Chapter 3

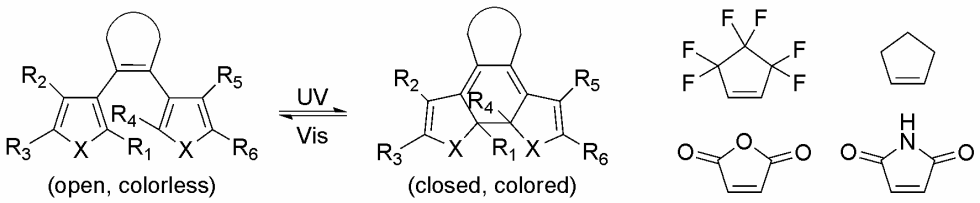
Synthesis and Photochromic Properties of New Thiol-Terminated Diarylethenes; Temperature Dependence of the Switching Process

This chapter deals with the synthesis and photochemical properties of diarylethene photochromic molecular switches. A number of new derivatives are presented bearing one or more acetyl protected thiol groups. The photochromic properties of the newly synthesized diarylethenes in solution were studied. The temperature dependence of the photochemical ring opening in solution between 115K and 290K was investigated. Suppression of the ring opening process, which is complete below a cut-off temperature, is observed with decreasing temperature. For the corresponding ring closing process no temperature dependence was observed. The results confirm the existence of a thermal activation barrier to photochemical ring opening of diarylethene photochromic molecules.[*]

[*] Part of this chapter has been published: D. Dulić, T. Kudernac, A. Pugžlys, B. L. Feringa, B. J. van Wees, *Adv. Mater* in press; T. Kudernac, D. Dulić, S. J. van der Molen, B. J. van Wees, B. L. Feringa , *Mol. Cryst. Liq. Cryst.* **2005**, *430*, 205.

3.1 Introduction

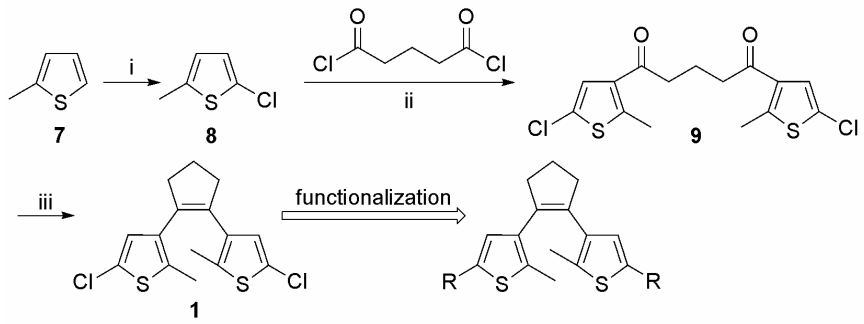
The rapidly growing interest in diarylethene-based molecular switches has stimulated the synthesis of a variety of new derivatives.[1] There are several possibilities of structural modifications of the photoswitching unit while photochemical processes, ring opening and ring closure, are preserved (Scheme 1). The unexpected loss of reversibility upon covalent anchoring of molecules **3**[2] and **6**[3] (Chapter 2, Scheme 1 and 2) to gold electrodes (discussed in Chapter 2) has aroused us to seek better candidates that would imitate the previously achieved high difference in conductance[2,3] of the closed and the open form while restoring the reversibility. The key problem of designing new diarylethene derivatives is to achieve a photochemically reversible and a thermally irreversible molecular system. Thermal back reaction is attributed to the loss of aromatic stabilization energy in the closed form.[1b] Consequently, it was concluded that the thermal stability of diarylethene-type photochromic compounds can be attained by introducing heterocyclic aryl groups, which have low aromatic stabilization energies. Thiophene, which has a relatively low aromatic stabilization energy, has thus become the most frequently used heterocyclic group in these photochromic compounds. Another structurally important element is the central double bond. Usually, cyclic olefins are used to prohibit cis to trans photoisomerization, which may compete with the photocyclization reaction. Several 1,2-bis(thien-3-yl) systems containing maleic anhydride, maleimide, perfluorocyclopentene, and cyclopentene units have been synthesized so far.[1] Both diarylmaleic anhydrides and diarylmaleimides are readily accessible but are sensitive to acidic conditions. Hence perfluorocyclopentene and perhydrocyclopentene bridging units are the most commonly used.



Scheme 1 *Left: general structure and switching cycle for diarylethenes. Right: different bridging units used for diarylethenes (X = S, O, NH).*

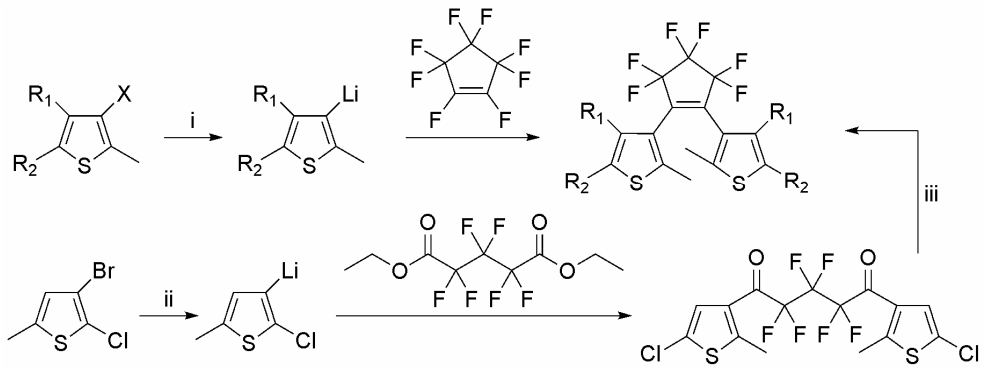
Few general synthetic approaches leading to perfluorocyclopentene and perhydrocyclopentene based switches have been developed. Well-established methodology leading to the 1,2-dithienylcyclopentenes based on titanium-mediated carbonyl coupling has been developed in our laboratories (Scheme 2).[4] The synthesis can be performed on a

multigram scale from relatively cheap starting materials. Compound **1** is synthesized starting from 2-methylthiophene, which was chlorinated at the 5-position with NCS in AcOH and benzene, followed by a Friedel–Crafts reaction with $AlCl_3$ and glutaryl chloride at 0 °C. The resulting 1,5-bis(5-chloro-2-methyl-3-thienyl)pentadione is used in a McMurry reaction with $TiCl_3(THF)_3$ and Zn in THF at 40 °C to provide **1**. The advantage of this approach is that the photochromic switch **1** can be functionalized easily in several ways. Compound **1** can, for instance, readily undergo a chlorine/lithium exchange at ambient temperature thus providing a versatile handle for the introduction of functionality.[4] Consequently, this method may provide both, symmetric or asymmetric dithienylcyclopentenes.



Scheme 2 *Reagents and conditions: i) NCS, AcOH, benzene, reflux, 80%; ii) $AlCl_3$, glutaryl chloride, CS_2, 0 °C, 94%; iii) $TiCl_3(THF)_3$, Zn, THF, 40 °C, 44%.*

A versatile synthetic route towards hexafluorocyclopentene dithienylethenenes is based on reaction of lithiated thiophenes with octafluorocyclopentene, resulting in switchable products by addition elimination reactions (Scheme 3). Various functionalities can be introduced by using substituted thiophenes. However, those functional groups must tolerate harsh lithiation condition in the final step. The expensive and rather volatile octafluorocyclopentene and the low yields commonly found in double substitution reactions of octafluorocyclopentene with lithiated thiophenes are major disadvantages. An alternative and more economic route leading to hexafluorodithienylethenens has been recently developed.[5] It follows the same synthetic strategy as for perhydrocyclopentene dithienylethenes shown in Scheme 2. The key step is an intramolecular McMurry coupling (Scheme 3) leading to dichloro derivative which can be further functionalized.

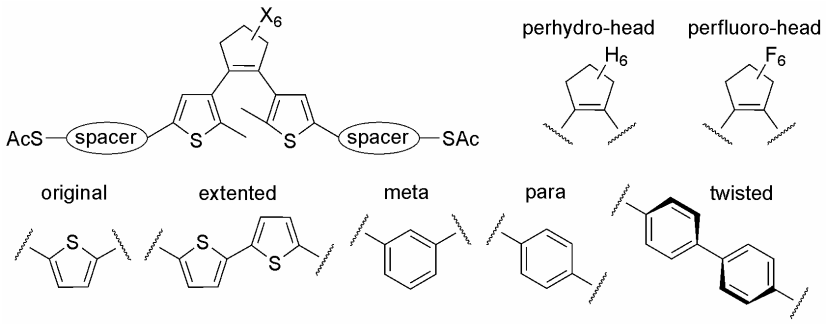


Scheme 3 *Two synthetic routes to perfluoro dithienylethenes. Top: original synthesis using octafluorocyclopentene.*[6] *Bottom: alternative synthesis forming a versatile dichloro-substituted switch used for further derivatization.*[5] *i) n-BuLi; ii) n-BuLi; iii) Zn, $TiCl_4$, (R_1= H and R_2= Cl).*

Photochromism of diarylethenes is the origin of the interest in these molecules. Photoswitching effects of diarylethenes are based on reorganization of the π-conjugated backbone of the molecule, which consequently leads to different physical properties. Knowledge of the key factors governing photochromic processes is essential for future utilization of diarylethenes as smart materials as well as in the fundamental understanding of the photo-processes involved. Hence, temperature dependent studies are necessary to reveal new aspects and limits of the switching process, as previously shown by measurements at elevated temperatures.[7] Additionally, determining possible switching restrictions at low temperatures is particularly important in view of carrying out conductance measurements at the single molecular level, which are restricted at room temperature because of the high mobility of the gold atoms constituting the electrodes in this type of experiments. In order to achieve stability of the metal/molecule/metal system it is often necessary to perform measurements at low temperatures.[8] The goal of the research described in this chapter is to develop fast and convenient synthetic strategies leading to various diarylethene derivatives bearing suitable anchoring groups which can be used for an attachment of these compounds to metallic surfaces and to study in detail the photochemical processes that diarylethene molecular switches undergo. In short, this chapter describes the synthesis of novel diarylethenes and their photochromic properties at ambient conditions as well as temperature-dependent kinetics studies revealing new restrictions to the switching process. Photochromic properties of the selected compounds described in this chapter are subjects of discussion in Chapter 4 and Chapter 5 upon their adsorption on a gold surface.

