Chapter 3
Photo- and Electrochemical Properties of SAMs of Diarylethenes on Semiconductive Surfaces

In this chapter, the syntheses and characterization of two functionalized diarylethene switches, one of which is attached to a coumarin fluorophore (compounds 3 and 4, respectively), are described. Both functionalized switches were immobilized on surfaces (i.e. quartz and ITO) using a triethoxysilane as the anchoring unit. The immobilized switch 3 can undergo multiple ring-opening and ring-closing reactions both electrochemically and photochemically driven. An important feature is that the state of the modified surface can be read ‘non-destructively’ by electrochemical readout. For diarylethene 4, the formation of self-assembled monolayers on ITO was found to be non-reproducible due to the instability of the monolayer on the surface employed. By contrast, the photochemical switching of fluorescence of the immobilized switch 4 was found to be reversible on quartz surfaces. The studies presented here show that intermolecular interactions have various consequences for the design of surfaces functionalized with dithienylethenes.

This chapter has been published in part in:
3.1 Introduction

A major challenge of molecular electronics is to design devices based on addressable molecular structures and to incorporate them into integrated circuits.\(^1\) As such self-assembled monolayers of photochromic compounds hold considerable potential in the development of molecular electronic and optoelectronic memory devices.\(^2\) Their ability to respond to an external stimulus places light-triggered molecular switches amongst the more promising of candidates as components for future molecular electronic devices. In particular, bistable diarylethene compounds are attracting increasing attention as a result of their good fatigue resistance and the reversibility of their photochemical- and redox-driven switching chemistry from the closed colored form to the open colorless form.\(^3\) Although the majority of investigations have focused on intrinsic molecular properties in solution, the ability to harness the rich and, often reversible photo- and redox chemistry of molecular systems requires that the functionality observed in solution is retained once immobilized on surfaces. In the context of the development of molecular electronics, it is essential to investigate how the properties of the dithienylethene molecular switches are modified, modulated, or degraded when they are attached covalently onto surfaces. In the following paragraphs, a short overview of the recent studies of dithienylethene switches on surfaces is presented.

3.2 SAMs of dithienylethene switches on a metal surface

In previous studies in our group, the potential of dithienylethene switches was first demonstrated in molecular electronic devices by studying the conductivity of a dithienylethene switch with thiophene groups as spacers and functionalized by two thiol groups chemisorbed on each of two electrodes of a mechanically-controlled break junction (MCBJ),\(^4\) as shown in Figure 1. This study demonstrates that the switching of a molecule from the closed to the open state results in a significant increase in resistance by three orders of magnitude, however the reverse process, switching from the open to the closed state was not observed. This limitation associated with the one-way switching of the dithienylethene unit in the MCBJ was rationalized as due to quenching of the excited state of the molecule in the open form by the gold electrodes.\(^5\)
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Figure 1. Schematic representation of a dithienylethene bridging two electrodes in the mechanically-controlled break junction (MCBJ).4

The reversible switching of a diarylene switch on a gold surface (Au 111) was investigated by STM6 for individual molecules modified with a phenyl spacer at the meta position of which a thiol group was attached, as shown in Figure 2. In its open form, the dithienylethene has similar charge transport properties and consequently the same apparent height as dodecanethiol. Therefore the open form of the dithienylethene switch cannot be distinguished within the SAM of dodecanethiol (Figure 2a). By contrast, the closed form is distinguished clearly by a higher apparent height (Figure 2b). The reversible photochemical switching of a meta-phenyl-linked dithienylethene has been confirmed by using the apparent height of the dithienylethene switch as a readout signal.

Figure 2. Schematic diagrams of photochemical switching of a dithienylethene anchored to Au(111). a) Apparent height STM images in the open form; b) closed form, the
dithienylethene presents a bright contrast, which is related to its better charge transport properties.\textsuperscript{6}

These studies of diarylethene switches on gold electrodes by MCBJ and STM suggest that the reversibility of the photochromic switching is directly related to the electronic communication between the switching unit and the substrate. Kudernac \textit{et al.}\textsuperscript{7, 8} reported further experiments to investigate this phenomenon, carried out with diarylethene incorporating a variety of the linkers attached to gold nanoparticles\textsuperscript{7}, and gold bead electrodes\textsuperscript{8} as shown in Figure 3. All three compounds display typical photochromic behavior when in solution. The photochromic properties of diarylethenes linked to gold nanoparticles via an aromatic spacer have been investigated. Depending on the spacer, bi-directional light induced switching of the diarylethene on gold was observed for compounds with a \textit{meta-} and \textit{para-} phenyl spacers and uni-directional photochromic reactions (ring opening) were observed in the case of a thiophene spacer. This demonstrates that small changes in molecular structure can have a significant impact on the overall photochemistry.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{Schematic representation of the molecular structure of dithienylethene with \textit{m-} phenyl, \textit{p-}phenyl and thiophene substituted thiol linked to gold nanoparticles and gold bead electrodes.}
\end{figure}

In 2007, Irie and co-workers\textsuperscript{9} reported a correlation between the plasmon absorption of the Ag nanoparticles and the fluorescence of a diarylethene using the system shown in Figure 4. On a silver surface, the diarylethene shows normal reversible photochromic reactions; however, the PSS from the open to the closed form decreases dramatically, indicating a decrease in the quantum yield of photocyclization. The quenching of the excited state was attributed to energy transfer from the diarylethene unit to the Ag nanoparticles, consequently the overlap between the absorption of the diarylethene and plasmon absorption of Ag nanoparticles is apparently an important factor in the quenching of photochemically excited states.
Photo- and Electrochemical Properties of SAMs of Diarylethenes on Semiconductive Surfaces

**Figure 4.** Diagram illustrating diarylethene SAMs on silver nanoparticles.\(^9\)

**Figure 5.** Self-assembled monolayers of diarylethene 1 on a gold electrode, (A) Cyclic voltammogram of a dithienylethene modified gold electrode; a) \(1_0\) monolayer-functionalized electrode, b) \(1_c\) after application of a potential of 0.35 V for 90 s, c) after irradiation at 570 nm for 15 min. (B) Peak current values obtained upon repetition of switching cycles.\(^10\)

Willner and co-workers\(^10\) have reported SAMs of diarylethenes \(1\) on a gold surface as a write-read-erase information processing unit, by using electrochemistry as a non-destructive read out method of the two different states of the diarylethene switch on a gold electrode, as shown in Figure 5. \(1_0\) undergoes an electrochemical cyclization to form \(1_c\) after application of potential at 0.35 V. The ring-closure product \(1_c\) also undergoes photochemical ring-opening to \(1_0\). It should be noted that \(1_c\) does not show any redox-response in the range of 0.0 V to 0.3 V. The self-assembly monolayer of \(1\) can be written and read electrochemically, and the information stored can be erased photochemically upon
irradiation with visible light. Thus, the electro- and photochemical properties of the monolayer-functionalized electrode reveals the sequential electro- and photochemical storage of information.

Self-assembled monolayers of diarylethenes have been shown recently to have a large and reproducible bidirectional conductance switching in a solid-state molecular device\(^\text{11}\) (Figure 6). SAMs of diarylethenes were coated with a highly conductive organic polymer top electrode to prevent the formation of short-circuits between the top and the bottom electrodes. Upon irradiation within a specific wavelength range, the conductance in these devices can be switched photochemically. Switching is not observed for devices without a SAMs of diarylethenes or with a monolayer of alkanethiol molecules that do not contain photoswitching units. Therefore these molecular devices can operate as an electronic ON/OFF switch and as a reprogrammable data storage moiety that can be written photochemically and read electronically.

