Dual photo- and redox- active molecular switches for smart surfaces
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Although bistability of molecular switches in solution is well established, achieving highly robust bistable molecular switching in self-assembled monolayers remains a challenge. Such systems are highly attractive as components in organic electronics and molecular based photo and electrochromic devices. In this chapter we report a remarkably robust surface confined bisthiaxanthylidene redox switch that shows excellent bistability, manifested in reversible changes in spectroscopic and electrochemical properties and in physical properties such as water contact angle changes (ca. 30° difference in water contact angle between the two redox states of a bisthiaxanthylidene self-assembled monolayer). The effect of surface immobilization of the overcrowded alkene bis-thiaxanthylidene on its photochromic, thermal and electrochemical properties is described. Surface immobilization is achieved by incorporating thiol- and alkylsiloxy-terminated “legs” on one of the tricyclic aromatic units. The molecular switch in its neutral and dicationic state, generated by bulk electrolysis, was characterized in solution, in the solid state and on surfaces by UV/Vis absorption, Fourier transform infrared, X-ray photoelectron and Raman spectroscopies and by cyclic voltammetry. In solution the redox switching to the dicationic state is achieved by oxidation at 1.2 V vs. SCE. Reduction of the dication at < 0.4 V results in initial formation of a highly unstable twisted conformation that reverts via a syn-folded conformational state to the most stable (anti-folded) conformer. Although the syn-folded state can be obtained by UV irradiation at < 0 °C, the twisted conformation is not observed in solution even at 200 K. Remarkably, in monolayers on electrodes this highly unstable form (which is generated by reduction of the dicationic state) is relatively stable even for several minutes. This stability is ascribed to the formation of densely packed monolayers in which the intermolecular interactions provide for a substantial barrier to thermal inter-conversion between the various conformational states.

The results presented in this chapter were published in:
3.1 Introduction

Bringing molecular bistability from solution to surfaces is without doubt one of the most exciting challenges in molecular switching currently, not least because of the potential to control surface properties with external stimuli such as light and redox reactions [1,2,3]. Such ‘smart’ surfaces, i.e. surfaces that are stimuli responsive, hold considerable potential application in areas as diverse as organic electronics [4,5,6], magnetic memory [7] and logic [8], bio-compatibility and cell culture on surfaces [9,10]. Achieving robust bistability, under repeated operation, either photo- or electrochemically, is essential for real applications and ideally a large hysteresis in the switching and thermal bistability is preferable, as is key to magnetic memory systems for example in the light induced spin cross-over systems [11]. In this regard the structurally simple overcrowded alkene bisthiaxanthylidene is an excellent candidate for redox control of surface properties due to its fascinating photo, thermal and redox driven switching behaviour [12].

The photochemical, thermal and electrochemical properties and the dynamic stereochemistry [13,14,15,16,17,18] of overcrowded alkenes [19,20,21,22,23,24,25] have captured the imagination of chemists for over 100 years [26]. Over the last decades this class of functional compounds has seen application in the development of functional molecular materials, molecular switches and devices. Most notable are the bistricyclic aromatic enylidenes (BAE) [27,28,29] and phenanthrylidenes [30,31,32,33], which were the basis for unidirectional light-driven molecular motors [31,33].

The thermal and photochemical properties of BAEs are highly sensitive to variations in molecular structure [34,35,36]. Indeed, even structurally simple BAEs show complex thermo-, photo- and electrochromic behaviour such as the bisthiaxanthylidenes 1, for which we reported recently the unprecedented three-state-switching of luminescence between blue, red and non-fluorescent states using a combination of electrochemical, photochemical and thermal stimuli (Figure 3.1) [12].

