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Synthesis of photochromic 6-aryl-substituted bis(benzothiophenyl)-perfluorocyclopentenes by the Suzuki–Miyaura cross-coupling

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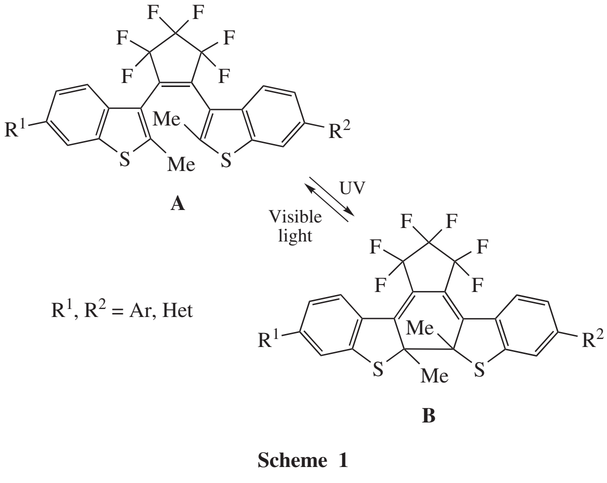
The Suzuki cross-coupling of 1,2-bis(6-iodo-2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene and (het)arylboronic acids depending on the reaction conditions affords bis- or mono-adducts. The latter on next cross-coupling with different boronic acid give unsymmetrical dihetarylethenes. Spectral-kinetic studies of the photoinduced cyclization of the compounds obtained were performed.

Dihetarylethenes represent a very promising heterocyclic chemotype due to their application in the fields of photonics and molecular electronics.[1] In particular, such compounds have been successfully used for the design of light-sensitive recording media for ultra high-density three-dimensional optical memory systems, polymers with photo- and electrically controlled conductivity, and optical switches.[2–5]

The photochromic interconversions of bis(benzothiophenyl)-perfluorocyclopentenes are outlined in Scheme 1. The UV irradiation leads to isomerization of the colourless open form **A** into a coloured cyclic form **B** that can be returned to its original state by visible light. A number of colouration–decolouration cycles exhibited by such dihetarylethenes proved to be rather high. For instance, in case of parent structure with $R^1 = R^2 = H$ these photochromic interconversions can be repeated more than 10^4 times. Another advantage of these compounds is a high thermal stability of the cyclic form.[6–8]

Nowadays, the design of new unsymmetrical diarylethenes with different aryl moieties is becoming an active and very promising area of research.[9–13] In particular, such compounds are of great interest for the development of fluorescence resonance energy transfer (FRET) systems.[14]



Scheme 1

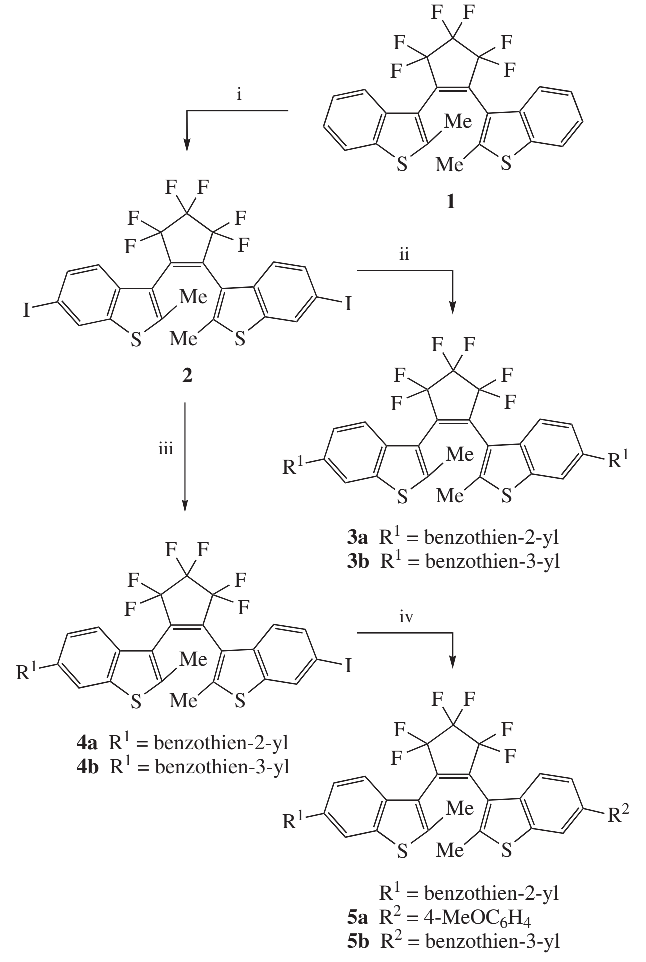
Synthetic transformations of parent bis(benzothiophenyl)-perfluorocyclopentene into its unsymmetrical derivatives have practically not been described so far. To the best of our knowledge, only a few examples of such mononitro- and monoformyl-substituted derivatives have been reported,[15–17] however, these syntheses were not regioselective giving mixtures of isomers.