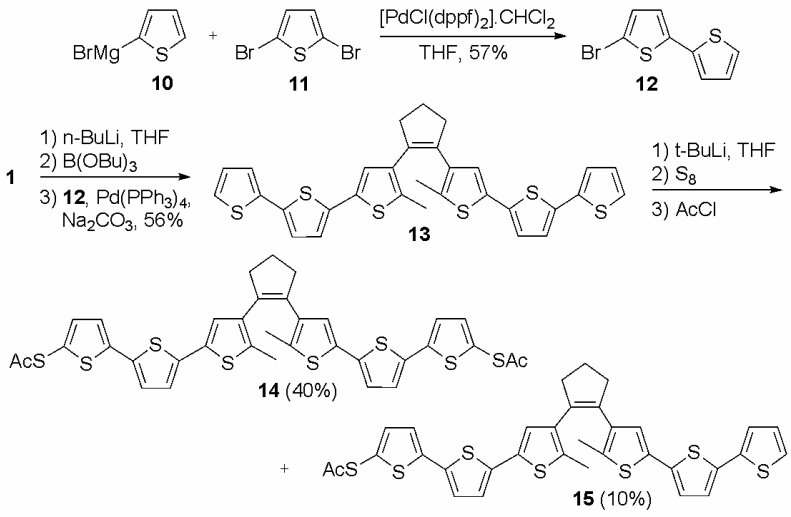
3.2 Synthesis of Thiol Terminated Diarylethenes

As discussed in Chapter 2, covalent attachment of thiophene-based switches **3** and **6** to a gold surface leads to the complete suppression of ring-closure and retardation of ring-opening. These effects of grafting photoactive molecules on gold have been attributed to the quenching of excited states of the molecules by gold surfaces and several quenching mechanisms have been proposed (see Chapter 2). A simple isolation of the central switching unit from the gold surface by introduction of a saturated aliphatic chain could be sufficient to preserve fully reversible behavior. However, electron transport would be substantially reduced and consequently the on-off ratio between conductance of the closed and open forms would be lowered. On our quest to find the best candidate for a reversible (surface bound) molecular switch we therefore needed to address both aforementioned issues. In order to preserve a fully reversible system after adsorption of a molecule on gold electrodes while keeping the conductance high, one could modify the electronic structure of the switch by careful variation of either the "head" group or the spacer unit (Scheme 4). If the hexahydrocyclopentene head group is exchanged by the electron withdrawing hexafluorocyclopentene group, both HOMO and LUMO levels are lowered, while the gap between them remains almost the same.[9] That would lead to the different alignment of molecular orbitals with the Fermi level of gold resulting in entirely new molecule-metal surface electronic coupling. The new alignment might influence the switching efficiency and due to the unchanged HOMO-LUMO gap the on-off ratio stays high. On the other hand one could choose to decrease the HOMO-LUMO gap *e. g.* by increasing the length of the conjugated system. This can be easily realized by modifying the spacer unit. The original design with a simple thiophene as a spacer can be substituted by two connected thiophene rings (Scheme 4). Another option to achieve full reversibility is to tune the extent of the electronic coupling of the central switching unit with the electrodes. A straightforward way of testing this is to examine an effect of the linearly conjugated spacer on the switching efficiency *versus* a cross conjugated spacer. For that purpose one can use *para* or *meta* di-substituted benzenes. Additionally, it should be possible to partially decouple the central switching unit from the anchoring group using a biphenyl spacer unit where the delocalization of electrons is hampered because of the twisted conformation. The following subsection will focus on the synthesis of the target molecules with the previously mentioned variations of the head group and spacer unit.



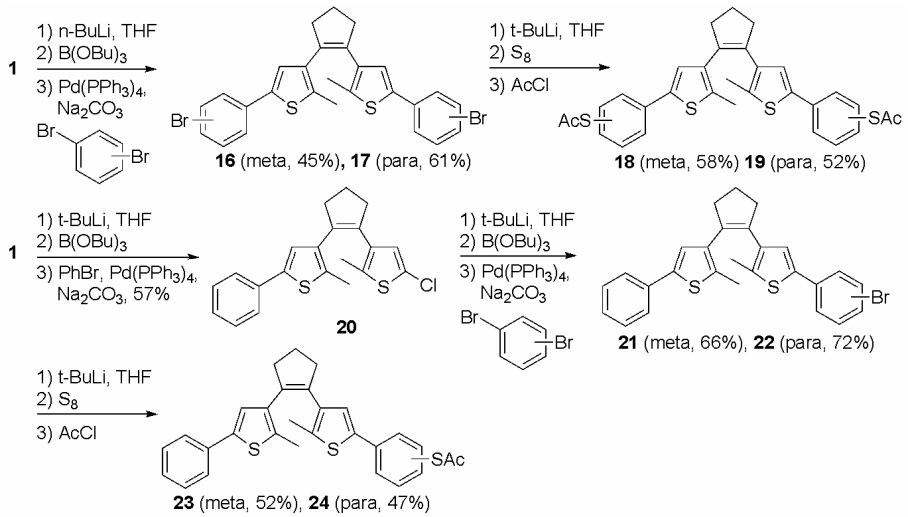
Scheme 4 *General scheme depicting possible variation of the head group or the spacer unit leading to modifications of the electronic structure of the switch.*

Perhydrocyclopentene-based switches **14** and **15** were synthesized following the strategy depicted in Scheme 2, employing compound **1** (Scheme 5). First, intermediate **12** was prepared by palladium catalyzed reaction of the Grignard reagent **10** and dibromide **11**. Treatment of compound **1** with *n*-butyllithium and subsequent reaction with tri-*n*-butylborate results in a boronic acid intermediate, which was reacted with compound **12** in the presence of a palladium catalyst providing **13** in 56% yield. Compound **13** was first lithiated and subsequent treatment with sulfur and acetyl chloride leads to formation of compound **14** as a main product and compound **15** as a side product of the reaction.



Scheme 5 *Synthetic route to compounds **14** and **15**. The final step gives compound **14** as a main product in 40% yield and compound **15** in 10% yield as a side product.*

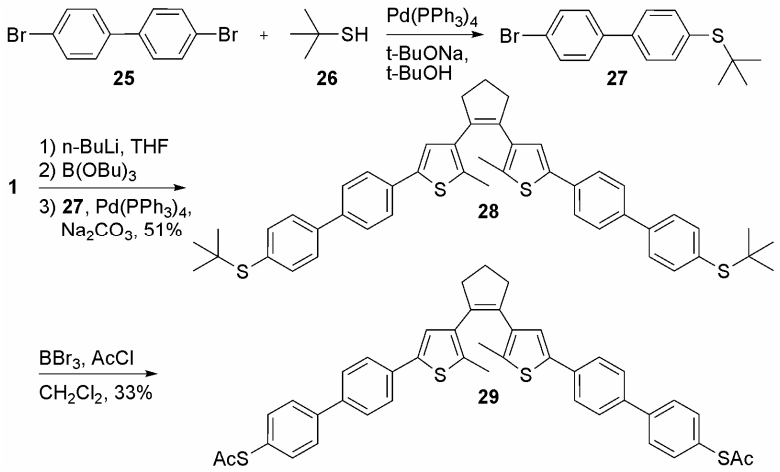
In order to have access to molecules that differ only in the position of the connection of the central switching unit with terminated thiol groups either in linearly conjugated or cross conjugated manner, compounds **18**, **19**, **23** and **24** were prepared (Scheme 6). In the synthesis of compounds **18**, **19**, **23** and **24,** brominated aryldithienylethenes were prepared as key intermediates. Subsequent lithiations can then be directed to selected sites. The overall strategy was based again on utilization of the versatile intermediate **1**. Two approaches, one towards symmetric and one to asymmetric switches yielded compounds **18**, **19**, **23** and **24**.



Scheme 6 *Synthetic route to symmetrically substituted compounds **18** and **19** and asymmetrically substituted compounds **23** and **24**. The final steps give yields of 58% of meta substituted **18**, 52% of para substituted **19**, 52% of **23** and 47% of **24**.*

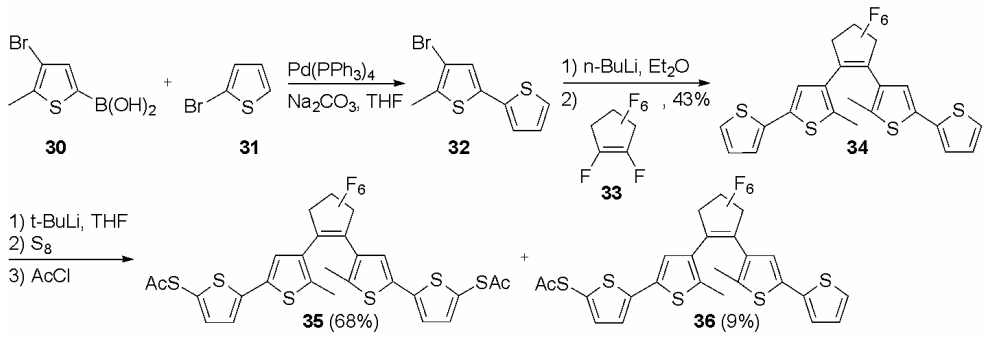
In all so far synthesized diarylethene compounds, sulfur was introduced in the last step. Those reactions give moderated yields and purifications are complicated by the presence of oligomeric sulfur species that are formed. An alternative could be to use intermediates, which already possess protected thiol groups. The protective group must tolerate the basic conditions involved in Suzuki coupling with derivative **1**. An acetyl protective group is not inert under the conditions that are usually employed for derivatization of **1** in a Suzuki coupling. In the course of reaction the acetyl group is being hydrolyzed and the deprotected thiol moiety poisons the palladium catalyst. For the synthesis of compound **29** (Scheme 7) possessing a twisted biphenyl spacer group we decided to test the aforementioned synthetic strategy. A use of a *t*-butyl as a thiol protective group and the conversion to S-acetyl in a synthesis of acetyl protected thiols has been described previously.[10] *t*-butylthiol

intermediate **27** was synthesized by reacting dibromobiphenyl **25** with *t*-butylthiol. Palladium catalyzed sulfenylation involves oxidative addition of the aryl halide to Pd, followed by nucleophilic attack of the thiolate anion on the adduct. The resulting compound **27** was then used in Suzuki coupling, without its thiol groups being deprotected. The *t*-butyl protected thiol groups of compound **28** were then deprotected using BBr_3 and re-protected with acetyl chloride in order to prevent any oxidative dimerization of the aromatic thiols. Compound **29** is formed in 33% yield, which is comparable to the results obtained *via* the previous strategy. However, if more complicated side groups are needed this strategy seems to be more favorable since the last step of the previous strategy involves lithiation, which might induce side reactions and is usually less tolerant towards functional groups.



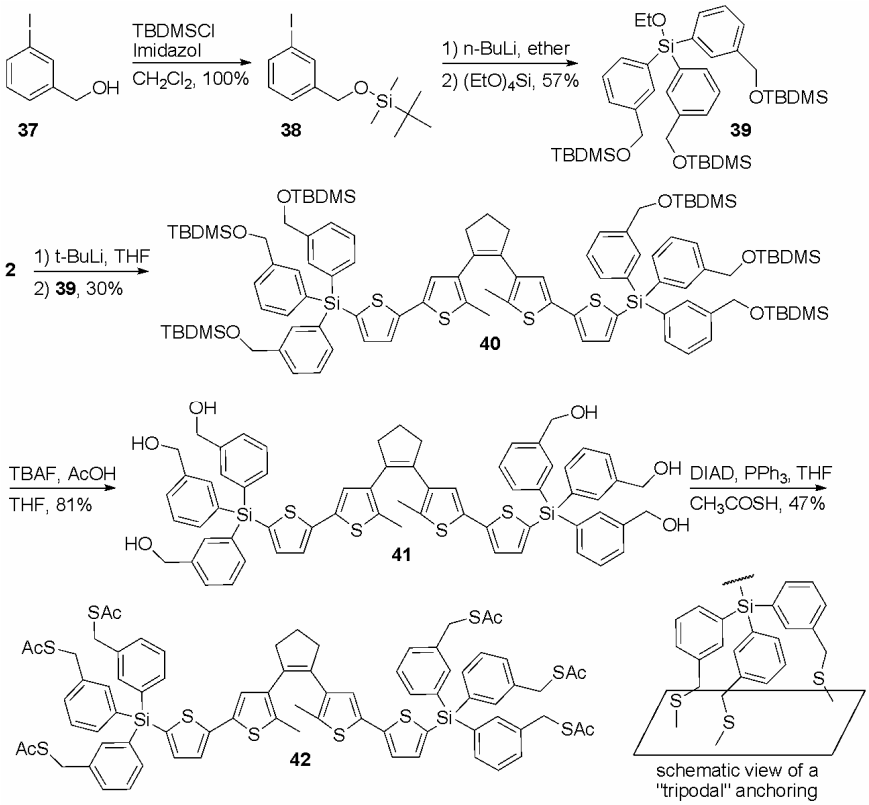
Scheme 7 *Synthetic route to compound **29**.*

For the synthesis of perfluorocyclopentene based compounds **35** and **36** (Scheme 8) the original strategy developed by Irie[6] (Scheme 3) was used. The key step is a reaction of lithiated thiophenes with octafluorocyclopentene. In order to prepare the intermediate **32**, palladium catalyzed coupling of boronic acid **30**[11] and bromide **31** was performed. Compound **32** was then reacted with *n*-buthyllithium and the lithiated intermediate reacted with octafluorocyclopentene **33** giving photochromic compound **34** in 43% yield. Compound **34** was next treated with *t*-buthyllithium followed by reaction with sulfur. Thiol groups of the thiol terminated intermediates were subsequently protected *in-situ* by acetyl moieties leading to both disubstituted compound **35**, as a main product, and monosubstituted **36** as a side product.



