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A new synthetic route to symmetrical photochromic diarylperfluorocyclopentenes

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Abstract: Symmetrical and photochromic diarylperfluorocyclopentene has been prepared by reaction of 3-lithio-5-chloro-2-methylthiophene with the ethyl ester of hexafluoroglutaric acid, followed by ring closure *via* a McMurry coupling. Compound **7** is a versatile intermediate for the development of photochromic materials.

Keywords: photochromism, diarylethenes, McMurry coupling

Diarylethenes constitute an important class of photochromic molecules. The switching process is thermally irreversible and the compounds show high fatigue resistance,[1] which are promising features for application in optical data storage,[2] molecular wires[3] and as molecular switches.[4,5] The most commonly used diarylethenes are the diarylperfluorocyclopentenes[6] followed by the bisarylmaleic anhydrides,[7] bisarylmaleimides,[8] and bisarylcyclopentenes.[9] Many functionalized diarylperfluorocyclopentenes have been synthesized.[1] They exhibit excellent photochromic behaviour and they are stable in the presence of air during cyclization at up to 80°C. Despite these attractive photochromic properties, the synthesis of these compounds is not trivial. The commonly used starting compound, octafluorocyclopentene, which is very volatile and expensive, has to undergo a double substitution reaction with a lithiated thiophene derivative. The yields are usually moderate at best, it is not easy to scale up the procedure, and a considerable amount of mono substituted perfluorocyclopentene product is formed.

Herewith we would like to present a new synthesis of symmetric diarylperfluorocyclopentenes based on the acylation of a thiophene derivative, followed by a McMurry coupling. *Via* this route a new diarylperfluorocyclopentene derivative has been

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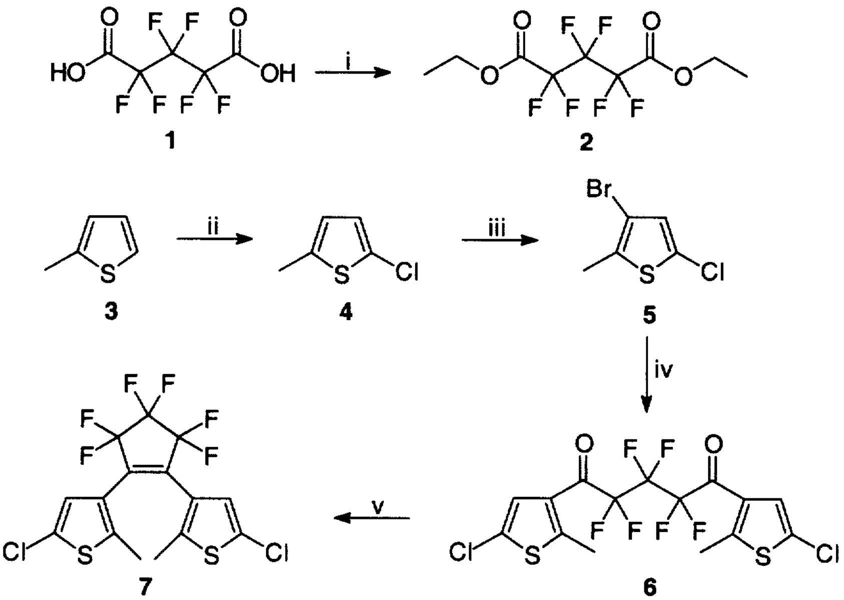
synthesized, which can easily be functionalized at the 5'-positions, and thus can be used as a building block for other functionalized diarylperfluorocyclopentenes.

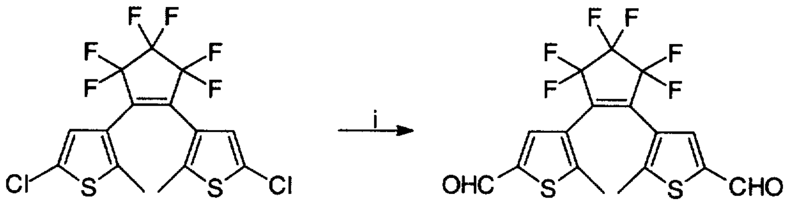
In the synthetic route presented here the relatively cheap hexafluoroglutaric acid **1** was used as a fluorine source, which was converted to its ethyl ester **2** (scheme 1). For the thiophene moieties 2-methylthiophene was used as the starting material, which was converted to 3-bromo-5-chloro-2-methylthiophene **5** by (i) chlorination at the 5-position with NCS in acetic acid and benzene and (ii) bromination at the 4-position with bromine in chloroform.