![Figure 3.1](image.png)

Figure 3.1 The interconversion between the three conformers of 1 (1A-1C) and the oxidized state 12+ is driven by a combination of light, heat and electrochemical oxidation/reduction (only trans isomers are shown for clarity) (left). Upon oxidation and reduction the change in conformation results in a 0.85 V hysteresis in the cyclic voltammogram (right, thin-layer CV, scan rate 0.1 V s⁻¹, glassy carbon electrode, initial potential is 0.0 V). The changes in molecular structure that accompany each redox process are shown schematically. Taken from [12]. Copyrights ACS 2006.
The overcrowded alkene dimethyl-bisthiaxanthylidene (1) can adopt any of three distinct conformational states – anti-folded (1A), syn-folded (1B) and twisted (1C); with the anti-folded (1A) conformation being the most thermodynamically favorable and the only conformation observed at 293 K in solution. Previously we have demonstrated that switching between the various conformational states can be achieved by the interplay of external stimuli, i.e. applied potential (electrochemical switching), temperature (thermal switching) and light (photochromic switching), Figure 3.1 [12]. The metastable syn-folded conformer (1B) can be obtained from 1A either by UV irradiation or an electrochemical oxidation/reduction cycle at temperatures below 0 °C [12]. The twisted conformer (1C) is too unstable for a significant population to be maintained even at 200 K in solution. The bisthiaxanthylum dication (1^{2+}), which is obtained from 1A by a two-electron oxidation, can be isolated from bulk electrolysis experiments as a stable red solid and has been characterized by single crystal X-ray structural analysis [12]. The structure of 1^{2+} is analogous to 1C with the upper and lower tricyclic groups orientated orthogonally with respect to each other (Figure 3.1).

Such a wide range of functionality, and excellent redox and photochemical robustness, in a single molecular species is a rather unique and highly attractive feature with regard to the preparation of responsive molecularly modified surfaces. This raises an important question: Can the switching properties in solution be reproduced when immobilized on a surface and does surface immobilization influence stability of less stable conformers and the rates of the transformations between the various states?

The importance of intermolecular interactions upon surface confinement was highlighted in a related BAE system reported recently by our group for a related blue fluorescent BEA in which the upper half contained a sulfur atom and the lower half a methylene unit [37]. In that case the compound underwent a 6-π electron pericyclic ring closing reaction followed by rapid irreversible dehydrogenation in the presence of molecular oxygen to form a photostable green fluorescent compound [38]. Immobilization of this irreversibly switchable blue fluorescent BEA on quartz and ITO surfaces however lead to the isomerization being inhibited by intermolecular energy transfer quenching. Such quenching was not observed in solution. In this case, the effect of immobilization of the photochrome as a monolayer on a surface was to change the kinetic competitiveness of the various excited state deactivation pathways compared with those observed in solution [12].
Figure 3.2 Structures of compounds used in this study (a) model compound 2 used to compare properties in solution with those observed on surfaces, (b) compounds 3 and (c) 4 used to form self-assembled monolayers on gold and monolayers on ITO and quartz, respectively.

For the overcrowded alkenes described here, such as 2-4A (see Figure 3.2), the large structural changes that accompany both photochemical and redox switching could give rise to cooperative or inhibitory effects at high packing densities when immobilized on surfaces as monolayers. Furthermore the proximity of molecules in a monolayer can profoundly influence the kinetics of inter- and intra-molecular reactions including rates of disproportionation [39] and energy transfer quenching [37]. Because of the large structural changes involved upon electrochemical switching, it can be expected [40] that in the closely packed environment of a Self-Assembled Monolayer (SAM), intermolecular interactions will modify the conformational properties of the compound and allow for the observation of highly conformational unstable species such as the twisted isomer 1C (Figure 3.1).

In the present chapter the effect of immobilization of analogues of 1, based on the BAE core and two ‘legs’ for surface attachment is investigated on a range of surfaces, with regard to changes in electrochemical, thermal and photochemical behaviour. Modification of the overcrowded alkene with thiol- or alkylsiloxy-terminated aliphatic ‘legs’ enables immobilization of the overcrowded alkenes 3 and 4 on gold, quartz and ITO surfaces (Figure 3.2), a strategy employed recently for a range of related overcrowded alkenes, especially the light driven molecular rotary motors [41]. The goal is to understand how packing in a SAM can be used to tune molecular properties beyond what is achievable with modifications in molecular structure. This aspect could open up new opportunities in the application of organic materials in organic electronics by generating functions and complex responses of surfaces to external stimuli.
3.2 Results and discussion

**Photochromism and redox switching in solution and solid state**

The synthesis and characterization of compounds 2-4 is reported elsewhere [42].

