

Photochromic Properties of Perhydro- and Perfluorodithienylcyclopentene Molecular Switches

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Various substituted phenylthienyl perhydro- and perfluorocyclopentenes have been synthesized in order to compare their spectroscopic and photochromic properties. The difference in the electron densities of the central cyclopentene moieties in the perhydrocyclopentene and perfluorocyclopentene molecular switches has only a small effect on the absorption maxima of the electronic spectra, but causes some subtle changes in substituent and solvatochromic effects. The photochromic behaviour is remarkably similar, and both type of switches combine excellent quantum yields (0.6) with high

degrees of photoconversion (> 0.85). The main difference is the lower photochemical and thermal stability of the perhydrocyclopentene molecular switches. It is concluded that in most studies the perhydrocyclopentenes are an excellent alternative for the perfluorocyclopentenes, while the perfluorocyclopentenes might be better suited for applications such as data storage, which depend critically on fatigue resistance and thermal stability.

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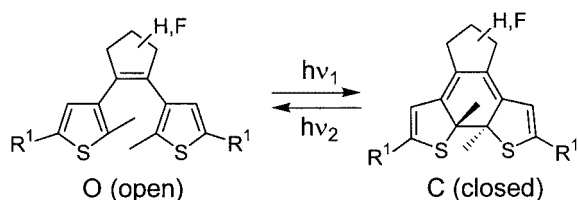
Introduction

In recent years there has been increasing interest in the synthesis, properties and application of organic photochromic materials as a possible basis for optoelectronic and photooptical devices. Diarylethenes with heterocyclic aryl groups belong to a new class of thermally irreversible photochromic switches.^[1–3] For switching purposes, the most commonly used diarylethenes are the diarylperfluorocyclopentenes,^[4] followed by the diaryl maleic anhydrides^[5] and bisaryl maleimides.^[6] Many functionalized derivatives of these compounds have been synthesized,^[1–3] and applications in, for example, reversible switching of liquid crys-

talline phases,^[7] colour pattern formation,^[8] electron transfer,^[9] and single-molecule fluorescence^[10] have been demonstrated. The photochemical switching process involves the thermally irreversible ring-closed product (Scheme 1) and both the open and closed compounds have high fatigue resistance. In particular, the perfluoro derivatives of diarylethenes display these excellent properties and are therefore most frequently used.^[11,12]

We have recently developed (dithienyl)cyclopentenes in which the fluorine substituents on the central cyclopentene ring are replaced by hydrogens.^[13] The synthesis of these so called ‘perhydrocyclopentene’ derivatives with R¹ = Cl can be performed on a large scale starting from cheap chemicals, and the basic switch can easily be derivatized to provide access to a wide variety of diarylcyclopentene photochromic switches by a convergent synthetic route.^[14] Because of their synthetic accessibility, these perhydrocyclopentene molecular switches thus possess major advantages over the perfluorocyclopentenes.

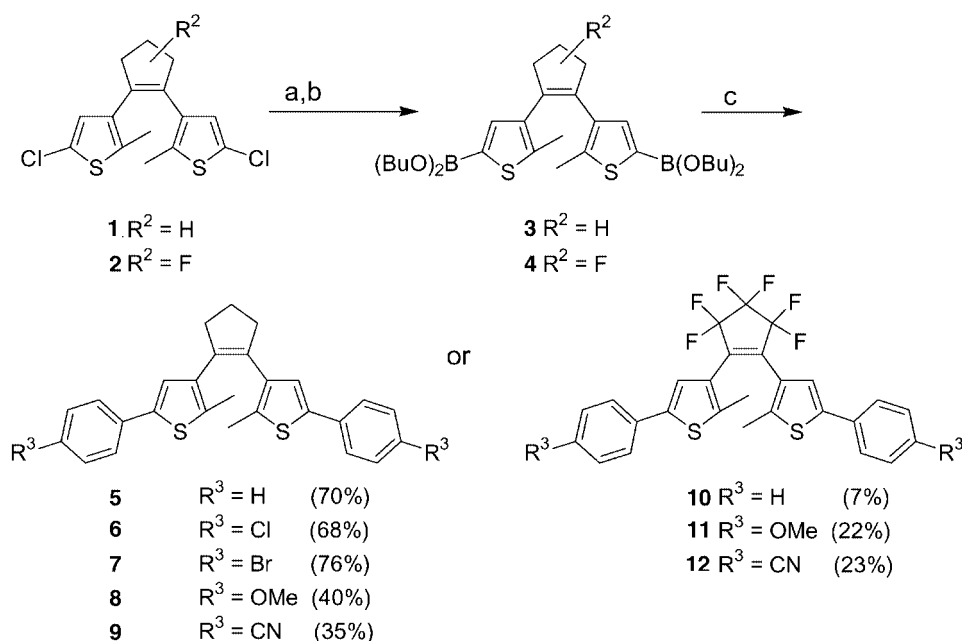
The important remaining question is whether these dithienylcyclopentene-based switches are also a suitable choice when it comes to their photochromic properties. Preliminary studies have revealed that they also exhibit excellent photochromic switching behaviour, provided that the correct substituents (i.e., moieties that extend the conjugation length of the switch) are present (R¹ in Scheme 1).^[13] Detailed insight into the photochemical processes was obtained by time-resolved spectroscopic and theoretical (DFT) studies on perhydrocyclopentene **5** (Scheme 2). These investigation revealed that the ring-closure reaction



