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A facile synthesis of dithieno[3,2-*b*:6,7-*b*]fluorenes *via* a tandem annulation–reduction†

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A concise and facile synthesis of 2,8-disubstituted dithieno[3,2-*b*:6,7-*b*]fluorenes starting from 2,7-dihydroxyfluorenone is reported. The key step involved is the tandem annulation–reduction of a 3,6-dichloro-2,7-di(alkynyl)fluorenone using $Na_2S{\cdot}9H_2O$ as a sulfur surrogate and reductant. The final dithiophene-fused fluorenes are obtained in reasonable yields (23–43%).

π-Conjugated polymers can be utilized as organic semiconductors, which are applicable as active materials in organic electronic devices, such as organic light emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaics (OPVs), and energy storage materials. In recent years, much attention has been devoted to preparing conjugated organic molecules and polymers containing fused heterocycles, especially those with thiophene and benzo[*b*]thiophene nuclei, which have found a huge number of applications in materials science. Thiophene-fused polycyclic (hetero)aromatics have aroused great interest due to their excellent charge transport properties. For example, thiophene- or benzothiophene-based derivatives have been applied in the fields of OLEDs and OFETs.[1,2,5a,6] In particular, acene-dithiophene systems with two thiophene rings fused at the ends of a carbocyclic acene, such as benzodithiophenes (BDTs),[3i,j] naphthodithiophenes (NDTs),[3k,l] and anthradithiophenes (ADTs),[3m–o] offer numerous advantages over other types of acenes, owing to the ease of functionalization at the α-position of thiophene, for typical transition metal catalyzed cross-coupling polymerizations such as the Suzuki, Stille and Yamamoto couplings or the direct (hetero)arylation polycondensation (DArP or DHArP) recently developed by Lerclerc and others.[3p,q] The integration of thiophene rings and carbocyclic acenes into a rigid and coplanar entity could enhance π-electron delocalization, and might also induce strong π–π stacking, useful for efficient charge transport in materials chemistry. These dithiophene-fused or thiophene-substituted acenes have been widely utilized as important p-cores for the development of semiconductors, from both small organic molecules and polymers, in the fields of organic field-effect transistors (OFETs) and organic photovoltaics (OPVs). Recently, Takimiya *et al.* successfully demonstrated the selective and efficient synthesis of several isomeric naphthodithiophenes (NDTs, Fig. 1), and fully investigated their properties. NDTs are commonly indicated as useful cores for optoelectronic devices, but have rarely been studied due to difficulties in their preparation and the limited availability of suitable precursors.[2d,e,3a–c] In contrast to dithiophene-fused carbocyclic acenes, the synthesis of dithiophene-fused heteroacenes has not been extensively studied, despite the fact that heteroatoms might have a strong and unique influence on the properties of small organic molecules or polymers. A few examples have been reported concerning dithiophene-fused carbazoles suitable for materials chemistry, for example, Geng *et al.* reported the synthesis of thiophene-fused congeners with dithieno-carbazoles as building blocks for the construction of semiconducting polymers for application as OFETs (Fig. 1, CDTs).[3g,h]

Therefore, any new strategy for the synthesis of benzothiophene cores represents an important development and particularly appealing are those syntheses that allow the easy and facially regioselective construction of five-membered rings fused to

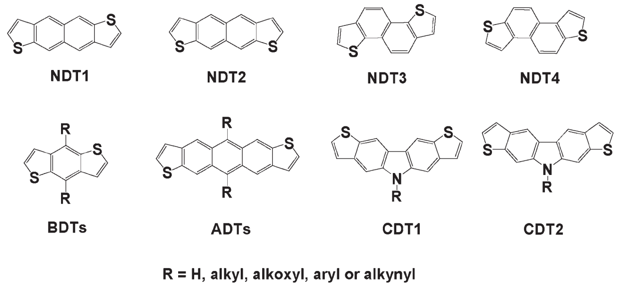

Fig. 1 Molecular structures of some representative dithiophene-fused carbocycles and heterocycles.