Scheme 8 *Synthetic route to hexafluorocyclopentene compounds **35** and **36**. The final step gives compound **35** as a main product in 68% yield and compound **36** in 9% yield as a side product.*

In addition to the compounds previously discussed, molecule **42** (Scheme 9) was designed as well. It addresses the same problem of the partial isolation of the switching unit from anchoring side groups. π-electrons are not delocalized through the whole molecule due to the presence of both a sp^3 hybridized silicon atom as well as six benzylic sp^3 carbon atoms. Adjacent acetyl protected thiol groups can be deprotected in the course of attachment of the molecule to gold electrodes and create stable "tripodal" anchoring (Scheme 9). This "tripodal" anchoring should have a beneficial effect on the stability of anchored molecules on gold electrodes (Scheme 9, right bottom). The stabile anchoring of molecules to metal surfaces is of great importance in the field of single molecule electronics.[12] For aromatic thiols inserted in *n*-dodecanethiol matrixes so-called stochastic switching has been observed in STM experiments (for more details, see Chapter 2). There is still no consensus on the origin of stochastic switching. However, Ramachandran *et al.* relate the phenomenon to instabilities of the Au–S bond.[13] Compound **42** with its "tripodal" anchoring hence addresses also basic problems of stability in single molecule electronics. The synthetic route to compound **42** is shown in Scheme 9. Tripod base **39** was synthesized as a crucial intermediate starting from *meta*-iodobenzylalcohol. The hydroxy group was first protected using TBDMSCl. Resulting compound **38** was then treated with *n*-butyllithium and the subsequent reaction with tetraethylorthosilicate gave tripod base **39**. Tripod base **39** was reacted with lithiated compound **2** (for the synthesis of compound **2,** see Chapter 2) to give molecular switch **40** in 30% yield. Six protected hydroxyl groups were then deprotected using *tert*-butylammonium fluoride following by Mitsunobu reaction with thioacetic acid as a nucleophile to give the desired compound **42**.



Scheme 9 *Synthetic route to compound* ***42***.

3.3 Room Temperature Photochromic Properties of Diarylethenes

3.3.1 Absorption Spectra and Photochemical Interconversion of Open and Closed Forms

In general, the open ring isomers of dithienylethenes have absorption bands at short wavelengths. Upon irradiation with UV light, new absorption bands appear at longer wavelengths, which are ascribed to the closed ring isomers. Most dithienylethenes show large spectral shifts upon photoisomerization from the open to the ring isomers.[1] In the closed ring isomers, π-electrons are delocalized through the whole molecule. The absorption spectra of the closed ring isomers depend on the substituents of the thiophene

rings. The absorption spectra of the open ring isomers also depend on the nature of the upper cycloalkene structures.

Figure 1 shows the UV/Vis absorption spectra of the open and closed forms of diarylethene derivatives **3, 6, 14, 15, 18, 23, 24, 29, 35, 36, 42** in toluene. Dynamic interconversion between the open and closed form can be achieved by irradiation at selected wavelengths (λ = 313 nm for the ring closure and $\lambda > 420$ nm for the ring opening). It should be noted that upon irradiation of the open forms with UV light in all cases a photostationary state (PSS) is obtained. Due to nonzero absorption of the closed form in the UV spectral region, both ring closure and ring opening take place after photoexcitation, leading to an equilibrium situation, the so called photostationary state (PSS), determined by the quantum yields of ring closing and ring opening processes. However, quantum yields obtained for diarylethenes showed that the cyclization is more efficient than the ring opening.[1] In the case of the presented compounds the PSSs were determined by ^{1}H NMR spectroscopy. In all cases no traces of the open forms could be detected suggesting that the ring closure process for all compounds reaches essentially full conversions.

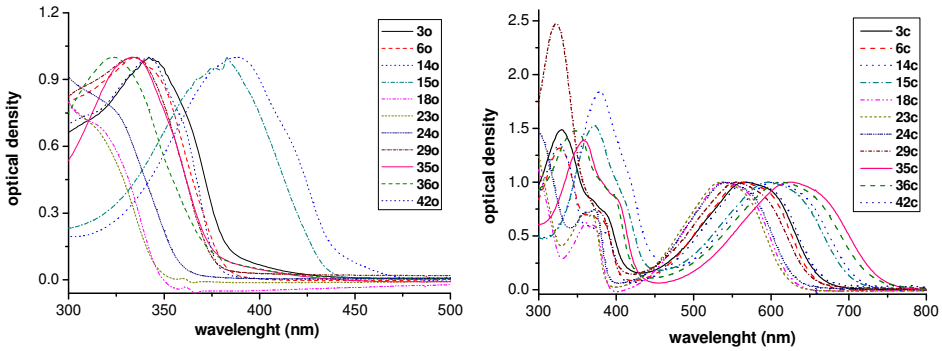


Figure 1 *Normalized absorption spectra of a) open forms and b) closed forms of the photochromic compounds taken in toluene.*

Table 1 shows the absorption maxima for the open and closed forms of the diarylethenes described in this chapter and their corresponding extinction coefficients. The importance of the effect of the substitution of cyclopentene bridging unit is demonstrated by comparing absorption spectra of perhydro compounds **3** and **6** and perfluoro compounds **35** and **36**. The absorption maxima of the open forms of all for compounds appear around a wavelength of 335 nm. However, the closed ring isomers of perfluoro derivatives show significant shifts in the UV/Vis absorption spectra to longer wavelengths in comparison with the perhydro derivatives. The effect of side-group substitution and length of

conjugation can be seen on the spectral changes for molecules **14** and **15** with respect to **3** and **6**. Both, the absorption maxima of the open and closed forms of **14** and **15** are shifted to longer wavelengths by 40 to 50 nm compared to **3** and **6**. Thioacetate moieties, if present as substituents on a benzene ring are responsible for small shifts in UV/Vis absorption (~7 nm for the open form and ~12 nm for the closed form) towards longer wavelengths.[9] Additionally the position of substitution on the benzene ring might be important as well. *Para*- substituted derivative **24** exhibits a bathochromic shift compared to *meta*- substituted derivative **23**. This observation suggests that the thioacetate group in the *meta*- position participates to a lesser extent in the delocalization of electrons within the molecular scaffold. Hence it can be anticipated that if molecules **23** and **24** are anchored on a metal electrode the central switching unit of molecule **23** will be partially isolated from the metal surface with respect to **24** and subsequently can be less prone to metal-assisted inhibition of the photoreactions. Compound **29** bearing the biphenyl spacer unit shows a spectral shift to longer wavelengths in comparison with "mono-"phenyl derivatives **18**, **19**. However the effect of one extra benzene ring is approximately four times less significant then for a thiophene ring in compounds **14** and **15**. This is due to the twisted orientation of two adjacent benzene rings. The delocalization of electrons is therefore less effective.

Table 1 *Photophysical properties of open and closed forms in toluene.*

Compound	Open form λ_{max}(abs) [nm] (ε [10^3 $cm^{-1}M^{-1}$])	Closed form λ_{max}(abs) [nm] (ε [10^3 $cm^{-1}M^{-1}$])	
3	342	331 (27), 372 (I, 14), 387 (S), 601 (S),	569 (21)
6	335 (32)	328 (28), 365 (I, 14), 369 (14), 386 (S), 602 (S)	562 (22)
14	388 (38)	379 (30), 419 (S), 431 (I, 11)	602 (17)
15	383 (41)	371 (32), 413 (S), 419 (I, 13)	596 (19)
18	323 (S)	340 (I, 10), 361 (17), 370 (17), 578 (S)	538 (28)
23	315 (S)	337 (I, 11), 360 (16), 369 (16), 569 (S)	537 (23)
24	327 (S)	346 (I, 11), 360 (S), 372 (14), 580 (S)	542 (19)
29	333 (55)	323 (52), 365 (I, 19), 385 (S), 606 (S)	555 (21)
35	334 (41)	352 (I, 29), 358 (30), 404 (S)	626 (21)
36	323 (41)	343 (I, 30), 348 (30), 400 (S)	614 (20)
42	342 (110)	327 (94), 369 (S), 370 (I, 40), 614 (S)	567 (69)

I=isosbestic point, S=shoulder

3.3.2 Fatigue Resistance

Photochromic reactions are often accompanied by rearrangement of chemical bonds. During the rearrangement, undesirable side reactions take place to some extent. This limits the number of cycles of photochromic reactions. Eventually, if one wants to use an optical switch for practical applications the performance has to be close to 100%. This need can be

illustrated with the following example: if there is an undesirable reaction which has a quantum yield of 0.001, then after 1000 switching cycles 63% of the initial switch is decomposed. Recently, decomposition products appearing after long irradiation have been shown for both perhydro[14] and perfluoro[15] cyclopentene-based switches.

Fatigue resistance can be measured in the following experiment; a toluene solution containing a diarylethene is irradiated with UV light of a certain wavelength, which can excite the open ring isomer, until the photostationary state is reached, and then the colored closed ring isomer is completely bleached by irradiation with visible light. This operation is repeated several times and the absorbance of the colored closed ring isomer is monitored. Figure 2 shows four repetitive switching cycles for compounds **6**, **23** and **36**. The absorption was monitored at 480 nm. A typical sign of photo-degradation is the decreasing intensity of the closed forms upon repetitive UV irradiation. However, photo-decomposed products might adsorb in the visible region close to the original adsorption peak of the closed forms as well. Therefore, it is also important to monitor the intensity after visible irradiation when the molecule should return to its open state. It can be seen that in all three cases (Figure 2) the intensity of the absorption increases after each visible irradiation, (lower values) suggesting that a photo-inactive side-product adsorbing in the visible region is formed. Judging from Figure 2 it is obvious that compound **6** is the most prone to photo-decomposition and after four switching cycles approximately 20% of the molecule is decomposed. Compounds **23**, bearing a phenyl spacer group, and perhydro derivative **36** show higher fatigue resistance, but photo-decomposition is still observed. Nevertheless, it should be noted that to reach PSS excessive UV irradiation is required due to the exponential nature of the process. It can be concluded that molecules with a phenyl spacer will benefit from higher fatigue resistance. The more electron withdrawing perfluorocyclopentene bridging unit is also responsible for the higher photo-stability of molecule.