![Figure 6](image)

**Figure 6.** a) Schematic cross section of the device layout of a large-area molecular junction in which the diarylethene is sandwiched between Au and PEDOT:PSS and b) Current density vs time for the in situ optical switching of a monolayer of diarylethenes, alternating between UV (2 min) and visible (4 min) light, illustrating a direct current modulation through the molecular junction.\(^\text{11}\)

The optoelectronic properties of SAMs of diarylethenes have been examined when immobilized on metal surfaces i.e. gold nanoparticles,\(^\text{7,12}\) silver nanoparticles,\(^\text{9}\) and bulk gold electrodes.\(^\text{6,8}\) The nature, length, and position of the anchoring group between the diarylethene moieties and metal surface have been shown to play an important role in controlling the reversibility of the photoreactions on metal surfaces. Inhibition of photochemical reactivity in certain cases was attributed to the quenching of the photoexcited state of the molecules by the electronic states of the metal surface.\(^\text{13}\) Therefore, it is essential to design suitably modified diarylethenes or to employ semiconductor surfaces, e.g. indium tin oxide (ITO) electrodes, to avoid quenching of the excited state by the
surface. The photo- and electrochemical properties of diarylethene SAMs, on non-metallic conductive surfaces had not been reported thus far. This prompted us to study the photo- and electrochemical properties of self-assembled monolayers of diarylenes on non-metallic surfaces, in order to achieve read/write/erase information storage with non-destructive read out. However, the development of practical read/write/erase memory devices depends, ultimately, on additional functions other than the molecular switching “write/erase” function (e.g. photochromism). Achieving a read/write memory device requires that a secondary physical signal, i.e. electrochemistry,\textsuperscript{14,15} IR,\textsuperscript{16} Raman,\textsuperscript{17} fluorescence spectroscopy\textsuperscript{18} etc., is available to read the state of the switch non-destructively. Diarylethene derivative \textit{Ho}, which was studied previously in our group,\textsuperscript{14} can undergo a reversible electrocyclic reaction to form \textit{Hc}, allowing for both photo- and electro-chromism (Scheme 1). Oxidation of \textit{Ho} generates the \textit{Ho}$^{2+}$ intermediate, which can undergo a thermal electrocyclization reaction to form \textit{Hc}$^{2+}$. The reduction of \textit{Hc}$^{2+}$ yields \textit{Hc}. Therefore, diarylethene switch \textit{Ho} was chosen as the basis for the design of a switchable system to study the photo- and electrochemical behavior at a semiconductor interface (ITO). However, that functionality is preserved on a surface is not the only consideration; efficient readout is required also.

Scheme 1. General scheme for electrochemical processes observed in dithienylethene based systems.

It should be possible to combine, e.g. an efficient fluorophore with the diarylethene switch, thereby having a unit with a high quantum yield of fluorescence ($\Phi \approx 1$ e.g. anthracene, porphyrin and coumarin) for the purpose of read out. Indeed a diarylethene has been used successfully as a switchable fluorescence quencher\textsuperscript{19} as shown in Figure 7. From previous studies in our group\textsuperscript{20}, it is known that a coumarin-dithienylethene 2 (Figure 7c) shows the properties of an effective fluorescence OFF/ON switch, by irradiation with UV and visible light, respectively. Furthermore the electrochemical properties of the switching unit are unaffected by the attachment of the coumarin unit. The combination of a diarylethene unit and a fluorophore opens the possibility of electro- and photochemical control of fluorescence output.
Figure 7. Schematic representation of a fluorophore – photochromic switch dyad. A) When the photochromic unit is in State 1, the fluorophore (F) is excited by $\lambda_1$ and emits light at longer wavelengths ($\lambda_2$). B) When the photochromic unit is in State 2, F is still excited by $\lambda_1$, however this excited state is quenched by the photochromic unit and emission is not observed. C) The coumarin-dithienylethene system 2.  

The use of a tricomponent system (surface-switch-fluorophore) should allow for electrochemistry or fluorescence spectroscopy to be used as the secondary physical signal for non-destructive readout. In this chapter, two types of diarylethene derivatives with and without a fluorophore substituent are designed for immobilization on metal oxide surfaces, quartz, and ITO (Scheme 2).

Scheme 2. Structures of dithienylethene switches used for surface immobilization.
3.3 Synthesis

Dithienylethene switch 3 was synthesized following the strategy depicted in Scheme 3. We used the triethoxysilane moiety as the anchoring group in compound 3 for immobilization onto a surface. Compound 8 was used for comparative studies in solution. Treatment of compound 5 with t-butyllithium and subsequent reaction with tri-n-butylborate provide a boronic acid intermediate, which was reacted with 4-bromo-methylbenzoate in the presence of a palladium catalyst providing 6 in 51% yield. The alkaline hydrolysis of compound 6 provided the acid functionalized switch 7 in 89% yield. Subsequently compound 7 was converted to compounds 8 and 3 by using N-methylmorpholine (NMM) and 2-chloro-4,6-dimethoxytriazine with the corresponding amine, n-propylamine and 3-aminopropyltriethoxysilane, respectively.

Scheme 3. Synthetic route to compounds 8 and 3.

For the synthesis of the coumarin-diarylethene switch 4 (Scheme 4), the intermediate compounds 9 and 12 were synthesized as reported previously. A Suzuki coupling was used between the diodo compound 9 and 4-carboxyphenylboronic acid 10 to obtain mono acid 11 in 52% yield. The amide coupling of mono acid 11 with dimethoxycoumarin 12 using 2-chloro-4,6-dimethyltriazine and NMM in CH2Cl2 yields compound 13 in 74% yield. A subsequent Suzuki reaction with 4-carboxyphenylboronic acid 10 yielded compound 14 in 38% yield. Finally, the desired compound 4 was prepared by amide
coupling of compound 14 to 3-aminopropyl-triethoxysilane in 50% yield. All compounds were purified by column chromatography and characterized with 1H and 13C NMR spectroscopy and (MALDI-TOF) mass spectrometry (see experimental section for details).

Scheme 4. Synthetic route to compound 4
3.4 Electronic properties of diarylethenes 8 and 2 in solution

Figure 8 shows the UV/Vis absorption spectra of the open and closed forms of diarylethenes 8 and 2. Dynamic interconversion between the open and closed state can be achieved by irradiation at selected wavelengths (λ = 365 nm for ring closing and λ > 500 nm for ring opening). Although the open states show absorption in the UV region only, the closed states show intense broad absorptions centered between 450 and 600 nm. It should be noted that upon irradiation of the open form, with UV light, in all cases a photostationary state (PSS) is reached.

Table 1 shows the absorption maxima for the open and closed forms of the diarylethenes, their corresponding molar absorptivity and the emission wavelength. As shown previously by Hurenkamp, the fluorescence of the coumarin component was not quenched by the open form of the diarylethene 2o (Figure 9). However, a large reduction in the intensity of coumarin fluorescence (> 98%) was observed in the ring-closed form. This decrease in fluorescence is due to quenching by 2c, indicating that energy transfer to the switch is efficient.

![Figure 8](image)

Figure 8. UV/Vis absorption spectra of 8 and 2 in open and closed form at room temperature (typical concentrations are 10^-5 M).
Figure 9. Fluorescence spectra ($\lambda_{ex}=380$ nm) of 2 in the open state (---), and PSS state (----).