Scheme 1. Photochromism in dithienylcyclopentene molecular switches

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Scheme 2. Synthesis of (arylthienyl)perhydro- and perfluorocyclopentene photochromic switches; reagents and conditions: a) *n*BuLi, THF, room temperature, b) B(OBu)₃, THF, room temperature, c) ArBr, [Pd(PPh₃)₄], 2 M Na₂CO₃(aq), ethylene glycol, THF, reflux

takes place with a time constant of 4.2 ps.^[15] Although this time constant compares well with that for the ring-closure reaction of perfluorodithienyl switches (1–3 ps, depending on the chemical structure of the switch),^[16–18] direct comparison between the photochromic properties of perhydrocyclopentenes and perfluorocyclopentenes can still not be made because of the different structures (substituent R¹ in Scheme 1) of the compounds used throughout these studies. It was therefore decided to synthesize a series of similarly substituted perhydro- and perfluorocyclopentenes^[19–23] (Scheme 2) and to compare their spectroscopic and photochromic properties. The first results from these studies are reported here.

Results and Discussion

It has recently been shown that 2,2'-(dichlorodithienyl)cyclopentenes **1** and **2** are easily accessible and versatile starting compounds for the synthesis of a wide range of functionalized (dithienyl)perhydro- and perfluorocyclopentenes.^[14] In order to obtain the desired phenyl derivatives of the two diarylethenes, **1** and **2** were first converted into the bis(boronate) esters **3** and **4**, respectively (Scheme 2). These compounds were used directly in the Suzuki reaction without any workup because it was found that the bis(boronate) esters **3** and **4** easily deboronize during isolation. Suzuki coupling with various aryl bromides gave the corresponding bis(arylthienyl)cyclopentenes in yields up to 76% after purification by column chromatography. It should be noted that application of switch **1** in place of the perfluoro switch **2** in the Suzuki coupling resulted in much

higher yields, even when Lehn's conditions were applied.^[24] The bis(arylthienyl)cyclopentene switches **5–12** were purified by chromatography, and the symmetric nature of the products due to the double Suzuki coupling was confirmed by ¹H NMR, ¹³C NMR, and HRMS.

The photochromic behaviour of the synthesized compounds was first studied by irradiation with a high-pressure mercury lamp with band-pass filters. The photochemical reactions were monitored by UV/Vis and ¹H NMR spectroscopy. Before irradiation, compounds **5–12** have strong absorptions in the UV region (Table 1), and the chemical shifts of the thienyl protons appear at positions characteristic for the aromatic thiophene group. These data show that compounds **5–12** are initially present as the ring-open isomers, as depicted in Scheme 1. The open form of the perhydro switch **5** and the corresponding perfluoro switch **10** have nearly the same absorption maxima, at 277 nm and 279 nm, respectively, in *n*-hexane (see Table 1, Figure 1), although the central double bond in **5** is relatively more electron-rich than in **10**. The presence of a cyano substituent, however, causes a bathochromic shift of this absorption in the case of the perhydrocyclopentene derivative **9** and a hypsochromic shift in that of the perfluoro derivative **12**. These opposite effects must be directly related to the different electron densities at the central double bond, and indicate that there is a significant electronic interaction between the phenylthienyl moiety and the central cyclopentene group.

Irradiation of solutions of compounds **5–12** at $\lambda = 313$ nm resulted in the appearance of a broad absorption band in the visible region, with λ_{max} ranging from 529 nm to 603 nm (Figure 1, Table 1). Upon irradiation, the ¹H

Table 1. Absorption spectroscopic data and photochemical conversions of compounds **5–12**

Compound ^[a]	λ_{\max} Open (ϵ) ^[b] <i>n</i> -Hexane	λ_{\max} Open (ϵ) ^[b] Toluene	λ_{\max} Closed (ϵ) ^[b] <i>n</i> -Hexane	λ_{\max} Closed (ϵ) ^[b] Toluene	Conv. ^[c] Toluene
5 ($R^3 = H, R^2 = H$)	277	[d]	529	531 (16.8)	0.95
6 ($R^3 = Cl, R^2 = H$)	281, 312	[d]	533	535 (16.7)	0.98
7 ($R^3 = Br, R^2 = H$)	284, 314	[d]	535	540 (16.4)	0.91
8 ($R^3 = OMe, R^2 = H$)	279, 309	[d]	529	528 (17.5)	0.86
9 ($R^3 = CN, R^2 = H$)	295, 332	299 (17.7) 355 (11.3)	570	569 (11.0)	0.99
10 ($R^3 = H, R^2 = F$)	279	[d]	569	592 (14.5)	0.76
11 ($R^3 = OMe, R^2 = F$)	290, 316	296 (37.2)	580	592 (17.5)	0.91
12 ($R^3 = CN, R^2 = F$)	271, 313	318 (49.7)	588	603 (18.5)	0.85

^[a] At room temperature before and after photoirradiation with 313 nm light. ^[b] λ_{\max} (nm), ϵ ($10^3 \text{ cm}^{-1} \text{ M}^{-1}$). The extinction coefficients of the closed form are obtained from the extinction coefficients of the PSS divided by the photoconversion. ^[c] Photochemical conversion given as molar fraction of the closed form [$X_{\text{closed}}/(X_{\text{closed}} + X_{\text{open}})$] in the PSS ($\lambda_{\text{irradiation}} = 313 \text{ nm}$) as determined by ^1H NMR in toluene solutions. ^[d] Determination of the absorption maxima was not possible because the bands were partly obscured by absorption of the solvent.

