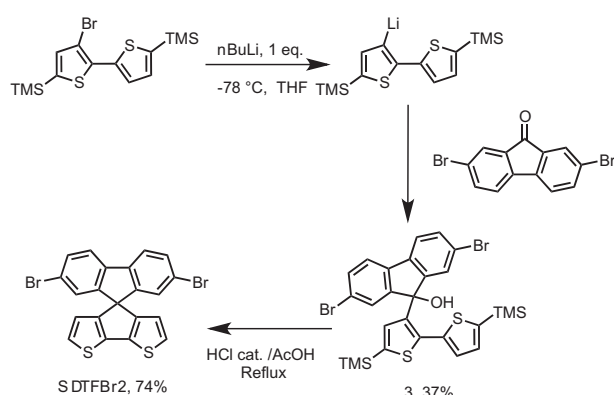
Figure 1. Target SDTF compounds.

metallic compound. The latter is subsequently cyclized in acidic conditions. Unfortunately, during this second step, an intermolecular oligomerization of the intermediate is also possible leading to the corresponding dimer as the major side product.⁷ If the ratio between dimer and desired spiro derivatives is strongly affected by the temperature and the concentration, it represents a major drawback for the preparation of spiroderivatives incorporating two or more thiophene moieties.

In order to circumvent this issue, more recently, Wu and co-workers suggested to protect the alpha positions of the thiophene units⁸ by silyl groups, and applied this strategy to the preparation of SDTF based dyes for DSSC. If this strategy does lead to SDTF as the main product, it implies successive protection/deprotection steps followed by halogenation and then functionalization, which is not propitious to straightforward and high yield synthesis. Moreover, the further derivatization of the SDTF motif is limited to the terminal positions of thiophene moieties more reactive than the phenyl ones. Consequently, we propose herein to prefunctionalize the terminal positions of π -conjugating systems by halogen atoms that may prevent intermolecular oligomerization, and also,

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Scheme 1. Synthesis of **SDTBr2F**.Scheme 2. Synthesis of **SDTFBr2**.

allow some large possibilities of further functionalization (halogen–lithium exchange, palladium mediated cross coupling reactions...). In this context, we report here our efforts to develop two Spiro[cyclopenta[1,2-*b*:5,4-*b'*]DiThiophene-4,9'-Fluorene] nodes prefunctionalized on their thiophenic (**SDTBr2F**) or benzenic **SDTFBr2** terminal positions by bromine atoms (Fig. 1).

To reach this objective, our synthetic approach consists in performing a nucleophilic addition with a lithiated or Grignard reagent on a pre-halogenated diarylcyclopentadienone compound.

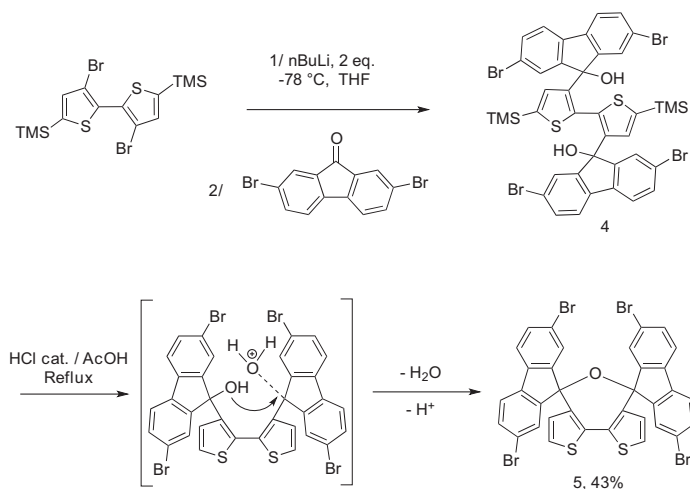
Moreover, it is worth noting that extended to bislithiated reactant, the strategy further allowed us to prepare a new and original 3D based dispiro-oxepine system. In order to illustrate the scope of possibilities in terms of functionalization offered by the presence of bromine, we briefly describe their functionalization with ethylenedioxythiophene (EDOT) units. Indeed corresponding EDOT end-capped compounds are susceptible to lead to materials exhibiting radically different properties. In this context, we carried out a comparative study of their electrochemical and spectroscopic properties.

Syntheses

SDTBr2F was obtained in three steps from 4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one.⁹ After bromination of the starting derivative in 72% yield using NBS,¹⁰ compound **1**, was reacted with the Grignard reagent of 2-bromobiphenyl affording the corresponding carbinol **2** in 79% yield. The latter was finally engaged in a cyclization reaction in refluxing acetic acid with a catalytic amount of hydrochloric acid yielding **SDTBr2F** in 53% (Scheme 1).

Conscious that applying a similar strategy to prepare the non-reported **SDTFBr2** derivative sounds unreasonable, we envisioned to follow the approach incompletely described by Kobayashi. However, in our hands the reaction of 2,7-dibromofluorenone with the 3-lithio-2,2'-bithiophene in situ generated from the addition of butyl lithium onto 3-bromo-2,2'-bithiophene only led to insoluble polymeric materials. Consequently and by analogy with the results of Wu et al., experiments were conducted from the silyl-protected monohalogenated 3-bromo-5,5'-ditrimethylsilyl-2,2'-bithiophene. Addition of a stoichiometric amount of BuLi followed by a slight excess of 2,7-dibromofluorenone allowed formation of the intermediate carbinol **3** as a white solid in 37% yield. Upon cyclization in the same conditions than previous experiments, the target **SDTFBr2** was obtained in 74% yield. Note that in this step, the trimethylsilyl protecting groups are also cleaved (Scheme 2).

As outlined in the introduction, Sinnige et al. initially described the preparation of **SDTF**. In their seminal work, the carbinol which conducts to **SDTF** by cyclization was synthesized from fluorenone and 3,3'-dilithio-2,2'-bithiophene. The requirement of bislithiated reagent to perform the simple addition on a fluorenone appearing quite surprising, one may postulate a partial hydrolysis of the dianion during the reaction. In order to confirm this supposition, the Sinnige conditions⁶ were reproduced in strict anhydrous conditions, starting from a ratio 1:1 of 2,7-dibromofluorenone

Scheme 3. Syntheses of carbinol **4** and dispiro-oxepine compound **5**.

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