Table 1 Absorption and emission spectra of the dithienylcyclopentene switches in the open state and at the PSS 365 nm.20

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance $\lambda_{max}$/ nm (10$^3$ $\varepsilon$/cm$^{-1}$ mM$^{-1}$)</th>
<th>Emission $\lambda_{max}$/ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>8o''</td>
<td>289(25.5)</td>
<td>-</td>
</tr>
<tr>
<td>8c PSS$^a$</td>
<td>287(22.9) 372(9.3) 547(12.4)</td>
<td>-</td>
</tr>
<tr>
<td>2o</td>
<td>287(29.3) 321(24.6)</td>
<td>420</td>
</tr>
<tr>
<td>2c PSS</td>
<td>285(25.9) 353(17.0) 541(14.9)</td>
<td>425</td>
</tr>
</tbody>
</table>

$^a$ recorded in CH$_2$Cl$_2$ at RT. $^b$ recorded in toluene at RT

3.5 Redox properties of diarylethenes 8 and 2 in solution

The solution redox properties of compound 8 and 2 in both open and closed forms are detailed in Table 2. As expected for both 8o and 2o an irreversible oxidation process (Figure 10) is observed at ~ 1.1-1.2 V vs SCE, which results in efficient ring closure to yield 8c$^{2+}$ and 2c$^{2+}$, respectively. The dications 8c$^{2+}$ and 2c$^{2+}$ can then be reduced, first to 8c$^{+}$ and 2c$^{+}$ at 0.78 V vs SCE and finally to 8c and 2c at 0.43 V vs SCE, respectively. The electrochemical properties of 8 and 2 are in agreement with those observed for their symmetric analogues.3
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![Graph showing cyclic voltammetry in CH₂Cl₂/0.1 M TBAPF₆ vs SCE of (inset) 8c and 2c scan rate 0.1 V s⁻¹. Glassy carbon working electrode and platinum wire counter electrode.](image)

**Figure 10.** Cyclic voltammetry in CH₂Cl₂/0.1 M TBAPF₆ vs SCE of a) 8o (inset) 8c, b) 2o (inset) 2c scan rate 0.1 V s⁻¹. Glassy carbon working electrode and platinum wire counter electrode.

<table>
<thead>
<tr>
<th></th>
<th>Open form E₁/₂ (V vs SCE)</th>
<th>Closed form E₁/₂ (V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1.15 (irr)</td>
<td>0.78, 0.42</td>
</tr>
<tr>
<td>2</td>
<td>1.18 (irr)</td>
<td>0.78, 0.43</td>
</tr>
</tbody>
</table>

*In CH₂Cl₂/ 0.1 M TBAPF₆ vs SCE, (irr) = irreversible*
3.6 Preparation and characterization of self-assembled monolayers of 3 and 4 on quartz slides.

The self-assembled monolayers of 3 and 4 were first studied on quartz slides in order to investigate the photochemistry of these compounds when attached to the surface. Prior to monolayer deposition, the quartz substrates were cleaned for 1 h in boiling ‘piranha’ (solution of 7:3 concentrated H$_2$SO$_4$ and 30% H$_2$O$_2$), rinsed several times with high-purity water and dried in a stream of dinitrogen. Formation of the self-assembled monolayers was achieved under an atmosphere of dinitrogen. The freshly cleaned substrate was immersed in a 1-5 mM solution of the adsorbate in dry toluene for 12 h at 80 °C. After the substrate had been removed from the solution, it was rinsed with toluene, dichloromethane and ethanol to remove any physisorbed material, and dried in a stream of nitrogen.

A first indication of the quality of the layers formed can be obtained from wettability studies (Table 3). Contact angle measurements were used to characterize the quartz slides at different stages. Cleaned quartz slides produced low water contact angles (5°) consistent with that of clean glass reported previously. Successive modifications with 3 and 4 caused the hydrophilicity of the surface to increase, leading to a water contact angle of 83° for 3-Q and 71° for 4-Q. These are similar to the contact angles of water observed on silicate surfaces derivatized with azobenzene based SAMs.

**Scheme 5.** Representation of self-assembled monolayers of 3-Q and 4-Q on quartz surfaces.
Photo- and Electrochemical Properties of SAMs of Diarylenes on Semiconductive Surfaces

UV-vis absorption spectroscopy is a valuable technique in the characterization of functionalized self-assembled monolayers. The use of quartz substrates that are transparent to 200 nm enables the detection of UV chromophoric groups. The UV-vis absorption spectrum of 3-Q and 4-Q clearly shows the presence of the diarylethene switch on the surface (Figure 11) with the characteristic absorption maxima at 287 and 290 nm, respectively. In addition to confirming the surface attachment of a chromophore through its characteristic absorption bands, UV-vis absorption spectroscopy can also be used in a quantitative manner. The Lambert-Beer law relates the absorption (A) to the surface density of the chromophores (Γ) as given in eq. 1. The value of the molar absorptivity (ε) of the chromophore can be determined from solution experiments. Usually, the molar absorptivity of a chromophore in a self-assembled monolayer is not known, hence values obtained from solution studies are used. By using the molar absorptivity obtained from solution, the surface densities of diarylethene 3-Q and 4-Q were estimated as 4.1 x 10^{-10} mol/cm² and 4.6 x 10^{-10} mol/cm², respectively (Table 3). The high packing of diarylethene 3 and 4 on the quartz surface is due to the formation of multilayers through pre-polymerization of triethoxysilane anchoring group before anchoring to the surface.

\[ A = ε . Γ \]  

**eq. 1.**

Table 3. Wettability and surface density of self-assembled monolayers on quartz.

<table>
<thead>
<tr>
<th></th>
<th>Sessile drop contact angle(°)</th>
<th>Surface density(\text{mol/cm}²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare quartz</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>3-Q</td>
<td>83</td>
<td>4.1 x 10^{-10}</td>
</tr>
<tr>
<td>C₈H₁₇Si(OEt)₃</td>
<td>102</td>
<td>-</td>
</tr>
<tr>
<td>4-Q</td>
<td>71</td>
<td>4.6 x 10^{-10}</td>
</tr>
<tr>
<td>4/C₈H₁₇Si(OEt)₃-Q</td>
<td>105</td>
<td>1.5 x 10^{-9}</td>
</tr>
</tbody>
</table>

* Sessile drop contact angle determined with water as the probing liquid. * Surface density determined by UV/Vis spectroscopy.

3.6.1 Photochemical and fluorescence switching of SAMs on quartz

Figure 11 shows the absorption spectra of 3o-Q and 4o-Q. Upon irradiation with UV light (365 nm), the absorption band in the visible region increases and a new maximum is found at 544 and 550 nm, respectively, indicating the formation of the closed form. 3-Q and 4-Q show similar absorption spectra with respect to those observed in solution (Table 4). Moreover, photochemical switching can be performed over several open/closing cycles as shown in Figure 11b (inset). However, compared to the unbound molecules, the ring closing reaction is less efficient. A number of factors could contribute to this phenomenon including a reduced effective interaction with light due to the restricted motion in a
packed monolayer, which is possible due to the high surface density of 3-Q and 4-Q or self-quenching of the chromophore in the monolayers.

Figure 11. UV-visible absorption spectra of a) 3-Q and b) 4-Q upon irradiation with UV light (365 nm), the inset shows repetitive photochemical switching when irradiation at 365 nm and > 500 nm, respectively.

Table 4. Absorption and emission spectra data for the dithienylethene switches in the open state and at the PSS on quartz surfaces

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; / nm</th>
<th>Emission λ&lt;sub&gt;max&lt;/sub&gt; / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3o-Q</td>
<td>287</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3c-Q PSS</td>
<td>287 375</td>
<td>544</td>
<td>-</td>
</tr>
<tr>
<td>4o-Q</td>
<td>290 328</td>
<td>417</td>
<td></td>
</tr>
<tr>
<td>4c-Q PSS</td>
<td>294 550</td>
<td>426&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

*The emission maximum determined in the mix-monolayer condition of 4c/C<sub>8</sub>H<sub>17</sub>-Q

The emission spectrum of 4o-Q is shown in Figure 12a. When excited at 360 nm only the open form was found to be fluorescent at 417 nm which is in agreement with measurements in solution (vide supra). However, when 4o-Q was irradiated with UV light to obtain a 4c-Q, quenching of the fluorescence was not observed (Figure 12b).
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Figure 12. a) Fluorescence spectra ($\lambda_{ex} = 360$ nm) of 4o-Q in the open state (---) and bare quartz as a blank (•••); b) Fluorescence spectra ($\lambda_{ex} = 360$ nm) of 4c-Q after irradiation with UV light.