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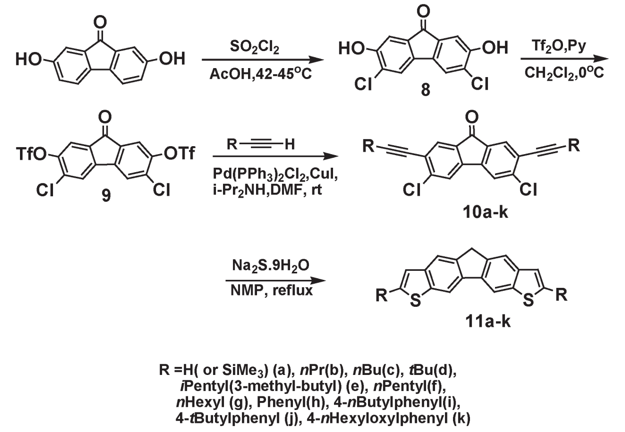
polycyclic aromatic hydrocarbons or heteroarenes. Currently there are three major approaches towards the synthesis of the benzothiophene unit: 1) the electrophilic cyclization reaction of an *o*-alkynyl thioanisole;[4] 2) the annulation of an *o*-haloalkynylbenzene with sodium sulfide at high temperature or a thiolation–annulation reaction within a transition-metal catalysed system;[5] and 3) the coupling cyclization reaction of *o*-bromoalkynylbenzenes with various thiol surrogates.[6] In these methods, the synthesis of key intermediates such as *o*-alkynyl thioanisole and *o*-haloalkynylarenes is difficult due to the limited number of suitable precursors. Other factors such as the solvent, temperature and the catalyst system can also play key roles in the ring formation of thiophene. For example, a high reaction temperature is an essential factor in Takimiya's procedure,[3a] in which 1-halo-2-(arylethynyl)arenes can be used as precursors to efficiently construct benzothiophene derivatives, especially dithiophene- or trithiophene-fused heteroarenes. Meanwhile, a transition metal catalyst such as in the CuI–TMEDA system can efficiently promote the synthesis of different benzothiophenes under mild conditions.[5b]

Due to the important roles of fluorene, thiophene and thiophene-fused polyaromatic hydrocarbons (PAHs) or polymers in materials science, the development of efficient and regioselective methods for the synthesis of hitherto unknown thiophene-fused fluorenones and their derivatives is of considerable current importance. These materials might offer important cores for further evaluation of thiophene-based semiconductors in the fields of solar cells and organic field transistors. As part of our continued interest in the construction of different sulfur-containing heterocycles such as thiophene-fused fluorenones, fluorenes and spirobifluorenes,[7] herein we report, to the best of our knowledge, the first synthesis of dithiophene-fused fluorenes using a well-designed synthetic route. In the context of our studies, we developed a novel and general protocol for the synthesis of 2,8-disubstituted dithieno[3,2-*b*:6,7-*b*]fluorenes, which provides novel and unprecedented access to target molecules that are difficult to prepare using other synthetic strategies, in terms of the number of synthetic steps and availability of key precursors.

The above mentioned methods for the construction of benzothiophene, generally require an *o*-haloalkynylbenzene, which can be prepared by the reaction of a 2-halo-1-iodobenzene or 2-halophenol triflate derivative with suitable acetylenes, under typical transition metal-catalyzed Sonogashira cross-coupling conditions. Due to the limited availability of 2,3,6,7-tetrahalofluorenones (*e.g.*, 2,7-dibromo-3,6-diiodofluorenone or 3,6-dibromo-2,7-diiodofluorenone, as well as their chloro congeners), we sought a different synthetic strategy that could be applied to dithieno-fluorenones. Inspired by Takimiya's procedures to obtain NDTs, we chose 2,7-dihydroxy-fluorenone as a starting material, which contains a central fluorenone component, with the further consideration that triflates derived from the hydroxy groups could act as excellent leaving groups in the palladium-catalyzed Sonogashira coupling.[5a,6]

In our case, in order to obtain suitable precursors like those reported by Takimiya, we decided to introduce two chlorides to 3 and 6 positions of the 2,7-dihydroxyfluorenone. The chlorination of 2,7-dihydroxy-fluorenone with sulfuryl chloride (SO_2Cl_2) in glacial acetic acid in the temperature range from 42 to 45 °C (strictly below 45 °C) proceeded smoothly to afford 3,6-dichloro-2,7-dihydroxy-fluorenone (**8**) in high yield (90%) as previously described.[8a,b] This was followed by a reaction with triflic anhydride (3.5 equiv.) in the presence of pyridine as a base in dichloromethane, to form the bis(triflate) (**9**) in an isolated yield of 93%.[5a,6,8c]