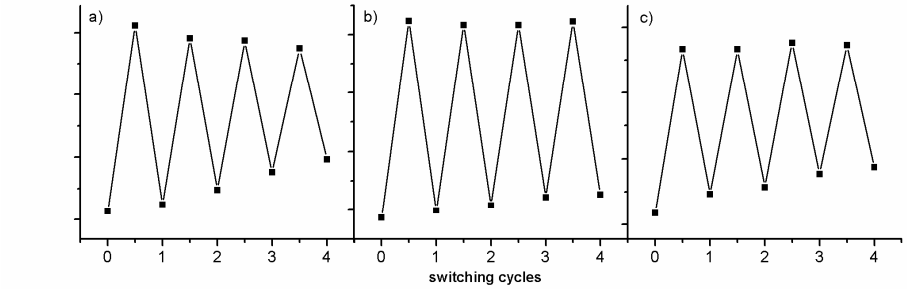


Figure 2 *Four successive switching cycles for compounds a)* ***6****, b)* ***23*** *and c)* ***36*** *monitored at* λ *= 480 nm in toluene. Switches are first illuminated with UV light (*λ *= 313 nm) until the PSS is obtained and subsequently illuminated with visible light (*$\lambda > 420$ *nm).*

3.4 Temperature Dependence of Diarylethene Photochromism

Temperature-dependent studies of photochemical processes in diarylethenes are essential for understanding the behavior of these molecular switches before they can be used in advanced technological applications. Furthermore, the observed suppression of the ring opening (*vide infra*) might have important implications for gating of photochromic processes. As for other photoreactions that have a photostationary state with less than 100 % of product, the ring closure process of diarylethenes occurs simultaneously to ring opening, since both forms absorb in the UV region. This phenomenon decreases total conversions.[16] On the other hand, if the ring opening can be blocked, total conversion increases.[17]

In this subsection, the temperature dependence of the photochemical behavior of dithienylcyclopentenes is discussed. The suppression of the ring opening process with decreasing temperature leads to the complete absence of the photoreaction below a cutoff temperature. By contrast, it is demonstrated that the reverse ring closure process shows no significant temperature dependence above 115 K. Two representative examples of dithienylcyclopentene photochromic switches have been investigated, the hexahydro compound **23** and hexafluoro compound **36**.

The UV/Vis absorption spectra at 115 K and 290 K of the switches **23** and **36** in isopentane solution are shown in Figure 3. The broad absorption bands with the maximum at λ = 590 nm for **36** and λ = 537 nm for **23** are characteristic of the closed form of the switch. At low temperature the vibrational structure in the absorption spectra becomes more apparent resulting in a sharpening of the absorption band and distinct absorption maxima are observed.

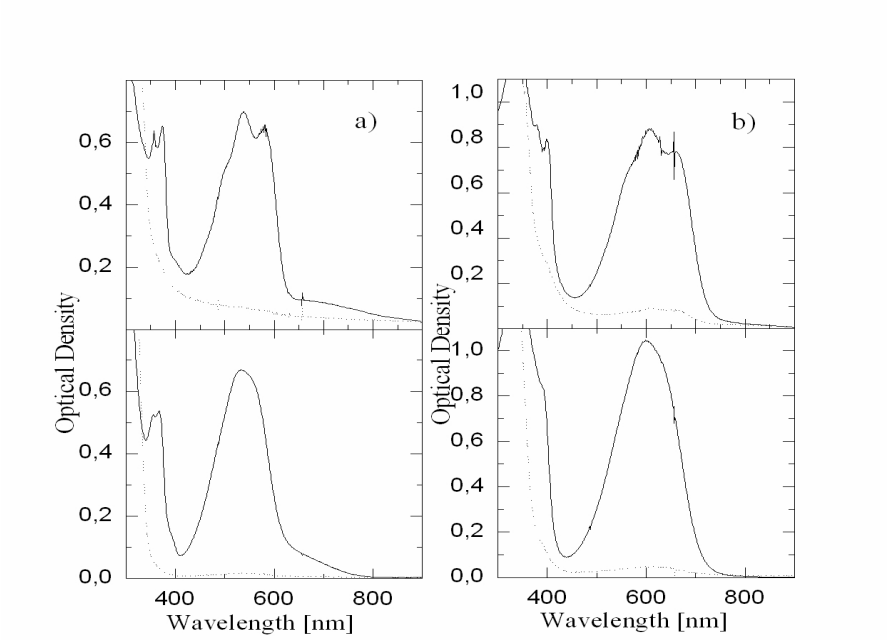


Figure 3 *Absorption spectra of the molecular switches: a) compound* ***23*** *in isopentane, concentration of 7.94 x 10^{-5} mol/L; solid line (—) closed form, dashed line (---) open form. Upper panel 115 K (isopentane at 115 K was used as a reference), lower panel 290 K (isopentane at 290 K was used as a reference); b) compound* ***36*** *in isopentane, concentration of 6.07 x 10^{-5} mol/L; solid line (—) closed form, dashed line (---) open form. Upper panel 115 K, lower panel 290 K.*

3.4.1 Ring-Closure Kinetics

In order to explore the effect of temperature on switching efficiency, the kinetics of the switching process was examined (for both ring closure and ring opening). At each temperature a solution containing the switch in the open form was used to obtain a reference spectrum (blank). Therefore, any absorption changes induced by irradiation are related to the evolution of the closed form. The time evolution of the differential absorption of the closed form was monitored to follow the kinetics of the switching reactions. To promote ring closure, UV light with λ = 313 nm was used until the photostationary state was reached.[18] The kinetics of this process at different temperatures is represented in Figure 4 for compound **23**. For each temperature a fresh solution was used. The data points are plotted for the wavelength corresponding to the maximum absorption of the closed form (λ

= 537 nm). The results demonstrate that the ring closure process is effectively temperature independent in the measured temperature range. Similar behavior was observed for compound **36** (monitored at λ = 590 nm).

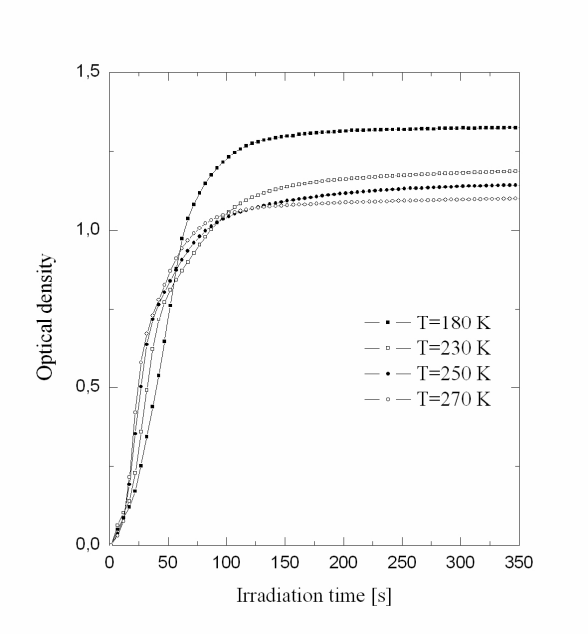


Figure 4 *Kinetics of the ring closure for switch* ***23*** *in isopentane obtained at λ = 537 nm for different temperatures.*

3.4.2 Ring-Opening Kinetics

The kinetics of the ring opening in isopentane were followed at the same wavelengths as ring closing, while irradiating with visible light λ = 546 nm. In contrast to the ring closure, the ring opening process is strongly temperature dependent, as shown in Figure 5. For both compounds **36** and **23** the ring opening process is suppressed completely at *ca*. 130 K for **36**, and around 120 K for **23**. The observed suppression of the ring opening might have important implications for gating of photochromic processes.

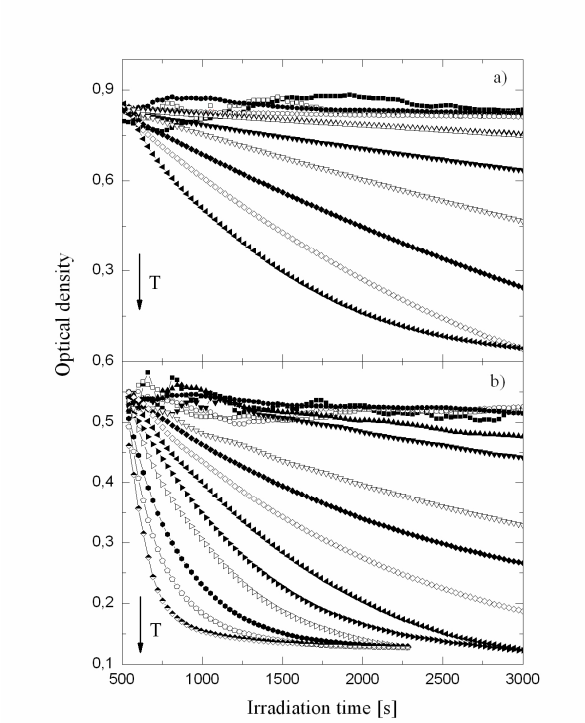


Figure 5 *Temperature-dependent kinetics of the ring opening process in isopentane: a) for compound* ***36*** *obtained at λ = 590 nm. Temperatures: 115, 130, 150, 170, 180, 190, 210, 230, 250, 270, 290 K; b) for compound* ***23*** *at λ = 537 nm. Temperatures: 115, 120, 125, 130, 140, 150, 170, 180, 190, 200, 210, 220, 230, 250, 270, 290 K. The curves are adjusted to the same value along the y-axis for clarity.*

3.4.3 Activation Energy Barrier

For each temperature the data points were plotted on a logarithmic scale, and the initial portion of the curve was fitted to determine the rate (K(T)) of ring opening. In Figure 6 the logarithm of the rate is plotted versus inverse temperature. The curves show two distinct components, a temperature-dependent region where photochemical ring opening is observed and a temperature independent region where photochemistry is not observed. From the slope of the temperature dependent component of the curve the thermal barrier of the ring opening is obtained. Although the observed rate of ring opening is dependent on the intensity of the light source, the exponential component of the fit is intensity independent. This has an important implication for determination of activation energies.

The validity of the approach taken is not immediately obvious. In the following section, it will be demonstrated that this approximation is justified under the low irradiation intensities employed.