The high intrinsic sensitivity of fluorescence spectroscopy\textsuperscript{28} makes it a valuable tool for the study of self-assembled monolayers. However, intermolecular interactions can influence the fluorescence properties of surface immobilized fluorophores,\textsuperscript{29} and the spectrum can provide information regarding the structure in the monolayers. In the present case, the fluorescence of 4o-Q might be affected by a high packing density of the fluorophore (coumarin), which opens the possibility for self-quenching between the coumarin moieties in the 4o-Q. This is consistent with the low PSS of the diarylethene 4c on quartz observed upon switching compared to that observed in solution. The low photostationary state of the closed form is attributed to the close packing so there is not enough space for photoisomerization in well-packed molecular film.\textsuperscript{30} Mixed monolayers of diarylethene 4 and octyl-triethoxysilane were used to separate the individual diarylethene molecules in the SAM layer. The same procedure as described above was used for the preparation of SAMs, and the substrates were immersed in 1:10 ratio of compound 4 and C\textsubscript{8}H\textsubscript{17}Si(OEt)\textsubscript{3}. The contact angle showed an increase in the hydrophobicity of the surface (105°) and the surface density is estimated to be 1.5 x 10\textsuperscript{9} mol/cm\textsuperscript{2} which is higher than that expected for the mixed SAMs as shown in Table 3 (\textit{vide supra}). This result can be explained by the polymerization of octyl-triethoxysilane prior to anchoring onto the surface in the presence of traces of H\textsubscript{2}O.\textsuperscript{26}
3.6.2 Photochemical switching of mixed-monolayer of 4/C₈H₁₇-Q

Figure 13a shows the UV-vis absorption of the mixed monolayer 4₀/C₈H₁₇-Q. Upon irradiation with UV light, the ring-closing isomer 4ₒ/C₈H₁₇-Q was observed to have a higher PSS than that of 4ₒ monolayer. This indicates that the photochromism of 4ₒ/C₈H₁₇-Q in a mixed monolayer system is more efficient than that of 4ₒ-Q. The fluorescence maximum of 4ₒ/C₈H₁₇-Q was observed at 417 nm (excitation at 360 nm). Coumarin fluorescence was quenched only partially by closing the dithienylethene 4c with UV irradiation (Figure 13b). In addition, the fluorescence of 4/C₈H₁₇-Q can be modulated several times by photochemically switching between the open and closed forms as shown in Figure 13b (inset). These results suggest that the self-quenching between the coumarin moiety on dithienylethene 4 in the SAMs can be avoided by using a mixed monolayer method. Although the mixed monolayer of 4/C₈H₁₇-Si(OEt)₃ can undergo fluorescence switching, it is not the optimal system to study the fluorescence switching on a surface due to the low PSS in both absorption and fluorescence spectra upon illumination compared to that observed in solution. Therefore, further investigation of the photochromic switching of surface tethered 4 is still required.

From these results, it is evident that SAMs of dithienylethenes 3 and 4 can be immobilized on a quartz surface and their functionality (photochemical properties) observed in solution is still retained once immobilized on the surface. In the following sections, the preparation of SAMs on indium-tin oxide (ITO) surfaces and their photo- and electrochemical properties to achieve the Read/Write/Erase system will be discussed.

![Figure 13.](image)

**Figure 13.** a) The UV-vis difference spectrum obtained by subtraction of the spectrum of 4c/C₈H₁₇-Q at PSS from the spectrum of 4₀/C₈H₁₇-Q upon the PSS was obtained by irradiation with 312 nm light, b) Fluorescence spectra of the 4ₒ/C₈H₁₇-Q and 4c/C₈H₁₇-Q (excitation at 360 nm), (inset) repetitive fluorescence switching during alternating irradiation at 312 nm and at 500 nm.
3.7 Preparation and characterization of self-assembled monolayers of 3 and 4 on ITO

Prior to monolayer deposition, ITO substrates were cleaned by sonication, first in acetone, then in dichloromethane, and finally in deionized water. Subsequently, each slide was immersed in a solution of 1:1:5 30% H2O2/NH4OH (30%)/H2O) for 1 h at 70 °C. The slides were washed with a large amount of water and dried in an oven at 100 °C for 4 h. The clean, hydrophilic slides were then stored in a desiccator for maximum of 24 h until further use.\(^{31}\) The monolayers were prepared by immersing the ITO substrates in a 0.5-5 mM solution of 3 and 4 in toluene which was subsequently heated at reflux overnight under N\(_2\). The silanized ITO (3-ITO and 4-ITO) samples were then washed with HPLC grade toluene, methanol, deionized water and isopropanol to remove the physiosorbed material and subsequently dried in a stream of N\(_2\).

<p>| Table 5. Wettability and surface coverage of self-assembled monolayers on ITO surfaces. |
|---------------------------------|---------------------------------|</p>
<table>
<thead>
<tr>
<th>Bare ITO</th>
<th>Sessile drop contact angle(°)(^{a})</th>
<th>Surface coverage(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-ITO</td>
<td>28</td>
<td>-</td>
</tr>
<tr>
<td>4-ITO</td>
<td>68</td>
<td>5.5 x 10(^{-11})mol/cm(^2)</td>
</tr>
</tbody>
</table>

\(^{a}\) Sessile drop contact angle determined with water as the probing liquid. \(^{b}\) Surface density determined by coulometric analysis. \(^{c}\) Not determined due to the instability of the monolayer on the ITO surface.

In wettability studies (Table 5), the water contact angle of bare ITO yielded a value of 28°, which is comparable to those reported elsewhere.\(^{26}\) The water contact angles on 3-ITO and 4-ITO samples were determined to be 80° and 68°, respectively. The increasing hydrophobicity indicates modification of the ITO substrate.

3.7.1 Cyclic voltammetry of 3-ITO

Cyclic voltammetry of 3o-ITO in 0.1M TABPF\(_6\)/CH\(_2\)Cl\(_2\) shows an irreversible oxidation at 1.1 V \{3o-ITO→3c\(^{2+}\)-ITO\}, which gives rise to two redox waves at 0.73 and 0.46 V vs SCE \{3c\(^{2+}\)-ITO→3c\(^{1+}\)-ITO→3c-ITO\} as depicted in Figure 14. Additionally, the cyclic voltammetry can be used to estimate the surface coverage\(^{32}\) of the diarylethene on the ITO as shown in eq 2.

\[ \Gamma = N/A \quad \text{eq 2} \]
Γ is surface coverage, N is number of molecules on ITO and A is the surface area of the electrode. The integral of the current peak (first redox wave at 0.46 V) gives the charge (Q) accumulated by the molecular layer on the electrode surface and the capacitance of the electrodes. Assuming that one electron corresponds to one molecule, and neglecting the capacitance, one can calculate the number of molecules on the ITO electrode as shown in eq 3.32

\[ N = \frac{Q}{nF} \]  

Herein \( n \) is the number of electrons involved in the reaction, and F is the Faraday constant. Coulometric analysis of the redox wave of 3-ITO yields a surface density of the diarylethene of 5.5x10\(^{-11}\) mol/cm\(^2\). The surface density of 3-ITO is similar to those observed on ITO immobilized SAMs of spiropyran and the roughness factor of 3o-ITO is estimated as 1.2 by atomic force microscopy (vide supra).

**Figure 14.** Cyclic voltammetry of a) \( \text{8o} \) (inset cyclic voltammetry of \( \text{8c} \)), b) \( \text{3o-ITO} \) at 0.1 V s\(^{-1}\) in CH\(_2\)Cl\(_2\) (0.1 M TBAPF\(_6\)).