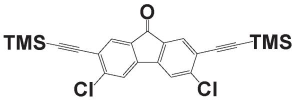
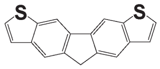
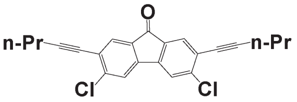
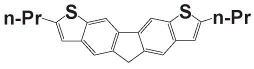
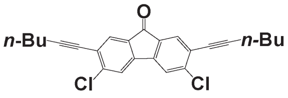
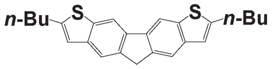
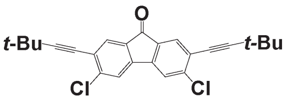
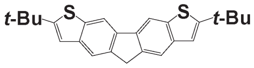
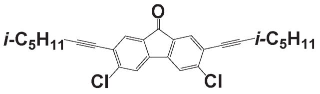
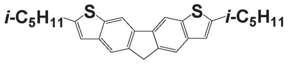
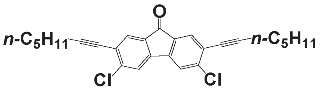
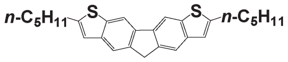
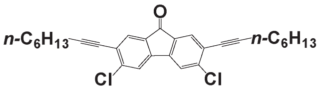
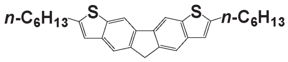
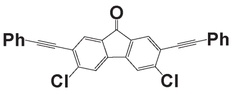
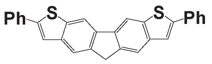
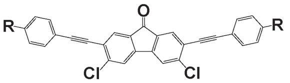
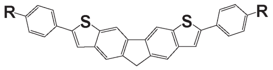
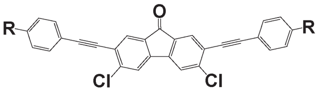
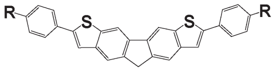
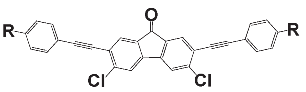
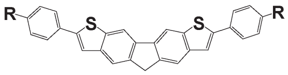


Scheme 1 The synthesis route to thieno-fluorenes.

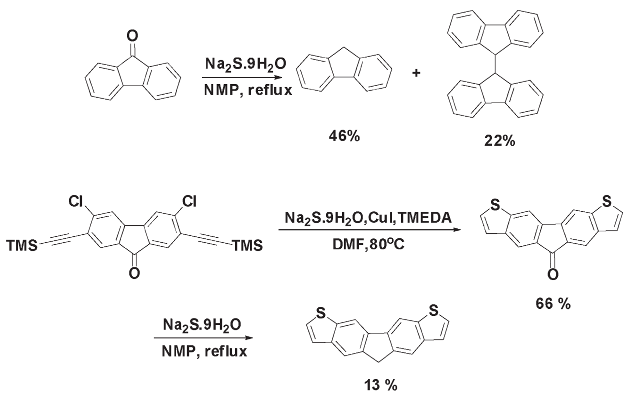
Next, reactions between bis(triflate) (**9**) and various ethynyl derivatives were carried out using the palladium-catalyzed Sonogashira coupling conditions, $Pd(PPh_3)_2Cl_2/CuI/{}^iPr_2NH$ in DMF, affording 3,6-dichloro-2,7-dialkynyl (or aryl-alkynyl) fluorenones **10a–10k**. Considering the solubility and functional group diversity, even alkyl or aryl acetylenes could be employed to perform this coupling reaction, all of the desired diethynyl derivatives could be obtained at room temperature. After the usual work up and purification by column chromatography, compounds **10a–10k** could be efficiently isolated in yields of 72–88%.[5a,6] With these intermediates in hand, our investigation began with the attempted annulation of substrate **10a** using $Na_2S\cdot 9H_2O$ in refluxing *N*-methylpyrrolindone (NMP) as described in Takimiya's procedure. A white solid product was obtained in an isolated yield of 25%. To our surprise, the methylene signal appeared as a singlet in the proton NMR spectrum (4.11 ppm, fluorene is at 3.92 ppm, see the ESI† for details). A carbonyl signal was also not found in the ^{13}C NMR spectrum, a signal for the methylene of fluorene was observed instead (35.82 ppm). Delighted by this unexpected result, we subsequently converted the other 3,6-dichloro-2,7-di(ethynyl)-fluorenones (**10b–10k**) into dithieno-fluorenes in the same manner. In all cases, the reactions proceeded smoothly to afford fluorenes **11a–11k** in isolated yields of 23–43%. (Scheme 1 and Table 1.)