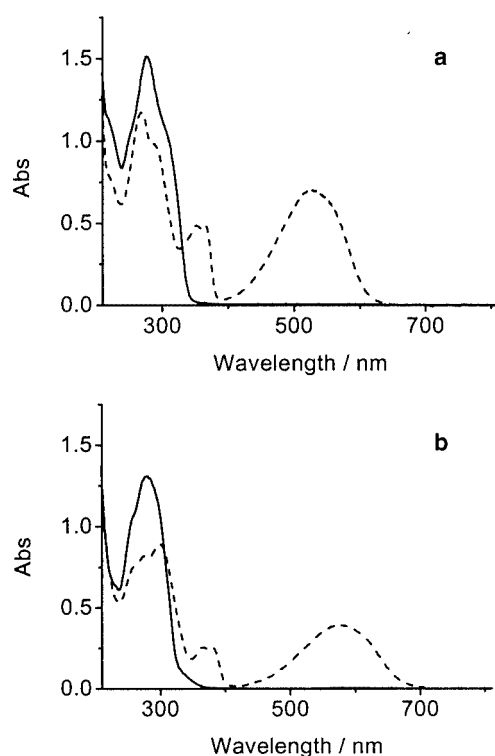


Figure 1. Absorption spectra of (a) perhydro switch **5** and (b) the corresponding perfluoro switch **10** in the open form (—) and in the photostationary state (PSS, ----) ($4.9 \times 10^{-5} \text{ M}$ (**5**) and $3.7 \times 10^{-5} \text{ M}$ (**10**) solutions in *n*-hexane at room temperature, PSS obtained by irradiation at 313 nm)

NMR spectra each showed conversion into a single new product with C_2 symmetry. The upfield shift of the thienyl hydrogens by 0.4–0.8 ppm is most pronounced, and indicates that the aromatic character of the thiophene moiety is lost. These spectral changes are characteristic for the formation of the closed forms (Scheme 1).^[1] The UV/Vis data for the closed forms of **5–12** are also summarized in Table 1. From the Table it is clear that the visible region spectral differences between the closed forms of the per-

hydro derivatives (**5, 8, 9**) on the one hand and the analogous perfluoro derivatives (**10–12**) on the other hand are more pronounced than the differences in the open forms, as is evident from the clear bathochromic shift of 30–60 nm found upon substitution of the hydrogens of the central cyclopentene ring by fluorine atoms. On comparison of the closed forms of the perhydro compounds **5–9**, it is evident that substituents at the *para* position of the phenyl group do not cause major changes of the absorption maxima in the visible region, and only the strongly electron-withdrawing cyano group induces a large bathochromic shift, of 40 nm. In the case of the closed perfluoro compounds, the changes due to substituent effects are only moderate and both the electron-donating methoxy and the electron-withdrawing cyano groups cause a bathochromic shift, suggesting that the ground state is stabilized though resonance with the methoxy or cyano groups. Comparison of the absorption maxima in *n*-hexane and toluene shows that the closed forms of the perfluoro derivatives **10–12** experience significant positive solvatochromic shifts, whereas with the perhydro derivatives **5–10** only small positive or negative solvatochromic shifts are observed. Apparently, the transition dipole moments differ significantly between the closed forms of the perhydro- and perfluorocyclopentene derivatives.^[25]

Irradiation of the closed forms of compounds **5–12** at $\lambda > 500 \text{ nm}$ in all cases resulted in the disappearance of the absorption band in the visible region and the restoration of absorption spectra of the open form, which establishes that the photochemical ring-opening/ring-closing process is fully reversible. Because of the non-zero absorption of the closed form in the UV spectral region, both ring closure and ring opening take place after photoexcitation in the UV region, producing a photostationary state (PSS), the position of which is determined by the quantum yields of ring closure and ring opening and the extinction coefficients of the open and closed forms at the wavelength of irradiation. The equilibrium ratios in the PSS ($\lambda_{\text{irradiation}} = 313 \text{ nm}$) could easily be obtained from the ^1H NMR spectra after the PSS had

been reached, and these values (as molar fractions of the closed form) are given in Table 1. For both the perhydrocyclopentenones **5–9** and the perfluorocyclopentenones **11** and **12** the molar fraction of the closed form is higher than 0.85 in the PSS upon irradiation at 313 nm.