Essentially the cyclic voltammetry of 3-ITO is equivalent to that observed for 8 in solution, however, as is expected for a modified surface the intensity of the Faradic current is directly dependent on the scan rate. Figure 15 shows a linear increase in current with increase of the potential scan rate (0.5-10 V s\(^{-1}\)), a plot of peak current against the scan rate (Figure 15b) was linear (\( R^2 = 0.9995 \)) thus indicating that the diarylethene is present as a surface confined redox system.34
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**Figure 15.** a) Representative cyclic voltammetric responses, at different scan rates of a SAM of a diarylene on ITO. The voltage scan rate was varied from 0.5, 0.75, 1, 2, 5, 10 V s⁻¹. b) Linear correlation of the peak current (A) versus the scan rate (V s⁻¹).

### 3.7.2 AFM image of 3o-ITO

The film morphology was studied by atomic force microscopy (Dimension, Digital Instruments). The characterization was performed under ambient conditions by tapping mode AFM on several samples of 3o-ITO and with different tips. The root mean square (RMS) surface roughness of the surface of 3o-ITO as measured by atomic force microscopy (AFM) on areas typically of 1x1 μm² was 12 nm. For Figure 16a, the effective area was calculated to be 0.7764 μm² by WsXM software, which corresponds to a roughness factor of 1.2. AFM phase contrast images have been shown to be sensitive to material surface properties, such as chemical composition. Figure 16b is the phase contrast image corresponding to the topography shown on Figure 16a. It shows a different contrast than that in Figure 16a which corresponds to uncovered or monolayer-covered ITO areas. The phase contrast reveals where ITO is covered by the monolayer: the organic monolayer covers small domains which are distributed over the whole surface, as reported by others.²⁵
3.7.3 Cyclic voltammetry of 4-ITO

Cyclic voltammetry of 4-o-ITO in 0.1M TBAPF₆/CH₂Cl₂ shows an irreversible oxidation wave at 1.3 V \{4-o-ITO→4c²⁺-ITO\}, which gives rise to two redox waves at 0.80 and 0.50 V vs SCE \{4c²⁺-ITO→4c¹⁺-ITO→4c-ITO\} as depicted in Figure 17a. However, a significant decrease in signal intensity for 4-ITO was observed upon repetitive cycling between 0.0 and 1.0 V, and the cyclic voltammogram of 4-ITO is not recovered after scanning between 0.0 to 1.3 V (Figure 17b and c, respectively). The loss of signal intensity is due to the instability of 4 on the ITO surface. In addition the fluorescence switching of 4 by using electrochemistry as the external stimulus could not be employed in these systems due to the overlap of the absorption spectrum of the coumarin (~ 420 nm) and ITO (~ 400 nm). In contrast to 4, self-assembled monolayers of 3 can be prepared reproducibly on ITO, indicating that the coumarin moiety of 4 may affect the stability of the molecule on the surface. From these results, a coumarin-dithienylethene switch is not a suitable system to study its photo- electrochemical switching on the surface with either quartz or ITO. Hence a new design of the dithienylethene switch-fluorophore combination would be required for further investigations of the fluorescence switching on ITO by electrochemistry (i.e. in a switch-perylene²⁰ system the fluorescence switching at 600-700 nm can be modulated in solution). The next section will only discuss the photo- and electrochemical properties of 3 on ITO electrodes.
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Figure 17. Cyclic voltammetry of a) 3o-ITO in CH2Cl2, b) repetitive cycles between 0.0 – 1.0 V, and c) after repetitive cycles between 0.0 to 1.0 V, the Faradic current of 4o-ITO is not observed in 0.1M TBAPF$_6$ at 0.5 V s$^{-1}$.

3.8 Electrochemical and photochemical switching of 3-I TO

The cyclic voltammetry of the 3o-ITO shows no Faradic processes between -0.2 to 0.6 V i.e. no process attributable to the closed state isomer. Irradiation of 3o-ITO results in photocyclization of 3o-ITO to 3c-ITO with the appearance of a reversible redox wave at 0.45 V, i.e. the 1st oxidation of 3c-ITO (Figure 18). A complete disappearance of the redox process at 0.45 V, i.e. restoration of 3o-ITO was observed after irradiation of the electrode at $\lambda > 420$ nm for 30 min. This process can be continued over several cycles of photochemical switching of the monolayer between states 3o-ITO and 3c-ITO, however, it is apparent that with each cycle the signal in the closed state diminishes considerably as shown in the inset of Figure 18. Moreover, the water contact angle of the surface decreases
from 80° before irradiation to 58° after four cycles of photochemical switching. The decrease in the intensity of the redox wave of 3c-ITO over several cycles can be attributed to the instability of the anchoring silyl group of the dithienylethene switch on the surface due to the liberation of F⁻ from the supporting electrolyte, rather than an inherent electrochemical instability of 3c-ITO (vide infra).

Indeed, this instability can be circumvented by using TBA(CF₃SO₄) as the supporting electrolyte. The first redox wave of the closed-state could be used to read the state (closed or open) of the switch; the signal of the open and closed form was observed upon irradiation with UV and visible light as shown in Figure 19. In addition, the decrease in intensity of the 1st oxidation wave of 3c-ITO was not observed over four photochemical ‘close-open-close’ cycles (Figure 20). Furthermore, the water contact angle of the ITO glass after the four cycles with TBA(CF₃SO₄) as electrolyte showed only a modest change from 80° to 70°. Hence, under these conditions SAMs of 3-ITO show satisfactory stability.

Figure 18. Cyclic voltammetry of a) 3o-ITO and b) 3c-ITO after irradiation at 312 nm for 5 min. Inset: Repetitive photochemical switching of 3o-ITO to 3c-ITO in 0.1 M TBAPF₆/CH₂Cl₂ at scan rate 2 Vs⁻¹.
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**Figure 19.** Cyclic voltammetry of a) 3o-ITO and b) 3c-ITO after irradiation at 312 nm for 5 min. Inset: Repetitive photochemical switching of 3o-ITO to 3c-ITO in 0.1 M TBA(CF$_3$SO$_4$)/CH$_2$Cl$_2$, scan rate 2 V s$^{-1}$.

**Figure 20.** Photochemical switching of 3o-ITO, upon irradiation at 312 nm for 5 min, and subsequently with >400 nm (20 min). a) 3o-ITO, b) after 312 nm irradiation, c) after >400 nm irradiation, d) after 312 nm irradiation, e) after >400 nm irradiation f) after 312 nm irradiation, in 0.1 M TBA(CF$_3$SO$_4$)/CH$_2$Cl$_2$ at scan rate 2 V s$^{-1}$.
3.9 Electrochemical conversion of 3c-ITO to 3o-ITO (oxidative ring-opening)

Ring opening (oxidatively) of 3c-ITO is a thermodynamically disfavoured process however, it can occur through disproportionation of the monocation of the closed form 3c1+-ITO to the neutral state e.g. 3c-ITO and the dication 3c2+-ITO (i). The dication 3c2+-ITO is in equilibrium with 3o2+-ITO albeit with the closed form highly favoured (ii). In addition the dication 3c2+-ITO and 3o2+-ITO will undergo rapid electrochemical reduction to the monocation 3c1+-ITO and neutral 3o-ITO compounds, respectively, below 0.6 V. Although statistically unlikely, once ring opening does occur it is irreversible under the limited scanning range of 0-0.5 V. Hence, at high scan rates (>1 V s⁻¹) the extent of disproportionation of the monocation generated is low and the rapid reduction of the dication avoids ring opening. At slower scan rates the equilibrium is driven towards the open form 3o-ITO (iii) and overall ring open will be observed as shown in Scheme 6.