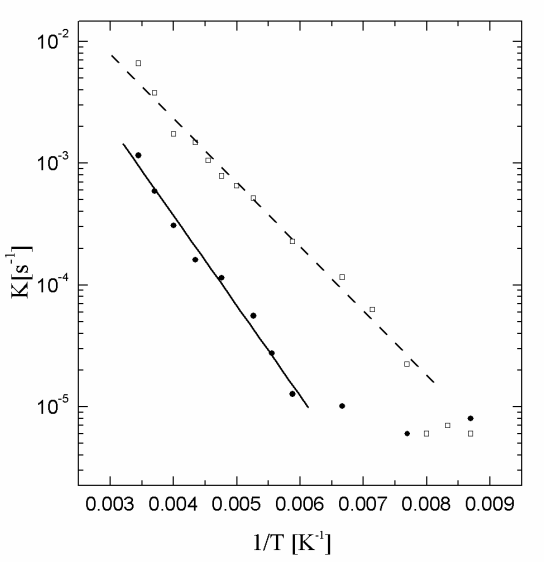


Figure 6 *Arrhenius plots for compound* ***36*** *(squares), and* ***23*** *(circles) with corresponding linear fits. The activation energies obtained from the Arrhenius plots are 104 meV (10.034 kJmol^{-1}, 838.8 cm^{-1}) for* ***23*** *and 147 meV (14.183 kJmol^{-1}, 1185.6 cm^{-1}) for* ***36****.*

In Figure 7 an illustrative diagram of the energy levels involved in the ring opening process is shown. Ring opening of the closed form requires first that the molecule is promoted to the THEXI state (thermally equilibrated excited state) upon irradiation with visible light, followed by the crossing of a thermal barrier. Semi-empirical quantum chemical computational methods[2] have predicted the existence of this barrier (also see, Chapter 2, Figure 8). So far, experimentally the thermal barrier and its importance in the photochemical processes have not been studied in detail. The only experimental studies describing the temperature dependence of the ring opening so far have been performed at elevated temperatures with very few data points.[19]

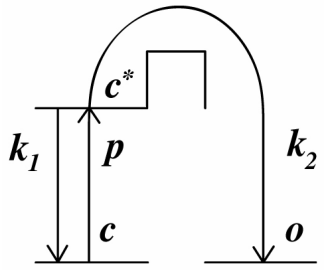


Figure 7 *Sketch of the energy levels of the ring opening process, where c, c* and o represents populations of the ground state and excited state of the closed form and ground state of the open form, respectively: p is the pump rate and k_1, k_2 are rates from excited to closed and excited to open state.*

The full set of differential equations that describes the ring opening dynamics is

$$\frac{dc(t)}{dt} = -p \cdot c(t) + k_1 \cdot c^*(t) \qquad (1)$$

$$\frac{dc^*(t)}{dt} = p \cdot c(t) - k_1 \cdot c^*(t) - k_2 \cdot c^*(t) \qquad (2)$$

$$\frac{do(t)}{dt} = k_2 \cdot c^*(t) \qquad (3)$$

Where *c(t)*, *c*(t)* and o(t) represent populations of the ground state and excited state of the closed form and ground state of the open form, respectively. $p=\sigma_0 \bullet I$ is the pump rate, σ_0 is absorption cross section, and I is intensity of light. k_1 and k_2 are rates from excited to closed and excited to open state, respectively, where $k_2 = k_2^0 \exp[(-\Delta E)/(k_B T)]$, with ΔE being the activation energy, k_B Boltzman constant, and T temperature. At steady state conditions when the pump intensity is very weak, the population of the excited state of the molecules in the closed form is proportional to the population of the ground state, $c^*(t) = a \times c(t)$, where $a << 1$. With this approximation Eqs.1,2 are reduced to

$$\frac{dc^*(t)}{dt} = -\frac{dc(t)}{dt} - k_2 \cdot c^*(t) \qquad (4)$$

$$\frac{dc(t)}{dt} = -c(t) \cdot \frac{a}{a+1} \cdot k_2 \qquad (5)$$

For $a << 1$ ($1 + a \approx 1$), Eq. 5 becomes

$$\frac{dc(t)}{dt} = -c(t) \cdot a \cdot k_2 \qquad (6)$$

With solution Eq.6

$$c(t) = c_0 \exp(-a \cdot k_2 \cdot t) \qquad (7)$$

By fitting our experimental data we obtain $K(t) = k_2$ x a. Since a does not depend on temperature, we can write

$$K(t) = k_2^0 \cdot a \cdot \exp(-\frac{\Delta E}{k_B T}) \qquad (8)$$

$$\ln(K(t)) = \ln(k_2^0 \cdot a) - \frac{\Delta E}{k_B T} \qquad (9)$$

Therefore, the data presented in Figure 6 can be fitted with a single exponent. The Arrhenius plot allows for determination of activation energies of ΔE =147 meV (14.183 kJmol^{-1}, 1185.6 cm^{-1}) for **36**, and ΔE =104 meV (10.034 kJmol^{-1}, 838.8 cm^{-1}). Different values of the activation energies indicate that the thermal barrier is sensitive to changes in molecular structure. It implies that further understanding of the barrier is necessary for optimization of switching properties. In particular, finding a way to reduce the barrier by an order of magnitude would significantly increase the switching rate (by a factor of 1000). On the other hand, the strong temperature dependence of the ring opening can be exploited for a control over the photochemical processes. Low temperatures would effectively block the ring opening while upon heating full reversibility could be restored. Such a gating would be particularly useful for systems where a UV irradiation results in a PSS with a low portion of the closed isomer. This is a result of the UV-induced ring opening reaction. However, if the ring opening is blocked at the particular temperature, UV irradiation would result in a complete conversion to the closed form.

3.5 Conclusions

In conclusion, in this chapter the synthesis of novel thiol terminated diarylethene-based molecular switches is described as well as their photochromic properties. A series of compounds with different spacers connecting the central switching unit with the anchoring groups has been synthesized. Photochemical and conductive properties of some of these compounds, once they are grafted on metal surfaces, will be discussed in detail in the

following chapters. All synthetic routes are straightforward and can be adapted for the synthesis of many different molecular switches with different functional groups. The photochromic behavior of all compounds in solution corresponds with the standard photochemical switching of diarylethenes. Both processes of ring closure and ring opening can be selectively addressed by light of different wavelengths and lead to high yields. The low temperature studies reveal the strong temperature dependence of the ring opening. On the other hand the ring closure is temperature independent within the measured temperature range. The strong temperature dependence of the ring opening implies that variation of temperature might be used for gating of photochromic behavior of diarylethenes.

3.6 Experimental Section

General Remarks

For general remarks see Chapter 2.

Low Temperature Measurements

UV/Vis absorption spectra were measured using a HP 8453 diode array UV/Vis spectrometer. In principle, the light from the spectrometer interacts with the molecules causing a photoreaction. However, repetitive acquisitions showed no detectable changes in the absorption spectra which we attribute to the weak intensity of the light source. A high pressure mercury lamp (200 W, Oriel) was used with 10 nm FWHM (full-width half maximum) band pass filters to switch the molecules from the open to the closed state and vice versa. Light beams with power densities of 0.094 mW/cm^2 for λ=546 nm were employed for ring opening, and 0.00354 mW/cm^2 for λ=313 nm to achieve ring closure. The power densities were measured (optical power meter Oriel 70260, Oriel, Stratford, USA) before and after the experiment for each temperature. In order to minimize artifacts due to diffusion the entire sample volume (1 cm^3) was irradiated. Temperature dependent measurements were performed between 115 K - 290 K, using liquid nitrogen cooled optical cryostat (Optistat, Oxford instruments). Isopentane solutions of both compounds, at a concentration of 6.07 x 10^{-5} mol/L for **36** and 7.94 x10^{-5} mol/L for **23** have been used.

5-Bromo-2,2'-bithiophene (12)

A solution of 2-bromothiophene (4.967 g, 24.92 mmol) in dry THF (5 ml) was added dropwise to Mg turnings (752 mg, 30.94 mmol) and a small I_2 crystal in dry THF (25 ml). When ca. 1 ml of the bromothiophene solution was added, the reaction started, and the mixture was kept under reflux during further addition. After complete addition, the mixture was stirred for 1h under reflux. The mixture was then transferred with a syringe to an

addition funnel and added slowly during 3 h to an ice-cooled mixture of 2,5-dibromothiophene (8.206 g, 33.91 mmol) and [1,1'-bis(diphenylphosphino)-ferrocene]dichloropalladium(II) ([$PdCl_2(dppf)_2$]; 250 mg, 0.306 mmol; 1 : 1 complex with CH_2Cl_2) in dry THF (50 ml). This mixture was stirred for 2h at 0° and for 16h at r.t. The solvent was evaporated and the residue suspended in AcOEt and washed with saturated aq. $NaHCO_3$ solution and brine. The aqueous layers were extracted with AcOEt and the organic layers dried ($MgSO_4$) and the solvents evaporated. Purification by flash chromatography (silicagel, hexanes) gave 4.229 g (57%) of **12**. Spectroscopic data were identical to those reported previously.[20]

1,2-Bis[5-(2,2'-bithiophen-5-yl)-2-methylthien-3-yl]cyclopentene (13)

To a solution of compound **1** (500 mg, 1.52 mmol) in THF (14 ml), kept under an inert N_2 atmosphere, *n*-BuLi (2.5 ml of 1.6 M solution in hexane, 4.00 mmol) was added. After 1h, $B(OBu)_3$ (1.2 ml, 4.60 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask compound **12** (1.512 g, 6.16 mmol), $Pd(PPh_3)_4$ (202 mg, 0.173 mmol), THF (10 ml), 2M Na_2CO_3(aq.) (8 ml) and ethylene glycol (10 drops) were preheated to 80 °C and the boronic ester solution was added slowly. The reaction mixture was heated under reflux overnight, diluted with diethyl ether (100 ml) and washed with water (100 ml). The aqueous layer was washed with an additional volume of ether (100 ml) and the combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuum. Three subsequent precipitations (silicagel, chloroform/*n*-hexane) afforded compound **13** (500 mg, 56 %) as a solid. M.p. 227-232°C (dec.); ^{1}H NMR (300MHz, $CDCl_3$) δ 1.97 (s, 6H), 2.00 (m, 2H), 2.82 (t, *J* = 7.3 Hz, 4H), 6.89 (s, 2H), 6.95 (t, *J* = 4.0 Hz, 2H), 7.00-7.05 (m, 6H), 7.14 (d, *J* = 5.1 Hz, 2H), 7.20 (d, *J* = 5.1 Hz, 2H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): 14.5 (q), 22.8 (t), 29.3 (q), 38.4 (t), 123.5 (d), 123.8 (d), 124.6 (d), 125.1 (d), 125.4 (d),132.5 (s), 134.4 (s), 134.6 (s), 136.4 (s), 136.5 (d), 137.5 (s), 143.6 (s) ppm; MS (EI): 588 [M+]; HRMS calcd. for $C_{31}H_{24}S_6$ 588.923, found 588.922.