The similarity of $^1$H NMR [42], FTIR and Raman spectra of compounds 2-3 (Figure 3.3) confirm that the peripheral nature of the difference between the two compounds has little, if any, effect on the structure of the BAE unit. $2^{2+}$ was prepared by electrochemical oxidation and isolated as described for $1^{2+}$ earlier (for preparation and $^1$H NMR of $2^{2+}$ see section 3.4).

![Figure 3.3](image)

Figure 3.3 (a) FTIR and (b) Raman ($\lambda_{exc} = 785$nm) spectra of 2A and 3A at 298 K.

The approach taken to immobilize the bisthiaxanthylidene (1) on electrode surfaces, *i.e.* by attaching alkoxy ‘legs’ to one half of the molecule, requires that a more appropriate model (*i.e.* compound 2) is employed to determine the solution properties being used as a reference point for determining the effect of immobilization in monolayers. As was observed for 1, irradiation at 365 nm at 273 K results in a decrease in absorption at 350 nm and an increase at 253 nm, corresponding to conversion from the *anti*-folded (2A) to the *syn*-folded (2B) conformational state (Figure 3.4). Warming to room temperature results in recovery of the original spectrum (2A). Conversion from 2A to 2B in the solid state (*i.e.* as thin films deposited on an ATR crystal) was confirmed by FTIR spectroscopy (Figure 3.4). Irradiation of 2A at 365 nm results in a decrease in the intensity of the ring breathing mode at the 1567 cm$^{-1}$, and a blue shift of the mode at 1457 cm$^{-1}$. The initial spectrum recovered after several minutes. Overall changes to the FTIR spectrum upon irradiation are minor, as expected considering that only a change in conformation and not bonding is occurring. Nevertheless, the changes observed demonstrate the possibility of photoswitching between 2A and 2B in the solid state.
Figure 3.4 (left) Conversion of 2A to 2B by irradiation at 365 nm at 273 K followed by the thermal recovery over 10 min monitored by UV/Vis absorption spectroscopy measured in solution at 273 K and (right) FTIR spectrum of 2A in the solid state at 293 K before and after irradiation at 365 nm; the difference spectrum (red line) is shown off-set.

In Figure 3.5 (left), the cyclic voltammogram shows that initially only 2A is present in solution, i.e. scanning initially from 0.7 V in a negative direction confirms the absence of 2\(^{2+}\) which has a reduction potential of 0.36 V. On the return cycle towards positive potentials an irreversible oxidation is observed at 1.21 V (vs. SCE), which on the subsequent scan towards negative potentials is accompanied by an irreversible reduction wave at 0.36 V. The redox behaviour was found to be independent of the solvent/electrolyte combination employed and is essentially the same as that observed for 1A (Figure 3.1).

Figure 3.5 Cyclic voltammetry of 2A (left) and 2\(^{2+}\)(PF\(_6\))\(_2\) in CH\(_2\)Cl\(_2\) (0.1 M TBAPF\(_6\)) (right). (inset: current vs. sqrt(scan rate)).
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Figure 3.6 UV/Vis spectroelectrochemistry during (a) oxidation from 2A to 2^2+ at 1.2 V vs. SCE and (b) reduction from 2^2+ to 2A at -0.3 V vs. SCE.