Note that in donor–acceptor unsymmetrical bis(benzothiophenyl)perfluorocyclopentenes bearing electron-donating and electron-withdrawing groups in different parts of the molecule[18] absorption shifts to a longer wavelength region through photochromism, accompanied by an increase in the molar absorption coefficients which are significantly greater than those of unsubstituted analogues. 1,10-Phenanthroline-modified bis(benzothiophenyl)perfluorocyclopentene bearing nitronyl nitroxide radical was used for the preparation of Cu^{II} complex possessing magnetic properties.[19]

Previously,[20] we have shown an opportunity for the regioselective incorporation of the only one substituent into 1,2-bis-(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene **1** by its electrophilic acylation with bromoacetyl chloride in the presence of pyridine. This approach resulted in a variety of new asymmetrically substituted dihetarylethenes through the further heterocyclizations of the haloacetyl moiety. We have found that substituents in the benzothiophene fragments can still have an impact on the course of electrophilic substitution despite of a noncoplanar structure of 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene core that hinders an efficient electron transfer through the bridged hexafluorocyclopentene C=C double bond.

Herein we report another example of successful regioselective synthesis of unsymmetrical structures based on displacement of iodo atoms in 1,2-bis(6-iodo-2-methylbenzo[*b*]thiophen-3-yl)-hexafluorocyclopentene **2** (Scheme 2) by means of the Suzuki–Miyaura cross-coupling. As a result, a number of novel 6,6′-substituted symmetrical and unsymmetrical diarylethenes have been prepared and their photochemical properties have been elucidated.

The starting 1,2-bis(2-methylbenzothiophen-3-yl)perfluorocyclopentene **1** was prepared by the reaction of the corresponding perfluorocycloalkene with the 3-lithium derivative of 2-methylbenzothiophene.[21,22] Compound **1** was found to react with iodine



Scheme 2 *Reagents and conditions*: i, I_2 (1 equiv.), H_5IO_6 (2.5 equiv.), AcOH, H_2SO_4, H_2O, 5 h, 70 °C, 76%; ii, R^1–B(OH)$_2$ (3 equiv.), Na_2CO_3, Pd(PPh$_3$)$_4$, THF/H_2O, 24 h, reflux, 60–80%; iii, R^1–B(OH)$_2$ (1.5 equiv.), Na_2CO_3, Pd(PPh$_3$)$_4$, THF/H_2O, 24 h, 50 °C, 50–60%; iv, R^2–B(OH)$_2$ (1.5 equiv.), Na_2CO_3, Pd(PPh$_3$)$_4$, THF/H_2O, 24 h, reflux, 40–45%.

in the presence of periodic acid in acetic acid to give the diiodo compound **2** in 76% yield.

Diarylethenes **3**–**5** were synthesized through the Pd(PPh$_3$)$_4$-catalyzed cross-coupling of **2** with boronic acids (see Scheme 2).[†] Depending on conditions, mono- or bis-substitution occurred, products **3** having been symmetrical. Monosubstitution was regulated by using a small excess (1.5 equiv.) of boronic acid. Further coupling of monoiodo derivatives **4** with different boronic acid led to unsymmetrical compounds **5**.

Results of the spectral-kinetic studies for the synthesized compounds are presented in Table 1. Figure 1(*a*) shows absorption spectra of the initial open form **A** (curve *1*) and photoinduced cyclic form **B** (curve *2*) for diarylethene **5a**, which are typical of other compounds of this family. One can see that the open form is characterized by the maximum of the structured absorption band at 309 nm. After UV irradiation two new absorption bands with maxima at 400 and 570 nm have appeared. At the same time decreasing in the intensity of the absorption band of the initial open form is observed.