Scheme 1. Reagents and conditions: i, ethanol, reflux, H^+, 99%; ii, NCS, acetic acid, benzene, reflux, 80%; iii, Br_2, $CHCl_3$, 93%; iv, n-butyl lithium, -78°C, **2**, 70%; v, $TiCl_3(THF)_3$, Zn, THF, 40°C, 55%.

Compound **5** then was lithiated at -78°C in ether using n-butyl lithium and subsequently a solution of **2** in ether was added at the same temperature.[10,11]
After acidic work-up diketone **6** was obtained in a good yield. Finally ring closure was achieved through a titanium mediated coupling using $TiCl_3(THF)_3$ and Zn in THF at 40°C, to provide **7**, which was purified by column chromatography.[12]

It is, of course, in principle possible to use thiophene derivatives other than **5** in this route provided that they can be lithiated exclusively at the 3-position. However, it was found that 3-bromo-5-chloro-2-methylthiophene **5** is an extremely versatile intermediate for the introduction of reactive groups at the 5'-positions of the diarylperfluorocyclopentenes. Compound **5** undergoes exclusive lithium-halogen exchange with the bromine at the 3-position at *-78°C*, whereas the chlorine substituent is not affected under these conditions. Compound **7** can easily undergo a lithium-chlorine exchange at *ambient temperature* thus providing a handle to introduce functionality. For example dialdehyde **8** is readily synthesized by double lithiation of **7** with n-butyl lithium followed by quenching with DMF.



7 **8**

Scheme 2. Reagents and conditions: i, n-butyl lithium, r.t., DMF, 66%.

In conclusion, we have accomplished an efficient synthesis of versatile intermediate **7**, which can be readily converted to other photochromic derivatives, and the synthesis can be performed on a relatively large scale with good yields.

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[11] **1,5-Bis(5'-chloro-2'-methylthien-3'-yl)hexafluoropentadione (6)**:n-Butyl lithium (1.6M in hexane, 5.4 ml, 8.64 mmol) was added to a stirred solution of **5** (1.75 g, 8.29 mmol) in anhydrous diethyl ether (25 ml) under nitrogen at -70°C. After 15 min. of stirring at the same temperature, the ethylester of hexafluoroglutaric acid (0.91 ml, 4.15 mmol) in anhydrous diethyl ether (2 ml) was added slowly at -80°C. The reaction mixture was quenched with hydrochloric acid (2N, 10 ml), extracted with ether (3 x 25 ml), washed with saturated sodium bicarbonate solution (1 x 25 ml) and H_2O (1 x 25 ml), dried (Na_2SO_4), filtered and the solvent evaporated under vacuum to yield a brown/reddish oil (1.36 g, 70%). ^{1}H NMR (200 MHz, 20°C, $CDCl_3$): δ_H 2.70 (s, 6H, CH_3), 7.31 (s, 2H, CH); ^{13}C NMR (500 MHz, 20°C,$CDCl_3$): δ_C 17.05 (q, CH_3), 110.37 (t, CF_2), 111.08 (t, CF_2), 125.80 (d, CH), 126.19 (s, C-Cl), 128.92 (s, C-CO), 155.37 (s, C-CH_3), 177.85 (s, C=O); ^{19}F NMR (500 MHz, 20°C,$CDCl_3$): δ_F -116.18(t, 4F, CF_2), -122.73 (t, 2F, CF_2);MS (EI): 467[M+]; IR (Nujol): 1696cm $^{-1}$ (C=O).

[12] **1,2-Bis(5'-chloro-2'-methylthien-3'yl)perfluorocyclopentene(7)**: Compound **6** (0.96 g, 2.06 mmol), $TiCl_3(THF)_3$ (1.50 g, 4.12 mmol), Zn dust (0.53 g, 8.24 mmol) and THF (25 ml) were stirred under nitrogen at 40°C for 1 h. The mixture was cooled, poured over a filter filled with silica gel and eluted with petroleum ether 40/60. A white solid (0.49g, 55%) was obtained after purification by chromatography over silica gel (petroleum ether 40/60). ^{1}H NMR (200 MHz, 20°C, $CDCl_3$): δ_H 1.88 (s, 6H, CH_3), 6.88 (s, 2H, CH); ^{13}C NMR (500 MHz, 20°C,$CDCl_3$): δ_C 14.29 (q, CH_3), 110.67 (t, CF_2), 117.73 (t, CF_2), 123.92 (d, CH), 125.36 (s, C-Cl), 127.88 (s, C-CH_3), 140.37 (s, C=C);^{19}F NMR (500 MHz, 20°C,$CDCl_3$): δ_F -114.78 (t, J=5.5Hz, J=5.0Hz, 4F, CF_2), -136.37 (t, J=6.2Hz, J=5.0Hz, 2F, CF_2); MS (EI): 436 [M+], mp.; 132°C.