UV/Vis absorption spectroelectrochemistry (Figure 3.6) shows the formation of 2^2+ upon oxidation at 1.2 V and the full recovery of the initial spectrum of 2A upon reduction at 0.0 V. In contrast to the methyl-substituted overcrowded alkene 1, for 2 the UV/Vis absorption spectrum of the dication is red shifted and shows more clearly that the lowest energy absorption is a superposition of several distinct absorption bands. This is expected considering that the upper and lower halves are non-equivalent due to the alkoxy substituent in the lower half of the molecule. 2A can be converted to the dicationic state (2^2+) by preparative (bulk) electrolysis (and isolated as a PF_6^- salt, see ^1H NMR in Figure 3.19). The cyclic voltammetry of 2^2+ is in agreement with that of 2A with the reduction of 2^2+ being observed at _ca._ 0.3 V and the current scaling with the square root of the scan rate (Figure 3.5). In contrast to the photochemical conversion of the anti-folded 2A to the syn-folded 2B, the oxidation of 2A to 2^2+ results in large changes in the FTIR (Figure 3.7a) and XPS spectra (Figure 3.7b) as well as in the UV/Vis absorption spectrum. The changes in the FTIR spectrum are consistent with the large changes in structure that accompany oxidation. The S 2p region of the XPS spectrum of the film of 2 contains only one doublet component at 163.6 eV, as expected for neutral sulfur atoms [43]. However, for a film of 2^2+ the major S 2p component (70%) was at 165.1 eV and is assigned to the S^1+ oxidation state [43]. A minor component (ca. 15%) assignable to the neutral form, 2 (S2p_3/2 at 163.6 eV) is observed. The S 2p_3/2 peak of sulfur in a higher oxidation state was observed at 166.9 eV. Therefore, from the XPS measurements it is apparent that oxidation results in a considerable change (ca. 1.5 eV) in the binding energy of the sulfur 2p doublet, consistent with localization of the positive charge on the sulfur atoms, and relatively minor changes in the carbon region (not shown).
In summary, it can be concluded that, with respect to 1, the introduction of the two alkoxy-groups does not perturb the basic photo- and electrochemistry of the overcrowded alkene substantially.

**Surface functionalization by self-assembly of switchable molecules**

Surfaces modified with self-assembled monolayers of 3 were characterized by ellipsometry, contact angle measurements and XPS. The expected thickness of the SAM of 3, composed of molecules perpendicularly oriented to a gold surface, is 1.75 nm. A thickness of $1.6 \pm 0.05$ nm was determined by ellipsometry and from this it can be inferred that the molecules are tilted at $24^\circ \pm 3^\circ$ with respect to normal to the surface. Contact angle (CA) measurements with water gave values of $78^\circ \pm 3^\circ$ for 3-Au and $74^\circ \pm 3^\circ$ for 4-ITO, which when compared with bare Au ($83 \pm 3^\circ$) and ITO ($30 \pm 3^\circ$), are in agreement with the immobilization of 3 and 4 as monolayers on the respective surfaces.

Additional information on the composition of the monolayer and the bonding of the molecules to the surface was obtained by XPS. A survey scan shows the fingerprint of the expected elements (S, C, O, Au) only. From the attenuated intensity of the gold photoelectron emission peak, the thickness of the molecular film was estimated to be $1.4 \pm 0.1$ nm, which is in agreement with the data from ellipsometry and the theoretical length of the molecule. The spectra of the S $2p$ and C $1s$ core level regions are shown in Figure 3.8.
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Figure 3.8 X-ray photoemission spectra of the S 2p (a) and C 1s (b) core level regions of 3-Au. Data and fits are shown (for details see text). Inset: binding energies of the components, their full width at half maximum (FWHM) and relative contribution.

The sulfur 2p spectrum contains two contributions, one at a binding energy of 161.9 eV of the 2p3/2 level, corresponding to the S-Au bond, and another at 163.6 eV assigned to the sulfur bound to the carbon of the bisthiaxanthylidene part of the molecule [44,45,46,47]. The intensity ratio between these components S\textsubscript{S-Au}/S\textsubscript{S-C} – 33/67% is in agreement with the expected attenuation of the S-Au component in a well packed monolayer and implies formation of a monolayer only. Peaks at higher binding energy corresponding to oxidized species were not observed, as expected for a densely packed SAM of 3A [44].

The overcrowded alkene (3-Au, Figure 3.1) consists of seven chemically non-equivalent carbon atoms. The closely spaced peaks originating from C-O and C-S bonds cannot be distinguished in the spectra; the same holds for aromatic and aliphatic carbon contributions. As a result, the peak at BE 284.4 eV is attributed to the aliphatic and aromatic parts (24 atoms) of the molecule accounting for 67% of the C 1s signal [48]. The component at 285.8 eV corresponds to the twelve C-O, C-S bonds, which makes up 27.3% of the carbon signal. The two carbonyl carbon atoms produce a peak at 288.5 eV and contribute 5.4% to the total C 1s signal. The satellite peak at 291 eV is assigned to π-π* shake-up of the aromatic parts of the molecule [49].