\[
\begin{align*}
\text{(i)} & \quad 2(3c^+\text{-ITO}) \rightarrow 3c\text{-ITO} + 3c^{2+}\text{-ITO} \\
\text{(ii)} & \quad 3c^{2+}\text{-ITO} \rightarrow 3o^{2+}\text{-ITO} \\
\text{(iii)} & \quad 3o^{2+}\text{-ITO} + 3c\text{-ITO} \rightarrow 3o\text{-ITO} + 3c^{2+}\text{-ITO}
\end{align*}
\]

Scheme 6. Electrochemical processes leading to electrochemical ring closing and ring opening of 3c-ITO/3o-ITO, upon repetitive cycles between 0.0 to 0.65 V vs SCE

Figure 21 shows the oxidative ring-opening of 3c-ITO to 3o-ITO. The loss of signal intensity for 3c-ITO (Figure 21a) was observed after repetitive cyclic voltammetry between 0.0-0.6 V at 0.1 V s⁻¹ due to the formation of 3o-ITO (Figure 21b). Indeed a complete recovery of the redox wave of 3c-ITO is observed after irradiation with UV light (Figure 21c).
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Figure 21. Cyclic voltammetry of a) 3c-ITO (formed from 3o-ITO by irradiation with 312 nm light); b) 3o-ITO (after oxidative ring opening achieved by repetitive cyclic voltammetry between 0.0 and 0.6 V at 0.1 V s⁻¹) in TBA(CF₃SO₄)/CH₂Cl₂ at scan 0.5 V s⁻¹ and c) after irradiation of oxidatively opened 3o-ITO at 312 nm to 3c-ITO in 0.1 M TBA(CF₃SO₄) / CH₂Cl₂ at a scan rate of 2 V s⁻¹.

3.10 Conclusions

The electrochemical/photochemical properties of diarylene modified ITO electrodes reveal a robust system, where redox and/or optical switching allows for Write-Read-Erase function ability. The open form 3o-ITO can act as an information recording interface. The information is ‘written’ either photochemically or electrochemically (i.e. to produce the closed form 3c-ITO) and the information stored can be erased subsequently by either photochemical or electrochemical conversion from 3c-ITO to 3o-ITO. The information is ‘read out’ non-destructively by monitoring the reversible 1ˢᵗ oxidation of the closed form electrochemically in the potential range of 0.0 to 0.5 V. In the same potential window the open form 3o-ITO is electrochemically inert. Moreover this results demonstrate that robust immobilisation of monolayers of dithienylethene switches can be achieved on non-metallic interfaces, without loss of function. The ability to drive ring-opening and closing reactions oxidatively provides increased functionality to these photochromic surfaces compared with theirs solution behavior (Scheme 6).

Figure 22. A Write/Read/Erase information system based on dithienylethene on ITO.
In summary the immobilised diarylethene switch 3 can undergo multiple ring-opening and ring-closing reactions both electrochemically and photochemically and, importantly, the state of the modified surface can be read ‘non-destructively’ by electrochemistry (Figure 22). The tricomponent system (surface (ITO)-switch-coumarin) is not a suitable system to allow the use of electrochemistry and fluorescence spectroscopy as secondary physical signals for non-destructive readout as is evident from the instability observed for 4 on ITO surfaces. However, the optical switching of mixed monolayers of 4/C8H17Si(OEt)3-Q can be used to control fluorescence switching on quartz surfaces.

The present system for electrochemical control of fluorescence switching of dithienylethene 4 on an ITO surface was not successful and optimal conditions for surface modification requires the stability of monolayer on surface to be improve and for the PSS of molecules in the monolayer to be increased. For example, new anchoring functional groups (e.g. via click chemistry) or the longer alkyl spacers between the dithienylethene and surface would allow for an increasing the space between the molecules which could solve those problems. A new design of a dithienylethene switch-fluorophore combination would be required for further investigation of the photoswitching fluorescence on surfaces for instance with perylenes attached.

3.11 Acknowledgements

The synthesis of compounds 2 and 12 were performed by Dr. J. H. Hurenkamp. Dr. Nathalie Katsonis is acknowledged for assistance with AFM measurements.

3.12 Experimental Section

For information regarding synthesis and characterisation and general experimental details see Chapter 2

UV/Vis spectra were recorded (in solution or for polymer modified ITO slides) using a JASCO 570 UV-Vis-NIR spectrometer. Fluorescence spectra were recorded using a JASCO F7200 fluorimeter and a SPF-500C spectrofluorimeter manufactured by SLM Aminco. Contact angles were measured on a Krüss Drop Shape Analysis System DSA 10 Mk2. Electrochemical measurements were performed using a Model 630B or 760C Electrochemical Workstation (CH Instruments). Analyte concentrations were typically 0.5 to 2 mM in anhydrous CH2Cl2 containing 0.1 M tetra-butylammonium hexafluorophosphate (TBAPF6) or 0.1 M (TBACF3SO3). A Teflon shrouded glassy carbon, gold or platinum microelectrode, and indium tin oxide (ITO) coated glass (Präzisions Glass & Optik GmbH, Germany) was employed as a working electrode (CH Instruments), a Pt wire auxiliary electrode and Ag/AgCl ion quasi reference electrode or a SCE electrode were employed (calibrated externally using a 0.1 mM solution of ferrocene, all potentials reported are relative to SCE). Cyclic voltammograms were obtained at a sweep rate between 100 mV and 5000 mV/s.
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Methyl-4-(5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoate (6). Compound 5 (0.87 g, 2.36 mmol) in THF (40 ml) was treated with t-BuLi (2.36 ml, 1.5 M in n-pentane, 3.54 mmol) under a N2 atmosphere. After 1 h, B(OBu)3 (0.95 ml, 3.54 mmol) was added and the mixture was stirred for 1 h at room temperature. A separate flask was charged with methyl 4-bromobenzoate (0.76 g, 3.54 mmol), [Pd(PPh3)4] (81 mg, 0.07 mmol), THF (50 ml), aqueous Na2CO3 (2 M, 10 ml) and ethylene glycol (10 drops). The mixture was heated to 80 °C and the prepared boronic ester was added slowly. The reaction mixture was heated at reflux overnight, cooled to room temperature, diluted with diethyl ether (50 ml) and washed with H2O (50 ml). The aqueous layer was extracted with diethyl ether (50 ml). The combined organic layers were dried over Na2SO4. After evaporation of the solvent, the product was purified by column chromatography on silica gel (heptane) to afford 6 as a viscous oil (0.56 g, 51%). 1H NMR (400 MHz, CDCl3) δ 2.00 (s, 3H), 2.02 (s, 3H), 2.10 (m, 2H), 2.85 (t, J = 7.34, 7.69 Hz, 4H), 3.91 (s, 3H), 7.03 (s, 1H), 7.15 (s, 1H), 7.22 (t, J = 7.33, 7.34 Hz, 1H), 7.33 (t, J = 7.33, 8.07 Hz, 2H), 7.50 (d, J = 7.33 Hz, 2H), 7.54 (d, J = 8.43 Hz, 2H), 7.99 (d, J = 8.80 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 14.4 (q), 14.5 (q), 23.0 (t), 38.4 (t), 38.5 (t), 52.0 (q), 123.9 (d), 124.8 (d), 125.3 (d), 125.5 (d), 126.9 (d), 128.1 (s), 128.8 (d), 130.2 (d), 134.3 (s), 134.4 (s), 135.1 (s), 135.3 (s), 136.5 (s), 137.1 (s), 138.3 (s), 138.7 (s), 139.8 (s), 166.8 (s). EI-MS (m/z): 470 (M+); HRMS calcd for C29H26O2S2 470.1374, found 470.1399.