A favourable property of the (dithienyl)perfluorocyclopentenones is their excellent photostability (fatigue resistance^[1]). Repeated irradiation with UV and visible light revealed that the perhydrocyclopentenones are also very stable towards photochemical decomposition (Figure 2). The photostability of the photochromic switches was studied in more detail by continuous irradiation of solutions of **5** or **10** with a laser beam, while the build-up of the lowest-energy absorption band of the closed form was monitored with a weak probe beam, at 550 nm for **5** and at 615 nm for **10** (Figure 3, part a). The quantum yield of the ring-closure reaction upon excitation at 300 nm could then be obtained from the initial slopes of the absorption curves. Figure 3 (b) shows the initial part of the curves from Figure 3 (a) after conversion of the absorbance and time axes (Exp. Sect.). It can immediately be concluded that the quantum yields of **5** and **10** are nearly identical and equal to 0.6 (± 0.1). The absolute error is determined mainly by the accuracy with which the output power of the pump laser is measured. However, the value of 0.6 is in excellent agreement with the value of 0.59 reported previously for **10**.^[26]

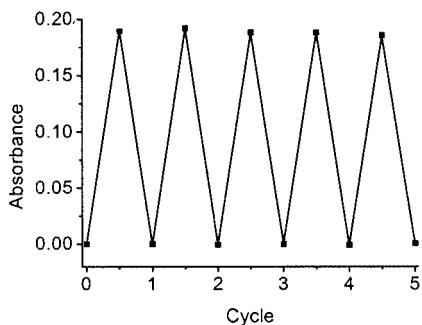


Figure 2. Cycling between the open and closed forms of the bis(*p*-cyanophenyl)-substituted cyclopentene switch **9** by repetitive irradiation at $\lambda = 313$ nm and $\lambda > 520$ nm at 25 °C in *n*-hexane. The ordinate shows the formation of the closed form as monitored by the absorbance at 570 nm

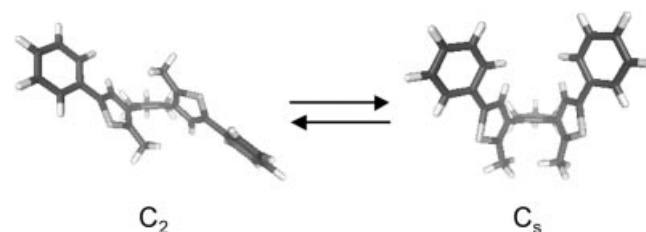
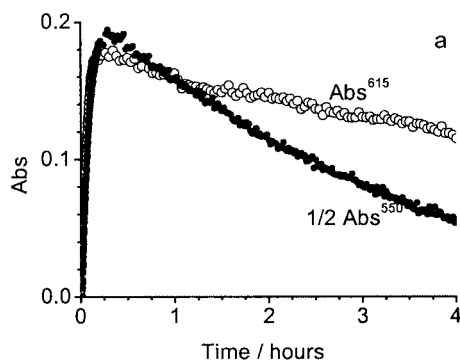


Figure 4. Two possible conformations of the open form of phenyl-substituted dithienyl cyclopentene switch **5**

From Figure 3 (a) it can be seen that the photostability of the switches is limited. According to Irie et al.^[29] the main pathway for decomposition takes place from the excited state of the closed form, which produces the scheme for photochromic reactions as shown in Equation (1), where *O*, *C* and *D* represent the concentrations of molecules in the open form (**5o**, **10o**), closed form (**5c**, **10c**) and decomposition products of **5** and **10**, and k_1 , k_2 and k_3 are the rate constants associated with the probability of ring-closure, ring-opening and photodecomposition, respectively.

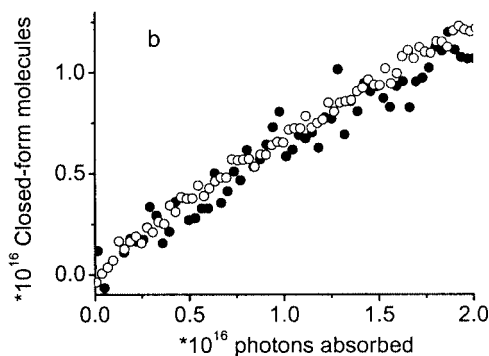


Figure 3. Photoconversion of **5** (●) and **10** (○) in cyclohexane at 25 °C by continuous irradiation with a laser at 300 nm (a); the formation of the closed form was monitored at 550 nm (**5**) and 615 nm (**10**); the conversion traces in (b) are calculated from the first minute of the curves shown in Figure 3 (a)

Since both open and closed forms absorb in the UV spectral region, the formation of **5c** (**10c**) from **5o** (**10o**) upon irradiation by UV light is a continuous process resulting in an equilibrium, the position of which is determined by the ratio between the rate constants k_1 and k_2 , which are dependent on the extinction coefficients of *O* and *C* at the excitation wavelength. The influence of rate constant k_3 on the equilibrium is negligible because k_3 is much smaller than k_1 and k_2 .