Most of the studied compounds are characterized by absorption bands of the open form located in the spectral region 320–336 nm, comparable molar extinction coefficients, the light-sensitivity value, ranked by the ratio $\Delta D^{\text{phot}}/D^{\mathbf{A}}$, as well as the ratio of constants for photocolouration and photobleaching processes

Table 1 Results of the spectral-kinetic studies for synthesized diarylethenes.[a]

Compound	$\lambda^{\mathbf{A}}_{\max}$/ nm	$\varepsilon^{\mathbf{A}}/10^{-4}$ dm^3 mol^{-1} cm^{-1}	$\lambda^{\mathbf{B}}_{\max}$/ nm	$\Delta D^{\text{phot}}/D^{\mathbf{A}}$	$k_{\mathbf{A}\text{-}\mathbf{B}}/k_{\mathbf{B}\text{-}\mathbf{A}}$	$t_{1/2}$/s
3a	335	4.5	575	0.5	4.8	3800
3b	320	5.5	570	0.2	4.2	2200
4a	335	5.0	560	0.2	3.9	3000
4b	332	3.5	553	0.1	3.9	3500
5a	309	2.0	570	0.3	3.8	1800
5b	330	3.0	575	0.3	3.6	2000

[a] $\lambda^{\mathbf{A}}_{\max}$ and $\lambda^{\mathbf{B}}_{\max}$ are the absorption maxima of the open-ring isomers in the UV region and the closed-ring isomers in the visible region, respectively; $\varepsilon^{\mathbf{A}}$ is the absorption coefficients of the open-ring isomers at the absorption maxima in the UV region; $\Delta D^{\text{phot}}/D^{\mathbf{A}}$ is a value of a photoinduced change of optical density at a maximum of the absorption band for the closed-ring isomers normalized to optical density at the maximum of open-ring isomers; $k_{\mathbf{A\text{–}B}}/k_{\mathbf{B\text{–}A}}$ is the ratio of rate constants for photocolouration ($\mathbf{A} \rightarrow \mathbf{B}$) and photobleaching ($\mathbf{B} \rightarrow \mathbf{A}$); $t_{1/2}$ is the time which is required for the irreversible decreasing photoinduced optical density in the photoequilibrium state under unfiltered light by half.

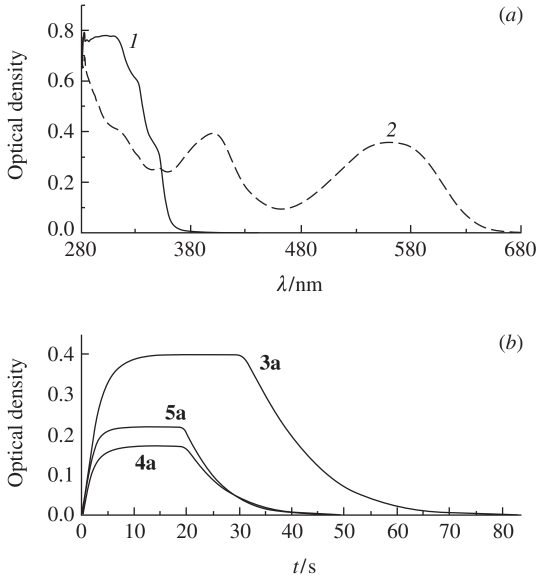


Figure 1 (*a*) Absorption spectra of photochromic compound **5a** in acetonitrile solution (4×10^{-5} mol dm^{-3}) (*1*) before and (*2*) after UV irradiation with a UFS-1 light filter ($\lambda_{\max}$ 320 nm) for 10 s; (*b*) kinetic curves of colouration/decolouration of compounds **3a**, **4a** and **5a**.

($k_{\mathbf{A\text{–}B}}/k_{\mathbf{B\text{–}A}}$). An exception is unbalanced diarylethene **5a** containing the electron-donating substituent, for which the maximum of the absorption band of the open form is hypsochromically shifted.

The most long-wavelength absorption bands of the cyclic forms are observed for symmetric diarylethenes **3a**, **3b**, **5b** and the unbalanced compound **5a**. Unbalanced diarylethenes containing electron-withdrawing substituent **4a** and **4b** exhibit a hypsochromical shift. Diarylethenes **3b**, **5a** and **5b** show the smallest resistance to irreversible photo-induced transformations. Thus, most of the obtained symmetric and unbalanced diarylethenes are characterized by comparable spectral-kinetic properties. The detected differences for several compounds can be explained by influence of substituents and the geometric factor affecting the system of conjugated bonds in the cyclic form.

In summary, a new approach to the synthesis of unsymmetrical 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)-substituted hexafluorocyclopentenes has been developed based on the iodination–Suzuki cross-coupling protocol. All dihetarylethenes obtained are promising for applications in the fields of photonics and molecular electronics.

[†] For synthesis and characteristics of compounds **3a**,**b**, **4a**,**b** and **5a**,**b**, see Online Supplementary Materials.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.03.007.

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