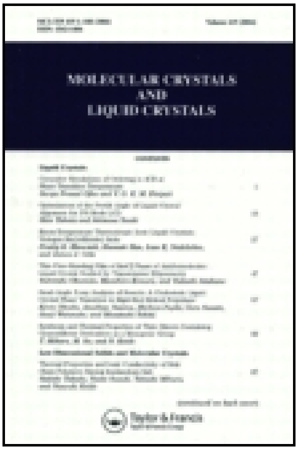

Molecular Crystals and Liquid Crystals

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Molecular Switches Get Wired: Synthesis of Diarylethenes Containing One or Two Sulphurs

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Molecular Switches Get Wired: Synthesis of Diarylethenes Containing One or Two Sulphurs

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Two series of novel diarylethenes, the first containing one and the second two acetyl protected thiol groups, were synthesised in two and three steps from an easily available known intermediate. Newly synthesised compounds present ideal examples of model substrates for photochromic studies on metal surfaces.

Keywords: diarylethene; gold surface; photochromism; synthesis

INTRODUCTION

There has been an increasing interest in the implementation of small organic molecules into the field of nanoelectronics in the last decades [1]. In the infinite "pool" of organic compounds, a replacement for conventional switches [2], rectifiers [3], wires [4] and transistors [5] has been found. The necessity to respond to external stimuli makes switches the most challenging part of these efforts. Photochromic

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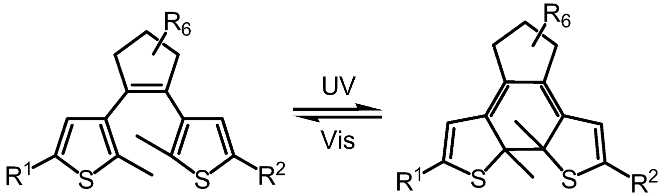


FIGURE 1 Typical photoreaction of dithienylethenes.

switches exhibit reversible photo-induced transformation between their two isomeric forms whose absorption spectra are different [6]. Among these, 1,2-dithienylethenes maintain a prominent position because of their exceptional thermal stability and fatigue resistance [7] of the photochromic reaction (Fig. 1), and they seem to be promising candidates for various photo-devices.

The incorporation of small molecules into the integrated circuit remains an unsolved task. Employing single-molecule techniques such as Mechanically controllable break junction [8] and Scanning electron microscopy (STM) [9], researchers have been able to combine a single molecule with metallic electrodes and thus simulate the integration. We have published a first attempt to incorporate dithienylethenes between two nanoscopic gold electrodes and to study their electronic and photochromic properties on a single molecule level [10].

In order to explore the published system more, we synthesised two new molecules. The design of the recently studied molecule **1a** and the two new molecules **1b, c** incorporating two sulphur atoms proposed for these experiments, was mainly influenced by the necessity to create a strong bond between gold and molecules and by the possibility to vary the conducting character of the spacer from the well-conducting thiophene to the meta substituted benzene ring providing only cross-conjugation. Moreover, molecules **2a, b, c** incorporating one sulphur atom were synthesised and these might be used for further experiments, better explaining the events happening in the metal-molecule system, such as STM measurement or the use of absorption spectroscopy on the monolayer protected gold nanoparticles modified by those sulphur derivatives.

RESULTS AND DISCUSSION

The synthetic strategy for both symmetrical and asymmetrical molecules was based on a palladium catalysed cross-coupling reaction between arylhalides and arylboronic acid [11]. Starting from the known 1,2-Bis(5-chloro-2-methylthien-3-yl)cyclopentene **3** [11], the

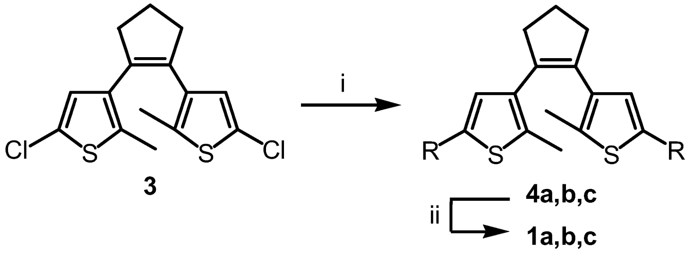
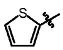
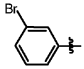
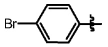
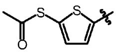
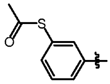
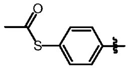


FIGURE 2 Synthetic route to compounds **1**. i) a) n-BuLi, THF, b) $B(OBu)_4$, c) ArBr, $Pd(PPh_3)_4$, Na_2CO_3, THF, reflux, ii) a) t-BuLi, THF, −78°C, b) S_g, −78°C, c) AcCl. (for R see Table 1).

TABLE 1 Substituents and Yields of Compounds **4** and **1**

Compd.	**4a**	**4b**	**4c**	**1a**	**1b**	**1c**
R						
Yield[%]	66	53	56	33	41	39

series of compounds **4a, b, c** (Fig. 2) was prepared with satisfactory yields (Table 1). The final products **1a, b, c** were synthesised by treatment with n-butyllithium followed by the addition of sulphur and the protection with acetyl chloride giving moderate yields.

The general procedure for the preparation of **4** and **1** is as follows. To a solution of compound **3** (0.729 mmol) in THF (7 ml), kept under an inert atmosphere, n-BuLi (1.92 mmol, 1.6 M in hexane) was added.