Equation (1) predicts a biexponential evolution of the concentrations *C* and *D* with the rate constants k_a and k_b , where k_a and k_b represent the growth and decay of the absorption of *C* at visible wavelengths,^[30] respectively, and fulfil the relations $k_a + k_b = k_1 + k_2 + k_3$ and $k_a \cdot k_b = k_1 \cdot k_3$. Biexponential fits of the absorption curves presented in Figure 3 yield rate constants $k_a = 5.5 \times 10^{-3} \text{ s}^{-1}$ and $k_b = 3.1 \times 10^{-5} \text{ s}^{-1}$ for **5**, and $k_a = 3.9 \times 10^{-3} \text{ s}^{-1}$ and $k_b = 8.1 \times 10^{-5} \text{ s}^{-1}$ for **10**. The larger value of k_a in the case of perhydrocyclopentene **5** reveals that the equilibrium situation is reached more rapidly than in the case of the perfluorocyclopentene **10**, while the ratio between the k_b values obtained for the two analogues indicates that the photostability of the perfluorinated analogue is roughly 2–3 times higher than that of the nonfluorinated compound.

Whereas the photochemical conversion between the open and closed forms proceeds with high quantum yields, the thermal interconversion is very slow for most perfluorocyclopentene switches. It has been reported that the thermal ring opening of **10c** in the crystalline phase has a half-life time of approximately 1900 years at 30 °C and 3.3 h at 150 °C.^[20] Because the lifetimes could have been influenced by crystal packing forces, the thermal stabilities of the closed forms of **5** and **8–12** were studied in toluene solution by ¹H NMR spectroscopy. For the perfluorocyclopentenenes **10–12**, the thermal conversion into the open form was found to be negligible (< 2%) after 14 h at 100 °C, indicating that the perfluoropentenenes are also thermally very stable in solution. The closed forms of perhydrocyclopentenenes **5** and **9** also showed excellent thermal stabilities, with half lives of 66 h and 40 h, respectively, for ring opening at 100 °C. Only the closed form of **8** is significant less stable at elevated temperatures, but has still a half-life time of 3 h at 100 °C. It should be noted that the thermal conversion of the closed form to the open form is a clean process in all cases, with no sign of any decomposition products in the ¹H NMR spectra.

In conclusion, various derivatives of perhydro- and perfluorocyclopentene photochromic switches have successfully been prepared by a Suzuki coupling of boronylated dithienyl perhydro- (**3**) and perfluorocyclopentene (**4**) with aryl bromides bearing electron-withdrawing or -donating substituents. It is to be expected that this route should be well suited for the convergent synthesis of other functionalized perhydrocyclopentene molecular switches, but less suitable for the corresponding perfluorocyclopentenenes because of the lower yields of the Suzuki coupling. The differences in the electron densities of the central cyclopentene moieties of the perhydrocyclopentene and perfluorocyclo-

pentene molecular switches have only a small effect on the absorption maxima of the electronic spectra, but cause subtle changes in substituent and solvatochromic effects. The photochromic behaviour is remarkably similar, and both types of switch combine excellent quantum yields (0.6) with high levels of photoconversion (> 0.85). The main difference is the lower photochemical and thermal stabilities of the perhydrocyclopentene molecular switches, but they can still undergo multiple switching cycles without notable photodecomposition, whereas the half lives for thermal interconversion between the open and closed forms are in all cases exceeding 3 h at 100 °C. It is therefore concluded that the perhydrocyclopentenenes should be excellent alternatives for the perfluorocyclopentenenes in most studies on diarylethene photochromic switches, but the perfluorocyclopentenenes might be better suited for applications such as data storage, which depend critically on fatigue resistance and long-term thermal stability.

Experimental Section

General Procedures: Melting points were determined with a Büchi melting point apparatus or a Mettler FP1 melting point apparatus and are uncorrected. ¹H NMR spectra were recorded at 200 MHz, 300 MHz or 500 MHz, ¹³C NMR spectra were recorded at 50.3 MHz, 75.4 MHz or 125.7 MHz, and ¹⁹F NMR spectra were recorded at 188.2 MHz or 470.3 MHz. All spectra were taken at ambient temperature. The residual protons from the solvent are taken as an internal reference and the chemical shifts are reported relative to TMS. Mass spectroscopy was performed by CI⁺, DEI or EI⁺ ionization procedures. The dithienylethenes are sometimes hard to sublime and only by means of DEI (desorption electron ionization) it was possible to obtain the mass spectra in these cases. Derivatives synthesized starting from compounds **1** and **2** are light-sensitive and so were exclusively handled in the dark, in brown glassware, with column chromatography being performed under yellow light.

Materials: Reagents and starting materials were used as supplied. The solvents were distilled and dried before use, if necessary, by standard methods. Aldrich silica gel grade 9385 (230–400 mesh) was used for column chromatography.

General Procedure for the Suzuki Reactions Starting from **1**

1,2-Bis(5'-dibutoxyboryl-2'-methylthien-3'-yl)cyclopentene (3): Compound **1** (1.75 g, 5.3 mmol) was dissolved in anhydrous THF (12 mL) under nitrogen, and *n*BuLi (4.5 mL of 2.5 M solution in hexane, 11 mmol) was added at once by syringe. This solution was stirred at room temperature for 30 min, and B(*n*BuO)₃ (4.3 mL, 16 mmol) was added at once. The resulting solution was stirred at room temperature for 1 h and used directly in the Suzuki cross-coupling reaction without any workup because boronic acid **3** was found to be hydrolysed during isolation.