4-(5-Methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoic acid (7). Compound 6 (0.56 g, 1.21 mmol) was added to 50 mL of MeOH/H2O/THF (1:1:3 v/v/v). The suspension was stirred at room temperature for 10 h. The mixture was acidified carefully by dropwise addition of 2 M aq. HCl. The aqueous layer was extracted with dichloromethane (3x50 ml). The combined organic layer was washed with sat. aq. NaCl, dried over Na2SO4, and the solvent removed in vacuo. The product was recrystallized from dichloromethane/methanol, to yield compound 7 as a brown solid (0.49 g, 89%). 1H NMR (400 MHz, CDCl3) δ 2.00 (s, 3H), 2.03 (s, 3H), 2.10 (m, 2H), 2.86 (t, J = 7.34, 7.33 Hz, 4H), 7.03 (s, 1H), 7.18 (s, 1H), 7.23 (m, 1H), 7.33 (t, J = 7.70, 7.33 Hz, 2H), 7.50 (d, J = 7.70 Hz, 2H), 7.58 (d, J = 8.43 Hz, 2H), 8.06 (d, J = 8.70 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 14.4 (q), 14.5 (q), 23.0 (t), 38.4 (t), 38.5 (t), 52.0 (q), 123.9 (d), 124.9 (d), 125.3 (d), 125.8 (d), 127.0 (d), 128.8 (d), 130.2 (d), 134.3 (s), 134.4 (s), 135.2 (s), 136.5 (s), 136.7 (s), 137.2 (s), 138.1 (s), 139.6 (s), 139.8 (s), 171.4 (s). EI-MS (m/z): 456 (M+); HRMS calcd for C28H24O2S2 456.1217, found 456.1201.

4-(5-Methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)N-propylbenzamide (8). Compound 7 (100 mg, 0.22 mmol) was suspended in CH2Cl2 (5 ml) and the mixture cooled to 0 °C. Subsequently N-methylmorpholine (30 μl, 0.22 mmol) was added and the compound dissolved. Next, 2-chloro-4,6-dimethoxytriazine (46 mg, 0.22 mmol) was added. The reaction mixture was stirred for 2 h at 0 °C, and a second equivalent of N-methylmorpholine (30 μl, 0.22 mmol) was added followed by propylamine (43 μl, 0.44 mmol). Stirring was continued for 1 h at 0 °C, and subsequently overnight at room temperature. CH2Cl2 (50 ml) was added and the solution was washed with, respectively, 1M aq. HCl (2 x 20 ml), brine (1 x 20 ml), saturated aqueous bicarbonate solution (1x20 ml) and H2O (1x20 ml). The organic phase was dried over Na2SO4 and after evaporation of
the solvent a solid was obtained. After purification by column chromatography (EtOAc:heptane = 5:95) a solid compound was obtained (48 mg, 43%). H NMR (400 MHz, CDCl3) δ 0.98 (t, J = 7.33, 7.70 Hz, 3H), 1.64 (m, 2H), 2.00 (s, 3H), 2.02 (s, 3H), 2.09 (m, 2H), 2.85 (t, J = 7.70, 7.33 Hz, 4H), 3.41 (m, 2H), 6.15 (br, 1H), 7.03 (s, 1H), 7.10 (s, 1H), 7.22 (m, 1H), 7.33 (m, J = 7.33, 7.70 Hz, 2H), 7.50 (d, J = 6.97 Hz, 2H), 7.53 (d, J = 8.43 Hz, 2H), 7.72 (d, J = 8.43 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 11.4 (q), 14.0 (q), 14.5 (q), 22.9 (t), 23.0 (t), 38.4 (t), 38.5 (t), 41.7 (t), 123.9 (d), 125.0 (d), 125.1 (d), 125.3 (d), 126.9 (d), 127.4 (d), 128.4 (d), 128.7 (d), 131.7 (d), 132.8 (s), 134.3 (s), 134.4 (s), 134.4 (s), 135.0 (s), 135.8 (s), 136.5 (s), 137.0 (s), 137.3 (s), 138.3 (s), 139.7 (s), 166.9 (s). EI-MS (m/z): 497 (M+); HRMS calc for C31H31NOS2 497.1846, found 497.1843.

4-(5-Methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)-N-(2-(triethoxysilyl)ethyl)benzamide (3).

Compound 7 (100 mg, 0.22 mmol) was suspended in CH2Cl2 (5 ml) and the mixture was cooled to 0 °C. Subsequently N-methylmorpholine (30 μl, 0.22 mmol) was added and the compound dissolved. Then 2-chloro-4,6-dimethoxytriazine (46 mg, 0.22 mmol) was added. The reaction mixture was stirred for 2 h at 0 °C, and then another equivalent of N-methylmorpholine (30 μl, 0.22 mmol) was added followed by n-propylamine (43 μl, 0.44 mmol). Stirring was continued for 1 h at 0 °C, and subsequently overnight at room temperature. The reaction mixture was filtered and the solvent was removed in vacuo. After purification by flash column chromatography (1:1 EtOAc : n-heptane) a viscous oil was obtained (0.11 g, 75%). H NMR (400 MHz, CDCl3) δ 0.70 (m, 2H), 1.22 (m, 9H), 1.75 (m, 2H), 1.99 (s, 3H), 2.00 (s, 3H), 2.08 (m, 2H), 2.86 (m, 4H), 3.45 (m, 2H), 3.83 (m, 6H), 6.51 (br, 1H), 7.03 (s, 1H), 7.10 (s, 1H), 7.23 (m, 1H), 7.32 (m, J = 7.33, 7.79 Hz, 2H), 7.51 (m, 4H), 7.73 (d, J = 8.43 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 14.2 (q), 14.5 (q), 22.9 (t), 23.0 (t), 38.4 (t), 38.5 (t), 42.2 (t), 58.5 (t), 124.8 (d), 124.8 (d), 125.6 (d), 127.3 (s), 130.9 (d), 133.7 (s), 134.4 (s), 135.0 (s), 135.8 (s), 136.5 (s), 137.0 (s), 137.3 (s), 138.3 (s), 139.7 (s), 166.9 (s). EI-MS (m/z): 659 (M+); HRMS calc for C34H45NO4S2Si 659.2559, found 659.2566.

4-(4-(2-(5-Iodo-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)benzoic acid (11).

An oven-dried round-bottomed flask and condenser were placed under a nitrogen atmosphere and charged with 4-carboxylphenylboronic acid 10 (0.3 g, 1.8 mmol), compound 9 (1.85 g, 3.6 mmol), cesium carbonate (1.17 g, 3.6 mmol), and tetrakis(triphenylphosphine)palladium (60 mg, 51 μmol). The flask was evacuated and refilled with nitrogen three times, then toluene (150 ml) and methanol (150 ml) were added and the reaction mixture was heated at reflux for 18 h. When the reaction was completed, inorganic solids were removed by filtration through Celite and followed by washing with several portions of dichloromethane, and the solvent was removed by evaporation. The residue was subjected to chromatography on silica gel (ethyl acetate/n-heptane, 1:9) yielding product 11 as amorphous solid. (0.48 g, 52%). H-NMR (400 MHz, CDCl3) δ 1.94 (s, 3H), 2.00 (s, 3H), 2.09 (m, 2H), 2.84 (m, 4H), 6.96 (s, 1H), 7.13 (s, 1H), 7.56 (d, J = 8.43 Hz, 2H), 8.08 (d, J = 8.43 Hz, 2H); 13C-NMR (100 MHz, CDCl3) δ 14.2 (q), 14.5 (q), 22.9 (t), 23.0 (t), 38.4 (t), 68.3 (s) 124.8 (d), 124.8 (d), 125.6 (d), 127.3 (s), 130.9 (d), 133.7 (s),
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134.8 (s), 136.6 (s), 136.8 (s), 137.5 (d), 137.6 (s), 138.3 (s), 139.4 (s), 140.6 (s), 172.0 (s).
EI-MS (m/z): 506 (M+); HRMS (m/z), 505.9852, calcd 505.9871