Typically, one can approach the synthesis of thiophene-fused aromatic ketones or quinones such as anthrathiophenediones using the reaction between an *o*-halogenated arylacetylene and $Na_2S\cdot 9H_2O$ in a suitable solvent with or without a catalyst.[9] However, no example of a tandem cyclization–reduction with $Na_2S\cdot 9H_2O$ as the sole reagent, involving the direct reduction of the carbonyl group of the aromatic ketone or quinone during the

Table 1 The different dithieno[3,2-*b*:6,7-*b*]fluorenes synthesised

Entry	Precursor **10**	Product **11** (yield)
1		 25%
2		 40%
3		 43%
4		 27%
5		 36%
6		 32%
7		 42%
8		 24%
9	 R = *n*Bu	 23% R = *n*Bu
10	 R = *t*Bu	 27% R = *t*Bu
11	 R = O-nC_6H_{13}	 28% R = O-nC_6H_{13}

reaction process, has ever been reported. In order to prove the role of $Na_2S{\cdot}9H_2O$ as a reductant in this reaction, we first used fluorenone as a model, and found that the conversion of fluorenone could be completed with $Na_2S{\cdot}9H_2O$ in refluxing NMP, affording fluorene (46% isolated yield), with 9,9′-bifluorene as a separable by-product (isolated 22%). However, only part of fluorenone was consumed if the temperature was decreased to 110 °C. Further repetitions indicated that fluorenone could be fully recovered, if the same reaction was carried out at room temperature. For further validation of this unprecedented reduc-



Scheme 2 Reductions attempted to obtain fluorenes.

tion, dithieno[3,2-*b*:6,7-*b*]fluorenone (**14**) was synthesized *via* the CuI–TMEDA-catalyzed treatment of **10a** with $Na_2S·9H_2O$ in DMF at 80 °C (66% isolated yield), using the method reported by Zhang's group.[5b] Compound **14** could be converted to dithieno[3,2-*b*:6,7-*b*]fluorene (**11a**) with $Na_2S·9H_2O$ in refluxing NMP, albeit in quite a low yield (13%) (Scheme 2).

All products were characterized using spectroscopic methods such as NMR and mass spectrometry. The proton NMR signal for the methylene of the fluorenyl compounds generally appears at 4.00–4.20 ppm, while ^{13}C NMR signals for the methylene of the fluorenes range from 34.50 ppm to 36.00 ppm. The structure of **11f** was unambiguously confirmed using X-ray single crystal structure analysis (Fig. 2, see the ESI†).

In conclusion, we have described a novel and efficient route for the preparation of dithieno[3,2-*b*:6,7-*b*]fluorenes *via* a metal catalyst-free tandem annulation–reduction of suitable precursors with $Na_2S·9H_2O$ in a single step, where the formation of the two thiophene rings and the reduction of the fluorenone occur spontaneously during the reaction process. This result demonstrates that sodium sulfide can act as a surrogate for the annulation leading towards benzothiophene and a reductant for fluorenones or diaryl ketones, with the adoption of high temperature and a suitable solvent being key factors. The utilization of this strategy for the formation of other thiophene-fused carbocycles and heterocycles with extended π-conjugated systems, the reduction of ketones or quinones with sodium sulfide, and the application of the above described dithieno-fused fluorenes as key precursors in the construction of thiophene-based conjugated organic molecules and polymers suitable for solar cells and/or organic field transistors, are ongoing in our laboratory.

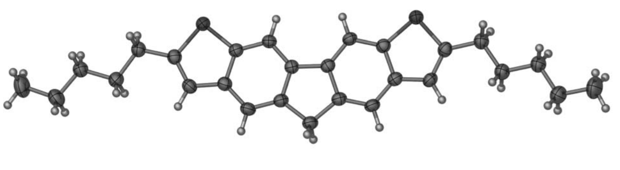


Fig. 2 The crystal structure of **11f**.

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