1,2-Bis(2'-methyl-5'-phenylthien-3'-yl)cyclopentene (5):^[14] Bromobenzene (1.1 mL, 9.3 mmol) was dissolved in THF (12 mL), and after addition of [Pd(PPh₃)₄] (0.37 g, 0.3 mmol), the solution was stirred at room temperature for 15 min. Aqueous Na₂CO₃ (23 mL, 2 M) and 6 drops of ethylene glycol were then added, and the resulting two-phase system was heated in an oil bath until reflux (60 °C). The solution of **3** was added dropwise by syringe over a few

min. After the addition was complete, the reaction mixture was heated at reflux for 2 h, and then allowed to cool to room temperature. Diethyl ether (50 mL) and H₂O (50 mL) were added, and the organic layer was collected and dried (Na₂SO₄). After evaporation of the solvent, the product was purified by column chromatography (SiO₂, hexane) to give a brown/yellowish solid (1.80 g, 70%). M.p. 84–85 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.98 (s, 6 H), 2.03–2.13 (m, 2 H), 2.84 (t, *J* = 7.5 Hz, 4 H), 7.03 (s, 2 H), 7.19–7.25 (m, 2 H), 7.32 (dd, *J* = 6.9, *J* = 7.5 Hz, 4 H), 7.49 (d, *J* = 7.2 Hz, 4 H) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 14.4 (q), 23.0 (t), 38.5 (t), 123.9 (s), 125.2 (d), 126.8 (d), 128.7 (d), 134.4 (s), 134.5 (s), 136.6 (s), 139.5 (s) ppm. C₂₇H₂₄S₂ (412.6): calcd. C 78.60, H 5.86; found C 78.65, H 5.90.

1,2-Bis[5'-(4''-chlorophenyl)-2'-methylthien-3'-yl]cyclopentene (6): The same procedure as described for **5** was followed, starting from **1** (1.00 g, 3.04 mmol), and *n*BuLi (5.0 mL of 1.6 M solution in hexane, 8 mmol), B(*n*BuO)₃ (2.3 mL, 8.3 mmol), 4-bromochlorobenzene (2.20 g, 12 mmol), [Pd(PPh₃)₄] (0.40 g, 0.3 mmol), aqueous Na₂CO₃ (17 mL, 2 M) and 6 drops of ethylene glycol. Purification of the product by column chromatography (SiO₂, hexane) gave a white solid (0.94 g, 68%). M.p. 113–114 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.97 (s, 6 H), 2.05–2.10 (m, 2 H), 2.81 (t, *J* = 7.5 Hz, 4 H), 6.97 (s, 2 H), 7.27 (d, *J* = 8.7 Hz, 4 H), 7.38 (d, *J* = 8.7 Hz, 4 H) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 14.4 (q), 23.0 (t), 38.4 (t), 124.3 (d), 126.4 (d), 128.9 (d), 132.6 (s), 133.0 (s), 134.7 (s), 134.9 (s), 136.7 (s), 138.4 (s) ppm. HRMS calcd. for C₂₇H₂₂Cl₂S₂ 480.054, found 480.050.

1,2-Bis[5'-(4''-bromophenyl)-2'-methylthien-3'-yl]cyclopentene (7): The same procedure as described for **5** was followed, starting from **1** (1.00 g, 3.04 mmol), and *n*BuLi (5.0 mL of 1.6 M solution in hexane, 8 mmol), B(*n*BuO)₃ (2.3 mL, 8.3 mmol), 1,4-dibromobenzene (3.40 g, 14.4 mmol), [Pd(PPh₃)₄] (0.40 g, 0.3 mmol), aqueous Na₂CO₃ (17 mL, 2 M) and 6 drops of ethylene glycol. Purification of the product by column chromatography (SiO₂, hexane) gave a yellowish solid (1.30 g, 76%). ¹H NMR (300 MHz, CDCl₃): δ = 1.97 (s, 6 H), 2.02–2.10 (m, 2 H), 2.81 (t, *J* = 7.5 Hz, 4 H), 6.98 (s, 2 H), 7.32 (d, *J* = 8.4 Hz, 4 H), 7.42 (d, *J* = 8.4 Hz, 4 H). ¹³C NMR (75.4 MHz, CDCl₃): δ = 14.4 (q), 23.0 (t), 38.4 (t), 124.4 (d), 126.8 (d), 131.8 (d), 133.4 (s), 133.6 (s), 134.7 (s), 135.0 (s), 136.8 (s), 138.4 (s) ppm. HRMS calcd. for C₂₇H₂₂Br₂S₂ 567.953, found 567.951.