1,2-Bis[5-acetylsulfan-5'-yl-(2,2'-bithiophen-5-yl)-2-methylthieny-3-yl]cyclopentene (14) and 1-[5-acetylsulfan-5'-yl-(2,2'-bithiophen-5-yl)-2-methylthieny-3-yl]-2-[(2,2'-bithiophen-5-yl)-2-methylthieny-3-yl]cyclopentene (15)

Compound **13** (300 mg, 0.509 mmol) was dissolved in THF (15 ml) and the solution was cooled to -80 °C. To this solution was added dropwise *t*-BuLi (0.75 ml of 1.5 M solution in *n*-hexane, 1.122 mmol). After 2h, S_8 (32.7 mg, 1.02 mmol) dissolved in THF (3 ml) was added and the mixture was allowed to reach slowly room temperature. After 2h the reaction mixture was cooled to 0 °C and acetyl chloride (0.145 ml, 2.04 mmol) was added. After 3h the mixture was diluted with dichloromethane, washed with water and the organic phase dried (Na_2SO_4) and concentrated. Subsequent chromatography (silicagel, *n*-hexane /

dichloromethane 3:2) afforded compound **14** (150 mg, 40 %) and compound **15** (33 mg, 10 %) as viscous yellow oils. **14**: ^{1}H NMR (300MHz, $CDCl_3$) δ 1.99 (s, 6H), 2.08 (m, 2H), 2.42 (s, 6H), 2.83 (t, *J* = 7.3 Hz, 4H), 6.91 (s, 2H), 6.95 (d, *J* = 4.0 Hz, 2H), 7.03-7.06 (m, 4H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.4 (q), 22.9 (t), 29.4 (q), 38.4 (t), 123.5 (d), 123.7 (d), 124.7 (d), 125.0 (d), 132.5 (s), 134.4 (s), 134.6 (s), 136.4 (s), 136.5 (d), 137.5 (s), 143.4 (s), 194.0 (s) ppm; MS (EI): 736 [M+]; HRMS calcd. for $C_{35}H_{28}O_2S_8$ 734.124, found 734.123. **15**: ^{1}H NMR (300MHz, $CDCl_3$) δ 1.98 (s, 6H), 2.07 (m, 2H), 2.42 (s, 3H), 2.82 (t, *J* = 7.3 Hz, 4H), 6.89 (s, 1H), 6.90 (d, 1H), 6.95 (d, *J* = 3.7 Hz, 2H), 7.00-7.02 (m, 1H), 7.03-7.06 (m, 3H), 7.10 (d, *J* = 4.0 Hz, 1H), 7.13-7.15 (m, 1H), 7.19 (m, 1H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.4 (q), 23.0 (t), 29.5 (q), 38.4 (t), 123.5 (d), 123.5 (d), 123.8 (d), 124.2 (d), 124.3 (d), 124.5 (d), 124.8 (d), 125.4 (d), 127.8 (d), 132.5 (s), 132.8 (s), 134.3 (s), 134.5 (s), 134.6 (s), 134.7 (s), 135.5 (s), 136.4 (s), 136.5 (s), 136.6 (d), 137.2 (s), 137.6(s), 143.5 (s), 193.3 (s) ppm; MS (EI): 662 [M+]; HRMS calcd. for $C_{33}H_{26}OS_7$ 661.021, found 661.022.

1,2-Bis[5-(3-bromophenyl)-2-methylthien-3-yl]cyclopentene (16)

To a solution of compound **1** (500 mg, 1.52 mmol) in THF (14 ml), kept under an inert N_2 atmosphere, *n*-BuLi (2.5 mL of 1.6 M solution in *n*-hexane, 3.99 mmol) was added. After 1h, $B(OBu)_3$ (1.2 mL, 4.56 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask compound 1,3-dibromobenzene (0.75 ml, 6.2 mmol), $Pd(PPh_3)_4$ (202 mg, 0.173 mmol), THF (10 ml), 2M Na_2CO_3(aq.) (8 ml) and ethylene glycol (10 drops) were preheated to 80 ^{o}C and the boronic ester solution was added slowly. The reaction mixture was heated under reflux overnight, diluted with diethyl ether (100 ml) and washed with water (100 ml). The aqueous layer was washed with an additional volume of ether (100 ml) and the combined organic phases were dried over Na_2SO_4 and concentrated. Purification by chromatography on silica gel (hexane) afforded compound **16** as a viscous oil (392 mg, 45 %). ^{1}H NMR (300MHz, $CDCl_3$) δ 1.99 (s, 6H), 2.09 (m, 2H), 2.84 (t, *J* = 7.3 Hz, 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.

1,2-Bis[5-(4-bromophenyl)-2-methylthien-3-yl]cyclopentene (17)

To a solution of compound **1** (500 mg, 1.52 mmol) in THF (14 ml), kept under an inert N_2 atmosphere, *n*-BuLi (2.5 ml of 1.6 M solution in *n*-hexane, 3.99 mmol) was added. After 1h, $B(OBu)_3$ (1.2 ml, 4.65 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask 1,4-dibromobenzene (1.453 g, 6.16 mmol), $Pd(PPh_3)_4$ (202 mg, 0.173 mmol), THF (10 ml), 2M Na_2CO_3(aq.) (8 ml) and ethylene

glycol (10 drops) were preheated to 80 °C and the boronic ester solution was added slowly. The reaction mixture was heated under reflux overnight, diluted with diethyl ether (100 ml) and washed with water (100 ml). The aqueous layer was extracted with an additional volume of ether (100 ml) and the combined organic phases were dried over Na_2SO_4 and concentrated. Purification by chromatography on silica gel (*n*-hexane) afforded compound **17** as a viscous oil (531 mg, 61 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.97 (s, 6H), 2.02-2.10 (m, 2 H), 2.81 (t, *J* = 7.5 Hz, 4H), 6.98 (s, 2H), 7.32 (d, *J* = 8.4 Hz, 4H), 7.42 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$): 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 $C_{27}H_{22}Br_2S_2$ 567.953, found 567.951.

1,2-Bis[5-(3-acetylsulfanylphenyl)-2-methylthien-3-yl]cyclopentene (18)

Compound **16** (200 mg, 0.351 mmol) was dissolved in THF (10 ml) and the solution was cooled to -80 °C. To this solution was added dropwise *t*-BuLi (0.56 ml of 1.5 M solution in *n*-pentane, 0.841 mmol). After 2h, S_8 (22.5 mg, 0.702 mmol) dissolved in THF (3 ml) was added and the mixture was allowed to reach slowly room temperature. After 2h the reaction mixture was cooled to 0 °C and acetyl chloride (0.099 ml, 1.404 mmol) was added. After 3h the mixture was diluted with dichloromethane, washed with water and the organic phase dried (Na_2SO_4) and concentrated. Purification by chromatography (*n*-hexane/dichloromethane 3:2) afforded compound **18** as a viscous oil (113 mg, 58 %). ^{1}H NMR (300MHz, $CDCl_3$) δ 1.98 (s, 6H), 2.08 (m, 2H), 2.42 (s, 6H), 2.84 (t, *J* = 7.3 Hz, 4H), 7.04 (s, 2H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.51-7.55 (m, 4H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.4 (q), 23.0 (t), 30.2 (q), 37.5 (t), 124.6 (d), 124.1 (d), 128.5 (s), 129.5 (d), 131.0 (d), 132.7 (d), 134.7 (s), 135.2 (s), 135.6 (s), 136.8 (s), 138.4 (s), 193.8 (s) ppm; HRMS calcd. for $C_{31}H_{28}O_2S_4$ 560.097, found 560.096.

1,2-Bis[5-(4-acetylsulfanylphenyl)-2-methylthien-3-yl]cyclopentene (19)

Compound **16** (200 mg, 0.351 mmol) was dissolved in THF (10 ml) and the solution was cooled to -80 °C. To this solution was added dropwise *t*-BuLi (0.56 ml of 1.5 M solution in pentane, 0.841 mmol). After 2h, S_8 (22.5 mg, 0.702 mmol) dissolved in THF (3 ml) was added and the mixture was allowed to reach slowly room temperature. After 2h the reaction mixture was cooled to 0 °C and acetyl chloride (0.099 ml, 1.404 mmol) was added. After 3h the mixture was diluted with dichloromethane, washed with water and the organic phase dried (Na_2SO_4) and concentrated. Purification by chromatography (*n*-hexane/dichloromethane 3:2) afforded compound **18** as a viscous oil (101 mg, 52 %). ^{1}H NMR (500MHz, $CDCl_3$) δ 1.97 (s, 6H), 2.06 (m, 2H), 2.47 (s, 6H), 2.82 (t, *J* = 7.2 Hz, 4H), 6.97 (s, 2H), 7.20 (d, *J* = 8.4 Hz, 4H), 7.38 (d, *J* = 8.4 Hz, 4H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.4 (q), 16.0 (q), 23.0 (t), 38.4 (t), 123.7 (d), 125.6 (d), 127.0 (d), 131.5 (s),

134.2 (s), 134.6 (s), 136.6 (s), 137.0 (s), 139.1 (s) ppm; MS (EI): 504 [M+]; HRMS calcd. for $C_{29}H_{28}S_4$: 504.108, found: 504.108.

1-(5-Chloro-2-methylthien-3-yl)-2-(2-methyl-5-phenylthien-3-yl)cyclopentene (20)

To a solution of compound **1** (2.25 g, 6.83 mmol) in THF (100 ml), kept under an inert N_2 atmosphere, *t*-BuLi (4.70 ml of 1.6 M solution in *n*-hexane, 7.51 mmol) was added. After 1h, $B(OBu)_3$ (2.77 ml, 10.3 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask bromobenzene (2.86 ml, 13.66 mmol), $Pd(PPh_3)_4$ (0.237 g, 0.21 mmol), THF (23 ml), 2M Na_2CO_3(aq.) (18 ml) and ethylene glycol (20 drops) were preheated to 80 ^oC and the boronic ester solution was added slowly. The reaction mixture was heated under reflux overnight, diluted with diethyl ether (200 ml) and washed with water (200 ml). The aqueous layer was washed with an additional volume of ether (200 ml) and the combined organic phases were dried over Na_2SO_4 and concentrated. Purification by chromatography on silica gel (*n*-hexane) afforded compound **20** as a sticky oil (1.95 g, 77 %). ^1H NMR (300 MHz, $CDCl_3$): δ 1.94 (s, 3H), 2.05 (s, 3H), 2.08-2.16 (m, 2H), 2.78-2.89 (m, 4H), 6.68 (s, 1H), 7.05 (s, 1H), 7.30 (t, *J* = 7.0 Hz, 1H), 7.37-7.42 (m, 2H), 7.55 (d, *J* = 7.0 Hz, 2H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.1 (q), 14.3 (q), 22.9 (t), 38.4 (t), 38.5 (t), 123.8 (d), 125.0 (s), 125.3 (d), 126.8 (d), 127.0 (d), 128.8 (d), 133.2 (s), 133.7 (s), 134.4 (s), 135.1 (s), 135.3 (s), 136.3 (s), 139.8 (s) ppm; MS (EI): 370 [M^+]; HRMS: calcd. for $C_{21}H_{19}S_2Cl$ 370.062, found 370.063.

1-[5-(3-Bromophenyl)-2-methylthien-3-yl]-2-(2-methyl-5-phenylthien-3-yl)cyclopentene (21)

To a solution of compound **20** (1 g, 2.70 mmol) in THF (35 ml), kept under an inert N_2 atmosphere, *t*-BuLi (2.13 ml of 1.5 M solution in *n*-pentane, 3.20 mmol) was added. After 1h, $B(OBu)_3$ (1.09 ml, 4.05 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask 1,3-dibromobenzene (0.653 ml, 5.40 mmol), $Pd(PPh_3)_4$ (0.094 g, 0.081 mmol), THF (15 ml), (aq.) 2M Na_2CO_3 (10 ml) and ethylene glycol (15 drops) were preheated to 80 ^oC and the boronic ester solution was added slowly. The reaction mixture was heated under reflux overnight, diluted with diethyl ether (200 ml) and washed with water (200 ml). The aqueous layer was washed with an additional volume of ether (200 ml) and the combined organic phases were dried over Na_2SO_4 and concentrated. Subsequent chromatography on silica gel (*n*-hexane) afforded compound **21** as a viscous oil (0.88 g, 66 %). ^1H NMR (300 MHz, $CDCl_3$): δ 2.01 (s, 6H), 2.08-2.13 (m, 2H), 2.84-2.89 (m, 4H), 7.05 (s, 1H), 7.06 (s, 1H), 7.16-7.26 (m, 2H), 7.32-7.42 (m, 4H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.66 (s, 1H) ppm; ^{13}C NMR (75.4, $CDCl_3$): δ 14.4 (q), 14.4 (q), 23.0 (t), 38.4 (t), 122.9 (s), 123.8 (d), 123.9 (d), 124.8 (d), 125.3 (d), 127.0

(d), 128.1 (d), 128.7 (d), 129.7 (d), 130.2 (d), 134.3 (s), 134.4 (s), 135.0 (s), 135.4 (s), 136.5 (s), 136.8 (s), 137.8 (s), 139.8 (s) ppm; HRMS: calcd. for $C_{27}H_{23}S_2Br$ 490.042, found 490.043.