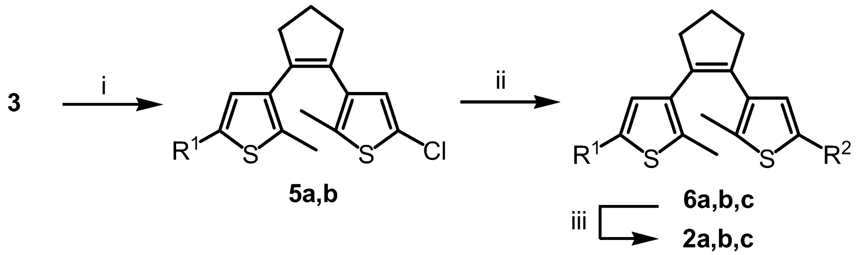
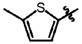
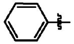
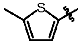
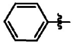
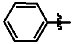
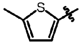
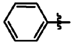
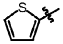
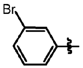
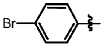
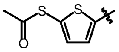
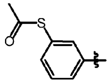
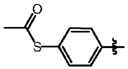


FIGURE 3 Synthetic route to compounds **2**. i) and ii) a) n-BuLi, THF, b) $B(OBu)_4$, c)ArBr, $Pd(PPh_3)_4$, Na_2CO_3, THF, reflux; iii) a) t-BuLi, THF, − 78°C, b) S_g, − 78°C, c) AcCl. (for R see TABLE 2).

TABLE 2 Substituents and Yields of Compounds **5**, **6** and **2**

Compd.	**5a**	**5b**	**6a**	**6b**	**6c**	**2a**	**2b**	**2c**
R1								
R2	Cl	Cl						
Yield[%]	68	77	72	66	76	57	52	56

After 1 h, $B(OBu)_3$ (2.19 mmol) was added to produce a bis-boronic ester intermediate. A separate flask was charged with aromatic halide (2.98 mmol), $Pd(PPh_3)_4$ (0.083 mmol), THF (5 ml), (aq.) 2 M Na_2CO_3 (4 ml) and ethylene glycol (5 drops). The mixture was heated to 80 °C and the performed boronic ester was added slowly. The reaction mixture was boiled under reflux overnight, diluted with diethyl ether (50 ml) and washed with water (50 ml). The water layer was washed with an additional volume of ether (50 ml) and the combined organic phases were dried over Na_2SO_4 and concentrated. Subsequent chromatography on silica gel (hexane) afforded compounds **4** [12].

Compounds **4** (0.236 mmol) were dissolved in THF (5 ml) and the solution was cooled down to −78°C. To this solution t-BuLi (0.520 mmol, 1.5 M in pentane) was added dropwise and the mixture was stirred for 2 h, after which S_8 (0.472 mmol) dissolved in a small portion of THF was added. The reaction mixture was stirred at −78°C for 1 h and then allowed to reach room temperature and stirred for an additional 1 h. The reaction mixture was cooled down to −20°C and acetyl chloride (0.944 mmol) was added. The reaction was allowed to slowly reach room temperature and stirred overnight. The reaction was diluted with dichloromethane (50 ml) and the organic phase was washed with water and brine. The organic phase was dried and concentrated. Subsequent chromatography on silica gel (hexane/dichloromethane) afforded **1**. All compounds were identified by ^1H NMR, ^{13}C NMR and MS.

The synthesis of the asymmetrical derivatives **2a, b, c** follows exactly the same sequence of the two palladium catalysed couplings and sulphuration (Fig. 3). However, the first coupling step requires four times higher dilution to provide products **5a, b** with good yields (Table 2) and high selectivity for the mono substitution.

In conclusion, the general synthetic strategy leading to either symmetrical or asymmetrical derivatives incorporating one or two sulphurs can be adopted to many new compounds, taking into account the final desired properties, by varying the spacer unit and changing the position of sulphur groups. The newly synthesised compounds are currently being subjected to various photochemical experiments on gold surfaces. Relevant information will be reported.

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(b) for a single molecule switching also see: Irie, M., Fukaminto, T., Sasaki, T., Tamai, N., & Kawai, T. (2002). *Nature, 420*, 759.

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[12] **4a)** mp. 204–208°C decomp. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94 (s, 6H), 2.04 (m, 2H), 2.79 (t, $J = 12.5$, 4H), 6.87 (s, 2H), 6.95 (t, $J = 6.5$, 2H), 7.03 (d, $J = 4.5$, 2H), 7.13 (d, $J = 8.5$, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.3 (q), 22.9 (t), 38.5 (t), 122.9 (d), 123.7 (d), 124.5 (d), 127.6 (d), 133.0 (s), 134.0 (s), 134.5 (s), 136.3 (s) ppm. HRMS calcd. for $C_{23}H_{20}S_4$ 424.045, found 424.045.

4b) ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99 (s, 6H), 2.09 (m, 2H), 2.84 (t, $J = 7.3$, 4H), 7.02 (s, 2H), 7.19–7.21 (m, 2H), 7.33–7.41 (m, 4H), 7.64 (s, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.4 (q), 23.0 (t), 38.4 (t), 122.9 (s), 123.9 (d), 124.8 (d), 128. 2 (d), 129.7 (d), 130.3 (d), 134.7 (s), 135.4 (s), 136.5 (s), 136.8 (s) ppm. HRMS: calcd. for $C_{27}H_{22}S_2Br_2$ 567.953, found 567.953.

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