1,2-Bis[5'-(4''-methoxyphenyl)-2'-methylthien-3'-yl]cyclopentene (8): The same procedure as described for **5** was followed, starting from **1** (0.74 g, 2.3 mmol), and *n*BuLi (1.9 mL of 2.5 M solution in hexane, 4.7 mmol), B(*n*BuO)₃ (3.1 mL, 12 mmol), 4-bromoanisole (0.56 mL, 4.5 mmol), [Pd(PPh₃)₄] (0.31 g, 0.25 mmol), aqueous Na₂CO₃ (15 mL, 2 M) and 6 drops of ethylene glycol. Purification of the product by column chromatography (SiO₂, hexane/CH₂Cl₂, 1:1) gave a brown/yellowish solid (0.43 g, 40%). ¹H NMR (CDCl₃, 300 MHz): δ = 1.97 (s, 6 H), 2.01–2.11 (m, 2 H), 2.82 (t, *J* = 7.5 Hz, 4 H), 3.81 (s, 6 H), 6.90 (s, 2 H), 6.86 (d, *J* = 8.9 Hz, 4 H), 7.41 (d, *J* = 8.9 Hz, 4 H) ppm. ¹³C NMR (CDCl₃, 75.4 MHz): δ = 14.4 (q), 23.0 (t), 38.5 (t), 55.4 (q), 114.2 (d), 123.0 (d), 126.6 (d), 127.5 (s), 133.4 (s), 134.6 (s), 136.6 (s), 139.5 (s), 158.8 (s) ppm. HRMS calcd. for C₂₉H₂₈O₂S₂ 472.153, found 472.153.

1,2-Bis[5'-(4''-cyanophenyl)-2'-methylthien-3'-yl]cyclopentene (9): The same procedure as described for **5** was followed, starting from **1** (0.74 g, 2.3 mmol), and *n*BuLi (1.9 mL of 2.5 M solution in hexane, 4.7 mmol), B(*n*BuO)₃ (3.1 mL, 12 mmol), 4-bromobenzonitrile (0.81 mL, 4.5 mmol), [Pd(PPh₃)₄] (0.31 g, 0.25 mmol), aqueous

Na₂CO₃ (15 mL, 2 M) and 6 drops of ethylene glycol. Purification of the product by column chromatography (SiO₂, hexane/CH₂Cl₂, 1:4) gave a brown/yellowish solid (0.37 g, 35%). M.p. 126–127 °C. ¹H NMR (CDCl₃, 300 MHz): δ = 2.01 (s, 6 H), 2.05–2.15 (m, 2 H), 2.84 (t, *J* = 7.5 Hz, 4 H), 7.12 (s, 2 H), 7.54 (d, *J* = 8.4 Hz, 4 H), 7.59 (d, *J* = 8.4 Hz, 4 H) ppm. ¹³C NMR (CDCl₃, 75.4 MHz): δ = 14.6 (q), 23.0 (t), 38.4 (t), 110.0 (s), 118.9 (s), 125.3 (d), 126.0 (d), 132.6 (d), 134.8 (s), 137.1 (s), 137.1 (s), 137.6 (s), 138.5 (s) ppm. HRMS calcd. for C₂₉H₂₂N₂S₂ 462.121, found 462.122.

General Procedure for the Suzuki Reactions Starting from **2**

1,2-Bis(5'-dibutoxyboryl-2'-methylthien-3'-yl)perfluorocyclopentene (4): The same procedure as described for **3** was used, starting from **2** (0.20 g, 0.5 mmol) and *n*BuLi (0.66 mL of 1.6 M solution in hexane, 1.1 mmol), and B(*n*BuO)₃ (0.41 mL, 1.5 mmol). The resulting solution was also used directly in the Suzuki cross-coupling reaction without any workup, because boronic acid **4** is hydrolysed during isolation.

1,2-Bis(2'-methyl-5'-phenylthien-3'-yl)perfluorocyclopentene (10):^[19] Bromobenzene (0.10 mL, 1.0 mmol) was dissolved in THF (8 mL) and, after addition of [Pd(PPh₃)₄] (35 mg, 0.03 mmol), the solution was stirred at room temperature for 15 min. Aqueous Na₂CO₃ (1 mL, 2 M) and 6 drops of ethylene glycol were then added, and the resulting two-phase system was heated to reflux (60 °C) in an oil bath. The solution of **4** was added dropwise by syringe over a period of several min. After addition was complete, the reaction mixture was heated at reflux for 2 h, and was then allowed to cool to room temperature. Diethyl ether (50 mL) and H₂O (50 mL) were added, and the organic layer was collected and dried (Na₂SO₄). After evaporation of the solvent the product was purified by column chromatography (SiO₂, hexane) to give a greenish solid (16 mg, 7%). ¹H NMR (300 MHz, CDCl₃): δ = 1.96 (s, 6 H), 7.28 (s, 2 H), 7.29 (d, *J* = 6.9 Hz, 2 H), 7.38 (dd, *J* = 7.2, *J* = 7.5 Hz, 4 H), 7.53 (d, *J* = 7.5 Hz, 4 H) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 14.5 (q), 120.5 (d), 122.4 (d), 125.6 (d), 127.9 (d), 129.0 (d), 133.3 (s), 141.3 (s), 142.2 (s) ppm. ¹⁹F NMR (188.2 MHz, CDCl₃): δ = −111.26 (t, *J* = 6 Hz, 4 F), −133.03 (m, 2 F) ppm. HRMS calcd. for C₂₇H₁₈F₆S₂ 520.075, found 520.075.