1-[5-(4-Bromophenyl)-2-methylthien-3-yl]-2-(2-methyl-5-phenylthien-3-yl)cyclopentene (22)

To a solution of compound **20** (1 g, 2.70 mmol) in THF (35 ml), kept under an inert N_2 atmosphere, *t*-BuLi (2.13 ml of 1.5 M solution in *n*-pentane, 3.20 mmol) was added. After 1h, $B(OBu)_3$ (1.09 ml, 4.05 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask 1-bromo-4-iodobenzene (1.53 g, 5.40 mmol), $Pd(PPh_3)_4$ (0.094 g, 0.081 mmol), THF (15 ml), (aq.) 2M Na_2CO_3 (10 ml) and ethylene glycol (15 drops) were preheated to 80 ^oC and the boronic ester solution was added slowly. The reaction mixture was heated under reflux overnight, diluted with diethyl ether (200 ml) and washed with water (200 ml). The aqueous layer was washed with an additional volume of ether (200 ml) and the combined organic phases were dried over Na_2SO_4 and concentrated. Purification by chromatography on silica gel (*n*-hexane) afforded compound **22** as a viscous oil (0.96 g, 72 %). ^1H NMR (300 MHz, $CDCl_3$): δ 2.00 (s, 3H), 2.01 (s, 3H), 2.06-2.11 (m, 2H), 2.81-2.87 (m, 4H), 7.01 (s, 1H), 7.03 (s, 1H), 7.23-7.25 (m, 1H), 7.31-7.36 (m, 4H), 7.43-7.51 (m, 4H) ppm; ^{13}C NMR (75.4, $CDCl_3$): δ 14.4 (q), 23.0 (t), 38.4 (t), 38.4 (t), 120.6 (s), 123.9 (d), 124.5 (d), 125.3 (d), 126.8 (d), 127.0 (d), 128.8 (d), 131.8 (d), 134.4 (s), 134.5 (s), 134.9 (s), 135.4 (s), 136.5 (s), 136.8 (s), 137.9 (s), 139.8 (s) ppm; HRMS: calcd. for $C_{27}H_{23}S_2Br$ 490.042, found 490.041.

1-[5-(3-Acetylsulfanylphenyl)-2-methylthien-3-yl]-2-(2-methyl-5-phenylthien-3-yl)cyclopentene (23)

Compound **21** (584 mg, 1.188 mmol) was dissolved in THF (25 ml) and the solution was cooled to -80 ^oC. To this solution was added dropwise *t*-BuLi (0.87 ml of 1.5 M solution in pentane, 1.307 mmol). After 2h, S_8 (38 mg, 1.188mmol) dissolved in THF (2 ml) was added and the mixture was allowed to reach slowly room temperature. After 2h the reaction mixture was cooled to 0 ^oC and acetyl chloride (0.17 ml, 2.376 mmol) was added. After 3h the mixture was diluted with dichloromethane, washed with water and the organic phase dried (Na_2SO_4) and concentrated. Purification by chromatography (*n*-hexane / dichloromethane 7:2) afforded compound **23** (301 mg, 52 %) as a viscous oil. ^1H NMR (300 MHz, $CDCl_3$): δ 1.99 (s, 3H), 2.00 (s, 3H), 2.05-2.15 (m, 2H), 2.43 (s, 3H), 2.85 (t, *J* = 7.3 Hz, 4H), 7.04 (s, 1H), 7.06 (s, 1H), 7.20-7.40 (m, 5H), 7.48-7.56 (m, 4H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.4 (q), 23.0 (t), 30.2 (q), 38.5 (t), 123.9 (d), 124.7 (d), 125.3 (d), 126.3 (d), 126.9 (d), 128.5 (s), 128.8 (d), 129.5 (d), 131.0 (d), 132.7 (d), 134.4 (s),

134.5 (s), 134.9 (s), 135.2 (s), 135.7 (s), 136.6 (s), 136.8 (s), 138.3 (s), 139.7 (s), 193.8 (s) ppm; HRMS: calcd. for $C_{29}H_{26}OS_3$ 486.115, found 486.114.

1-[5-(4-Acetylsulfanylphenyl)-2-methylthien-3-yl]-2-(2-methyl-5-phenylthien-3-yl)cyclopentene (24)

Compound **22** (1.3 g, 2.64 mmol) was dissolved in THF (50 ml) and the solution was cooled to -80 ^{o}C. To this solution was added dropwise *t*-BuLi (1.94 ml of 1.5 M solution in pentane, 2.91 mmol). After 2h S_8 (0.085 g, 2.64 mmol) dissolved in THF (4 ml) was added and the mixture was allowed to reach slowly room temperature. After 2h the reaction mixture was cooled to 0 ^{o}C and acetyl chloride (0.38 ml, 5.28 mmol) was added. After 3h the mixture was diluted with dichloromethane, washed with water and the organic phase dried (Na_2SO_4) and concentrated. Purification by chromatography (*n*-hexane / dichloromethane 7:2) afforded compound **24** (0.67 g, 47 %) as a viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 3H), 2.04 (s, 3H), 2.10-2.14 (m, 2H), 2.44 (s, 3H), 2.85-2.90 (m, 4H), 7.07 (s, 1H), 7.11 (s, 1H), 7.22-7.27 (m, 1H), 7.33-7.40 (m, 4H), 7.51-7.56 (m, 4H) ppm; ^{13}C NMR (75.4, $CDCl_3$): δ 14.4 (q), 14.5 (q), 23.0 (t), 30.1 (q), 38.4 (t), 38.5 (t), 123.9 (d), 124.9 (d), 125.3 (d), 125.8 (d), 125.9 (s), 126.9 (d), 128.7 (d), 134.3 (s), 134.4 (s), 134.8 (d), 134.9 (s), 135.4 (s), 135.6 (s), 136.5 (s), 136.9 (s), 138.5 (s), 139.7 (s), 194.1 (s) ppm; HRMS: calcd. for $C_{29}H_{26}OS_3$ 486.115, found 486.114.

4-Bromo-4'-tert-thiobutoxydiphenyl (27)

A solution of 4,4'-dibromodiphenyl (**25**) (5 g, 0.016 mol), *t*-butylthiol (1.8 ml, 0.016 mol), sodium *t*-butoxide (3 g, 0.032 mol) and $Pd(PPh_3)_4$ (0,56 g, 0.48 mmol) in *t*-butanol (200 ml) was heated at 65 ^{o}C under a nitrogen stream with stirring. After stirring for 4 h, the solvent was removed by rotary evaporation. From the residue the product was extracted into *n*-pentane. After washing with water, usual work-up and chromatography **27** (3.2 g, 64 %) was obtained as a white solid. M. p. 74-76 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 9H), 7. 46 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.56-7.60 (m, 4H) ppm; ^{13}C NMR (75.4, $CDCl_3$): δ 31.0 (q), 39.5 (s), 99.8 (s), 126.9 (d), 128.7 (d), 132.0 (d), 137.9 (d), 138.5 (s), 139.1 (s), 141.7 (s) ppm; HRMS calcd. for $C_{16}H_{17}S_{Br}$ 320.023, found 320.024.

1,2-Bis[5-(5-(4'-(tert-butylthio)biphenyl-4-yl)thiophen-2-yl))-2-methylthien-3-yl]cyclopentene (28)

To a solution of compound **1** (200 mg, 0.607 mmol) in THF (7 ml), kept under an inert N_2 atmosphere, *n*-BuLi (0.95 ml of 1.6 M solution in *n*-hexane, 1.518 mmol) was added. After 1h, $B(OBu)_3$ (0.489 ml, 1.821 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask **27** (390 mg, 1.214 mmol), $Pd(PPh_3)_4$ (70 mg, 0.061 mmol), THF (5 ml), 2M Na_2CO_3(aq.) (4 ml) and ethylene glycol

(5 drops) were preheated to 80 °C and the boronic ester solution was added slowly. The reaction mixture was heated 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. Purification by chromatography on silica gel (*n*-hexane) afforded compound **28** as a viscous oil (230 mg, 51 %). 1H NMR (300 MHz, $CDCl_3$): δ 1.33 (s, 18H), 2.03 (s, 6H), 2.13 (m, 2H), 2.83 (t, *J* = 7.3 Hz, 4H), 7.21 (s, 2H), 7.43 (d, *J* = 7.7 Hz, 4H), 7.57 (m, 8H), 7.62 (d, *J* = 7.7 Hz, 4H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.5 (q), 23.0 (t), 31.0 (q), 39.5 (s) 38.5 (t), 99.8 (s), 124.3 (d), 125.7 (d), 126.8 (s), 127.5 (d), 134.0 (s), 134.7 (s), 134.8 (d), 134.9 (s), 136.8 (s), 138.5 (s), 139.1 (s), 141.7 (s) ppm; HRMS calcd. for $C_{47}H_{48}S_4$ 740.264, found 740.261.

1,2-Bis[5-(5-(4'-(acetylthio)biphenyl-4-yl)thiophen-2-yl)-2-methylthien-3-yl] cyclopentene (29)

To a solution of **28** (75 mg, 0.101 mmol) and 0.10 ml AcCl in 5 ml of CH_2Cl_2 under an inert atmosphere, BBr_3 (0.019 ml, 0.202 mmol) was added. The reaction mixture was stirred overnight after which the reaction mixture was diluted with diethyl ether (10 ml) and poured onto 5 g of ice. The phases were separated and the aqueous layer was extracted with an additional volume of ether (20 ml) and the combined organic phases were dried with Na_2SO_4 and concentrated. Purification by chromatography (*n*-pentane/dichloromethane 3:2) produced **29** (24 mg, 33%) as a transparent colorless oil. 1H NMR (300MHz, $CDCl_3$): δ 2.03 (s, 6H), 2.12 (m, 2H), 2.45 (s, 6H), 2.87 (t, *J* = 7.3 Hz, 4H), 7.10 (s, 2H), 7.47 (d, *J* = 7.7 Hz, 4H), 7.58 (m, 8H), 7.64 (d, *J* = 7.7 Hz, 4H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.5 (q), 23.0 (t), 30.2 (q), 38.5 (t), 99.8 (s), 124.3 (d), 125.7 (d), 126.8 (s), 127.5 (d), 127.6 (d), 134.0 (s), 134.7 (s), 134.8 (d), 134.9 (s), 136.8 (s), 138.5 (s), 139.1 (s), 141.7 (s), 194.1 (s) ppm; HRMS calcd. for $C_{43}H_{36}O_2S_4$ 712.160, found 712.158.