4-(2-(4-(4-(2-(5-Iodo-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)benzoyl)piperazin-1-yl)-2-oxoethyl)-6,7-dimethoxy-2H-chromen-2-one (13)

Compound 11 (0.5 g, 1 mmol) was suspended in CH2Cl2 (20 ml) and placed in an ice bath. Subsequently N-methylmorpholine (0.10 ml, 1 mmol) was added and the solid material dissolved. Then 2-chloro-4,6-dimethoxytriazine (0.173 g, 1 mmol) was added. The reaction mixture was stirred for 2 h at 0 °C, and another equivalent of N-methylmorpholine (0.1 ml, 1 mmol) was added followed by compound 12 (0.328 g, 1 mmol). Stirring was continued for 1 h at 0 °C, and subsequently overnight at room temperature. CH2Cl2 (50 ml) was added and the solution was washed with, respectively, 1 M aq. HCl (2x30 ml), brine (1x30 ml), saturated aqueous sodium bicarbonate solution (1x30 ml) and H2O (1x20 ml). The organic phase was dried (Na2SO4), and the solvent was removed by evaporation. After purification by column chromatography (CH2Cl2/MeOH = 100:2) compound 13 was obtained as a solid (0.60 g, 74% yield). m.p. = 105-109 °C. 1H-NMR (400 MHz, CDCl3) δ 1.90 (s, 3H), 1.97 (s, 3H), 2.04 (m, 2H), 2.8 (m, 4H), 3.6 (br, 8H), 3.85 (s, 2H), 3.90 (s, 3H), 3.93 (s, 3H), 6.16 (s, 1H), 6.83 (s, 1H), 6.91 (s, 1H), 7.00 (s, 1H), 7.06 (s, 1H), 7.37 (dd, J = 8.06, 4.4 Hz, 2H), 7.50 (dd, J = 8.06, 2.94 Hz, 2H); 13C-NMR (100 MHz, CDCl3) δ 14.1 (q), 14.4 (q), 22.8 (t), 38.3 (t), 56.3 (q), 56.7 (q), 68.1 (s), 81.0 (d), 102.3 (d), 112.9 (d), 124.8 (d), 125.2 (d), 127.9 (d), 132.8 (s), 133.6 (s), 134.9 (s), 135.7 (s), 136.3 (s), 136.6 (s), 137.5 (d), 137.6 (s), 138.3 (s), 140.5 (s), 146.3 (s), 149.1 (s), 149.7 (s), 151.3 (s), 160.8 (s), 166.7 (s), 170.3 (s). MS (Maldi-tof) 842.1 (M+Na) C39H37IN2O6S2 calcd. C 57.07; H 4.54; N 3.41; S 7.81 found C 57.30; H 4.79; N 3.35; S 7.43

4-(4-(4-(2-(5-(4-(4-(2-(6,7-Dimethoxy-2-oxo-2H-chromen-4-yl)acetyl)piperazine-1-carbonyl)phenyl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)benzoic acid (14)

An oven-dried round-bottomed flask and condenser were placed under a nitrogen atmosphere and charged with 4-carboxylphenylboronic acid 10 (95 mg, 0.57 mmol), compound 13 (0.315 g, 0.38 mmol), cesium carbonate (0.37 g, 1.14 mmol), and tetrakis(triphenylphosphine)palladium (20 mg, 17 μmol). The flask was evacuated and refilled with nitrogen three times, and subsequently toluene (50 ml) and methanol (50 ml) were added and the reaction mixture was heated at reflux for 18 h. When the reaction was complete, the inorganic solids were removed by filtration through Celite, followed by washing with several portions of dichloromethane and the solvent was removed by evaporation. The residue was subjected to chromatography on silica gel (CH2Cl2/MeOH = 20:4) to yield product 14 (0.12 g, 38 %), m.p. = 121-125 °C. 1H-NMR (400 MHz, CDCl3) δ 2.00 (m, 8H), 2.87 (s, 4H), 3.51 (s, 4H), 3.64 (s, 4H), 3.83 (s, 2H), 3.84 (s, 3H), 3.87 (s, 3H), 6.14 (s, 1H), 6.82 (s, 1H), 7.09 (m, 3H), 7.33 (d, 2H, J = 6.6 Hz), 7.49 (m, 4H), 7.94 (s, 2H); 13C-NMR (100 MHz, CDCl3) δ 14.6 (q), 14.6 (q), 23.4 (t), 38.6 (t), 56.6 (q), 56.7 (q), 100.5 (d), 106.1 (d), 111.8 (s), 113.1 (d), 125.0 (d), 125.4 (d), 125.5, (d), 128.3 (d), 130.9 (d), 133.6 (s), 135.2 (s), 135.4 (s), 136.1 (s), 136.5 (s), 137.4 (s), 138.5 (s), 146.7 (s), 149.9 (s), 153.6 (s), 161.3 (s), 167.2 (s), 170.4 (s); MS (Maldi-tof) for C46H42N2O8S2 (M+Na) = 837.1
Compound 14 (40 mg, 0.049 mmol) was suspended in CH₂Cl₂ (5 ml) and the mixture was placed in an ice bath. Subsequently, N-methylmorpholine (5 μl, 0.049 mmol) was added and the solids dissolved. Then 2-chloro-4,6-dimethoxytriazine (10 mg, 0.049 mmol) was added. The reaction mixture was stirred for 2 h at 0 °C, and another equivalent of N-methylmorpholine (5 μl, 0.049 mmol) was added followed by 3-aminotriethoxypropylamine (22 μl, 0.098 mmol). Stirring was continued for 1 h at 0 °C and subsequently overnight at room temperature. CH₂Cl₂ (10 ml) was added and the solution was washed with, respectively, 1 M aq. HCl (2x10 ml), brine (1x10 ml), saturated aqueous sodium bicarbonate solution (1x10 ml) and H₂O (1x10 ml). The organic phase was dried (Na₂SO₄), and the solvent was removed by evaporation. After purification by column chromatography on silica gel (CH₂Cl₂/MeOH = 100:2) product 4 was obtained as viscous oil (25 mg, 50%).

1H-NMR (400 MHz, CDCl₃) δ 0.65 (m, 2H), 1.21 (t, J= 5.8, 6.9 Hz, 9H), 1.75 (m, 2H), 2.00 (s, 3H), 2.02 (s, 3H), 2.1 (m, 2H), 2.82 (m, 4H), 3.45 (m, 2H), 3.55 (s, 4H), 3.83 (m, 8H), 3.91 (s, 3H), 3.94 (s, 3H), 6.16 (s, 1H), 6.65 (s, 1H, N-H), 6.85 (s, 1H), 7.07 (m, 3H), 7.36 (d, J = 8.06 Hz, 2H), 7.51 (d, J = 7.70 Hz, 4H), 7.73 (d, J = 7.70 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 7.8 (t), 14.5 (q), 14.5 (q), 18.3 (q), 22.9 (t), 23.0 (t), 38.4 (t), 42.2 (t), 56.4 (q), 56.5 (q), 58.5 (t), 100.2 (d), 105.4 (d), 111.3 (s), 112.9 (d), 125.0 (d), 125.0 (d), 125.2 (d), 127.9 (d), 129.0 (d), 132.8 (s), 132.9 (s), 134.7 (s), 134.8 (s), 135.7 (s), 136.4 (s), 136.8 (s), 136.9 (s), 137.1 (s), 138.3 (s), 138.5 (s), 146.3 (s), 149.1 (s), 149.7 (s), 153.1 (s), 160.9 (s), 166.7 (s), 166.8 (s), 170.3 (s); MS (Maldi-tof) for C₅₅H₆₃N₃O₁₀S₂Si (M+Na) = 1040.4

3.13 References


Photo- and Electrochemical Properties of SAMs of Diarylenes on Semiconductive Surfaces

Chapter 3


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