1,2-Bis[5'-(4''-methoxyphenyl)-2'-methylthien-3'-yl]perfluorocyclopentene (11):^[20] The same procedure as described for **10** was followed, starting from **2** (0.10 g, 0.32 mmol), and *n*BuLi (0.32 mL of 1.6 M solution in hexane, 0.51 mmol), B(*n*BuO)₃ (0.22 mL, 0.78 mmol), 4-bromoanisole (0.08 mL, 0.6 mmol), [Pd(PPh₃)₄] (40 mg, 0.04 mmol), aqueous Na₂CO₃ (10 mL, 2 M) and 6 drops of ethylene glycol. Purification of the product by column chromatography (SiO₂, CH₂Cl₂/hexane, 1:2) gave a blue/grey solid (31 mg, 22%). ¹H NMR (CDCl₃, 200 MHz): δ = 1.93 (s, 6 H), 3.82 (s, 6 H), 6.90 (d, *J* = 9.2 Hz, 4 H), 7.14 (s, 2 H), 7.45 (*J* = 9.0 Hz, 4 H) ppm. ¹³C NMR (CDCl₃, 125.7 MHz): δ = 14.5 (q), 55.4 (q), 114.4 (d), 116.2 (s), 118.2 (s), 121.3 (d), 125.7 (s), 126.2 (s), 126.9 (d), 136.0 (s), 140.3 (s), 142.1 (s), 159.4 (s) ppm. ¹⁹F NMR (CDCl₃, 188.2 MHz): δ = −111.16 (t, *J* = 5.6 Hz, 4 F), −132.96 (m, 2 F) ppm. HRMS calcd. for C₂₉H₂₂F₆O₂S₂ 580.097, found 580.095.

1,2-Bis[5'-(4''-cyanophenyl)-2'-methylthien-3'-yl]perfluorocyclopentene (12): The same procedure as described for **10** was used, starting from **2** (0.10 g, 0.32 mmol), and *n*BuLi (0.32 mL of 1.6 M solution in hexane, 0.51 mmol), B(*n*BuO)₃ (0.22 mL, 0.78 mmol), 4-bromobenzonitrile (1.1 mL, 0.6 mmol), [Pd(PPh₃)₄] (40 mg, 0.04 mmol), aqueous Na₂CO₃ (10 mL, 2 M) and 6 drops of ethylene glycol. Purification of the product by column chromatography (SiO₂, first EtOAc/hexane, 1:2, then CH₂Cl₂/hexane, 1:2) gave a blue/grey solid (30 mg, 23%). M.p. 189–191 °C. ¹H NMR (CDCl₃,

200 MHz): δ = 1.97 (s, 6 H), 7.37 (s, 2 H), 7.58–7.68 (m, 8 H) ppm. ^{13}C NMR (CDCl_3 , 125.7 MHz): δ = 14.7 (q), 111.2 (s), 116.0 (s), 118.5 (s), 124.3 (d), 125.3 (s), 125.8 (d), 126.2 (s), 131.84 (s), 132.8 (d), 137.3 (s), 140.1 (s), 143.4 (s) ppm. ^{19}F NMR (CDCl_3 , 188.2 MHz): δ = –111.23 (t, J = 6 Hz, 4 F), –132.90 (m, 2 F) ppm. HRMS calcd. for $\text{C}_{29}\text{H}_{16}\text{F}_6\text{N}_2\text{S}_2$ 570.066, found 570.066.

Photochromic Behaviour: Solutions of switches **5**–**12** of known concentration were irradiated in a 1-cm quartz cuvette for UV/Vis measurements or in 5-mm Pyrex tubes for NMR experiments, using a 200 W mercury lamp (Oriel) with the appropriate filters (Andover Corporation Optical Filters). ^1H NMR experiments were performed on a Varian VXR-300 spectrometer. All measurements were carried out at room temperature except for the thermal stability tests of the closed forms.

Real Time Dynamics: The quantum efficiency of the ring-closure reaction and the photostability of the photochromic switches were measured by irradiation of a 1-mm cell, containing a solution of known concentration of **5** or **10** dissolved in cyclohexane, with UV light of power 285 μW at wavelength 300 nm. Simultaneously a weak probe (at 550 nm for **5** and at 615 nm for **10**) monitored the build-up of the lowest-energy absorption band of the closed form. Direct readout of the quantum yield is possible after conversion of the time and absorbance axes into numbers of absorbed photons and numbers of closed-form molecules, respectively. The time axis is converted by insertion of the known irradiation intensity I_0 and the absorbance of the open-form molecules at 300 nm into the relation:

$$(1 - 10^{-Abs}) I_0 t = N_{\text{photons}} \left(\frac{hc}{\lambda} \right)$$

where t is the time in seconds, N_{photons} the number of photons, h the Planck constant and c the speed of light. The absorbance of the open-form molecules at 300 nm is known exactly only at time $t = 0$. The absorbance axis is converted into numbers of closed-form molecules by the relation:

$$Abs(\lambda) = \varepsilon_{\text{closed}}(\lambda) \cdot \left(\frac{N_{\text{closed}}}{N_{\text{AV}} V} \right) \cdot l$$

with $\varepsilon_{\text{closed}}(\lambda)$ the extinction coefficient of the closed-form molecules at wavelength λ , l the length of the sample in cm, N_{closed} the number of closed-form molecules and V the volume of the sample.

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