1,2-Bis(2-methyl-5,2'-dithiophen-3-yl)perfluorocyclopentene (34)

A solution of **32** (2.5 g, 9.65 mmol) in dry ether (50 ml) was cooled to -80 °C under a nitrogen atmosphere. *n*-Butyllithium (6.33 ml, 1.6 M solution in hexane, 10.13 mmol) was added and after 2h, octafluorocyclopentene (**33**) (0.643 ml, 4.83 mmol) was added. The reaction mixture was stirred for 2h at -80 °C after which time the reaction was allowed to warm to ambient temperature. After an additional 2h, the reaction mixture was diluted with ether, washed with dilute hydrochloric acid (1 %), saturated aqueous sodium bicarbonate, and water, and extracted with ether (2 x 50 ml). The combined ether phases were then dried over Na_2SO_4, filtered and the solvent evaporated. Purification by chromatography (hexane) yielded solid compound **34** (1.1 g, 43%). Spectroscopic data were identical to those reported previously.[21]

1,2-Bis(5'-acetylsulfanyl-2-methyl-5,2'-dithiophen-3-yl)perfluorocyclopentene (35) and 1-(5'-Acetylsulfanyl-2-methyl-5,2'-dithiophen-3-yl)-2-(2-methyl-5,2'-dithiophen-3-yl)perfluorocyclopentene (36)

Compound **34** (1 g, 1.88 mmol) was dissolved in THF (20 ml) and the solution was cooled to -80 ^{o}C. To this solution was added dropwise t-BuLi (2.75 ml of a 1.5 M solution in *n*-pentane, 4.13 mmol). After 2h S_8 (0.120 g, 3.76 mmol) dissolved in THF (6 ml) was added and the mixture was allowed to reach slowly room temperature. After 2h the reaction mixture was cooled to 0 ^{o}C and acetyl chloride (0.53 ml, 7.52 mmol) was added. After 3h the mixture was diluted with dichloromethane, washed with water and the organic phase dried (Na_2SO_4) and concentrated. Subsequent chromatography (*n*-hexane / dichloromethane 3:2) afforded compound **35** (0.87 g, 68 %) as a main product and compound **36** (0.10 g, 9 %) as a minor product both as viscous oils. Compound **35:** ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.95 (s, 6H), 2.44 (s, 6H), 7.05 (d, *J* = 3.7 Hz, 2H), 7.11 (d, *J* = 3.7 Hz, 2H), 7.15 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4 (q), 23.0 (t), 30.2 (q), 38.5 (t), 123.9 (d), 124.7 (d), 125.3 (d), 126.3 (d), 126.9 (d), 128.5 (s), 128.8 (d), 129.5 (d), 131.0 (d), 132.7 (d), 134.4 (s), 134.5 (s), 134.9 (s), 135.2 (s), 135.7 (s), 136.6 (s), 136.8 (s), 138.3 (s), 139.7 (s), 193.8 (s) ppm; HRMS: calcd. for $C_{27}H_{18}O_2S_6F_6$ 679.953, found 679.952. Compound **36:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (s, 3H), 1.96 (s, 3H), 2.43 (s, 3H), 7.02 (dd, *J* = 5.1 Hz, 3.3 Hz, 1H), 7.06 (d, *J* = 4.0 Hz, 1H), 7.10 (d, *J* = 4.0 Hz, 1H), 7.12-7.14 (m, 2H), 7.16 (s, 1H), 7.24 (dd, *J* = 5.1 Hz, 1.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4 (q), 14.5 (q), 29.5 (t), 122.7 (d), 123.5 (d), 124.1 (d), 124.4 (d), 124.4 (s), 124.9 (d), 125.4 (s), 125.7 (s), 127.9 (d), 134.7 (s), 135.7 (s), 136.1 (s), 136.4 (d), 140.8 (s), 141.7 (s), 142.2 (s), 193.8 (s) ppm; HRMS: calcd. for $C_{25}H_{16}OS_5F_6$ 605.971, found 605.972.

tert-Butyl(3-iodobenzyloxy)dimethylsilane (38)

A mixture of 3-iodobenzyl alcohol (9.17 g, 39.2 mmol), TBDMSCl (7.1 g, 47 mmol), and imidazole (3.1 g, 47 mmol) was dissolved in CH_2Cl_2 (250 ml). The reaction mixture was stirred at room temperature for 2 h and then poured into H_2O. The organic layer was washed with H_2O (three times) and dried over $MgSO_4$ and the solvent removed in vacuo. The residue was filtered through a plug of silica gel to afford **38** as a clear oil (13.7 g, 100%). Spectroscopic data were identical to those reported previously.[22]

Ethoxytri-[3-tert-butyl-dimethylsilanyloxymethyl)phenyl]silane (39)

To a suspension of compound **38** (2 g, 5.74 mmol) in ether (30 ml) at -80 °C was added *n*-BuLi (3.59 ml, 5.74 mmol, 1.6 M in *n*-hexane) via a syringe. After the addition, the pale yellow slurry was stirred for 1 h and added via syringe to a precooled solution (-80 °C) of tetraethylorthosilicate (2.23 ml, 10.00 mmol) in ether (30 ml). The resulting clear solution

was stirred for 30 min at -78 °C and 3 h at room temperature. Subsequently, 1 N (aq.) HCl (5.74 ml, 5.74 mmol) was added. The organic layer was separated and washed with water (2x) and brine (1x). The aqueous solution was extracted with ether (2x). The combined organic fractions were dried over magnesium sulfate and filtered. Removal of the solvent in vacuo followed by flash chromatography (silicagel, *n*-hexane/CH_2Cl_2 1:1) gave **39** (0.80 g, 57% with respect to tetraethyl orthosilicate) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.05 (s, 18H), 0.89 (s, 27H), 1.22 (t, *J* = 7.0 Hz, 3H), 3.84 (q, *J* = 7.0 Hz, 2H), 4.72 (s, 6H), 7.34 (t, *J* = 8.0 Hz, 3H), 7.40 (d, *J* = 8.0 Hz, 3H), 7.49 (d, *J* = 8.0 Hz, 3H), 7.54 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.3 (q), 18.3 (s), 18.4 (q), 25.9 (q), 59.7 (t), 65.0 (t), 127.7 (d), 132.9 (d), 134.0 (d), 134.3 (s), 140.6 (s) ppm; HRMS: calcd. for $C_{41}H_{68}O_4Si_5$ 736.419, found 736.420.

1,2-Bis[5-(5-(tris(3-((tert-butyldimethylsilyloxy)methyl)phenyl)-silyl)-thiophen-2-yl)-2-methylthien-3-yl]cyclopentene (40)

An oven-dried 10 ml round-bottom flask was charged with **2** (46 mg, 0.109 mmol) and THF (3 ml). The solution was cooled to -80 °C. *t*-BuLi (0.16 ml, 1.5 M in pentane, 0.240 mmol) was added dropwise via a syringe. After the complete addition the reaction mixture was stirred at -78 °C for 2h. A precooled solution (-80 °C) of compound **39** (200 mg, 0.272 mmol) in THF (1 ml) was added dropwise via a syringe. The cooling bath was allowed to warm to room temperature overnight. The reaction mixture was poured into H_2O, and the mixture was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography (*n*-hexane/CH_2Cl_2/*t*-butyl-methylether 8:2:0.025) to afford **40** (59 mg, 30%) as a slightly yellow clear oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.03 (s, 36H), 0.87 (s, 54H), 1.85 (s, 6H), 2.03 (m, 2H), 2.77 (t, *J* = 3.3 Hz, 4H), 4.71 (s, 12H), 6.95 (s, 2H), 7.13 (d, *J* = 7.4 Hz, 2H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 6H), 7.41 (d, *J* = 7.4 Hz, 6H), 7.48 (d, *J* = 7.4 Hz, 6H), 7.52 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.3 (q), 18.3 (s), 18.4 (q), 25.9 (q), 59.7 (t), 65.0 (t), 124.4 (d), 124.9 (d), 127.7 (d), 130.5 (d), 131.7 (s), 132.4 (s), 132.9 (d), 134.1 (s), 134.3 (s), 134.4 (d), 134.7 (s), 135.5 (d), 136.3 (s), 137.2 (s), 140.6 (s), 145.1 (s) ppm; MS (ES): 1813.6 $[M+Li]^+$.

1,2-Bis[5-(5-(tris(3-(hydroxymethyl)phenyl)silyl)thiophen-2-yl)-thiophen-2-yl)-2-methylthien-3-yl]cyclopentene (41)

To the solution of **40** (58 mg, 0.032 mmol) in THF (10 ml) was added AcOH (0.015 ml, 0.257 mmol), followed by TBAF (1 M in THF, 0.257 ml, 0.257 mmol). The reaction mixture was stirred at room temperature for 28 h. The reaction mixture was poured into H_2O, and the mixture was extracted with EtOAc. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue was

purified by column chromatography (CH_2Cl_2/MeOH 20:1) to afford compound **41** (29 mg, 81%) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 6H), 2.08 (m, 2H), 2.77 (t, *J* = 7.7 Hz, 4H), 4.60 (s, 6H), 5.30 (s, 12H), 6.84 (s, 2H), 7.10 (d, *J* = 3.6 Hz, 2H), 7.15 (d, *J* = 3.6 Hz, 2H), 7.36 (t, *J* = 7.0 Hz, 6H), 7.42 (d, *J* = 7.0 Hz, 6H), 7.51 (d, *J* = 7.0 Hz, 6H), 7.54 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4 (q), 29.7 (t), 38.1 (t), 65.2 (t), 124.4 (d), 125.4 (d), 128.2 (d), 128.9 (d), 131.8 (s), 132.4 (s), 134.0 (s), 134.5 (d), 134.7 (s), 135.5 (d), 136.4 (s), 139.2 (d), 140.3 (s), 145.1 (s) ppm; MS (ES): 1122.2 $[M+H]^+$.

1,2-Bis[5-(5-(tris(3-(acetylthiomethyl)phenyl)silyl)thiophen-2-yl)-2-methylthien-3-yl]cyclopentene (42)

To a solution of PPh_3 (0.642 g, 2.448 mmol) in THF (15 ml), cooled to 0 °C, was added diisopropyl azodicarboxylate (DIAD) (0.482 ml, 2.448 mmol). A white precipitate formed after stirring at 0 °C for 5 min. The mixture was stirred at 0 °C for an additional 30 min, and then a solution of compound **41** (0.152 g, 0.136 mmol) and thiolacetic acid (0.174 ml, 2.448 mmol) in THF (10 mL) was added dropwise. The reaction mixture became orange, then green, and finally brown during the addition. The flask that held **41** was rinsed with THF (2 x 5 ml), and the liquid was also added to the reaction mixture. The reaction mixture was stirred in an ice bath throughout the addition, and the ice bath was then allowed to warm to room temperature. After 18 h, the reaction mixture was poured into H_2O and extracted with EtOAc. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, and filtered and the solvent removed in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 2:1) to afford **42** (0.093 g, 47%) as a colorless viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (s, 6H), 2.02 (m, 2H), 2.33 (s, 18H), 2.79 (t, *J* = 8.4 Hz, 4H), 4.11 (s, 12H), 6.96 (s, 2H), 7.16 (m, 4H), 7.33 (t, *J* = 7.3 Hz, 6H), 7.39 (d, *J* = 7.3 Hz, 6H), 7.44 (d, *J* = 7.3 Hz, 6H), 7.50 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4 (q), 22.8 (q), 30.3 (t), 33.5 (t), 38.7 (t), 124.4 (d), 124.9 (d), 128.3 (d), 130.5 (d), 131.7 (s), 132.8 (s), 133.9 (s), 134.4 (s), 134.5 (s), 135.0 (d), 136.3 (d), 136.4 (s), 137.1 (s), 139.2 (d), 145.1 (s), 195.0 (s) ppm; MS (ES): 1476.3 $[M+Li]^+$.

3.7 References and Notes

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