The carbon stoichiometry of the molecule gives a theoretical ratio between the intensities of the three spectral components as 24:12:2; experimentally a ratio 24.8:10:2 was found. The slightly lower contribution of the second component (C-O, C-S) can be rationalized by the attenuation of the two carbons bound to sulfur at the bottom (leg) position of the molecule and the neighbouring carbon bonded to oxygen.

Taken together, ellipsometry, contact angle and XPS spectroscopy confirm self-assembly of the overcrowded alkene switch as a densely packed monolayer on Au surfaces, attached via the sulfur legs with an orientation tilted ca. 24° with respect to the surface normal.
Photochemistry of monolayers on gold and quartz

The UV/Vis absorption spectrum of a monolayer of 4 assembled on quartz was measured in order to determine whether the photo-induced switching observed for 2 in solution (Figure 3.4a) was retained when immobilized on a solid surface. The UV/Vis absorption spectrum of 4-quartz shows absorption bands at ca. 230 nm, 300 nm and 350 nm in agreement with the spectrum of 2A. Irradiation of the modified quartz slide (4-quartz) at 365 nm for 30 min resulted in changes consistent with formation of the unstable syn-folded form 4B. The conversion is manifested in a decrease in absorbance at ca. 240 and 350 nm, and an increase in absorbance at 260 nm (Figure 3.9), in agreement with the changes observed in the UV/Vis absorption spectrum of 2 in solution (Figure 3.4a).

Due to the absorption of gold below 400 nm, monitoring of photochemical switching of a SAM of 3 on gold by UV/Vis absorption spectroscopy is not feasible. However, formation of the unstable syn-folded form 3B from 3A by irradiation with UV light should lead to a decrease in intensity of the oxidation wave at 1.2 V and the appearance of a new broader oxidation wave at ca. 1.1 V as observed for 2A, and previously for 1A [12], in solution. Irradiation of SAMs of 3A on both gold slide and gold bead electrodes for 60 min at 365 nm, however, did not result in any change to the cyclic voltammetry (Figure 3.9, right). This result demonstrates that the SAM is stable even under prolonged UV irradiation.

Figure 3.9 Left: UV/Vis spectrum of 4-quartz: initial (solid line) and after irradiation at 365 nm (dashed line). A difference spectrum is shown in the bottom part of the graph (dotted line). Arrows indicate changes upon irradiation. Right: Cyclic voltammetry (0.1 V s⁻¹) in CH₂Cl₂ (0.1 M TBAPF₆) of a SAM of 3 on gold (on mica) after irradiation at 365 nm for 1 h (only first cycle is shown).


**Cyclic voltammetry of monolayers on gold and ITO**

SAMs of 3 and monolayers of 4 on electrode surfaces allow for electrochemically induced transformation of the switch to be induced and studied by cyclic voltammetry, in addition to the determination of surface coverage (Γ) [50,51,52,53]. The electrochemically determined surface coverage of 3 on an Au electrode was found to be 1.5 x 10^{-10} mol cm^{-2}. The value obtained is consistent with monolayer formation, and found to be independent of the concentration of the compound (in the range 10^{-4}-10^{-7} M) in the solution from which self-assembly took place [54]. In contrast for 4-ITO, the concentration of 4 in solution plays an important role in monolayer formation (Γ; 10^{-11} - 10^{-12} mol cm^{-2}), as a result of the kinetics of chemisorption and the irreversibility of the process. The monolayers formed on gold (Γ = 10^{-10} mol cm^{-2}) are, in general, more dense than on ITO (Γ = 10^{-11} mol cm^{-2}).

The redox behaviour of both 3 and 4, when immobilized on a gold bead and on an ITO electrode, respectively, is shown in Figure 3.10. Even at low scan rates the cyclic voltammogram is stable over multiple cycles, indicating that oxidation to the dicationic state and the resulting increase in Coulombic repulsion between molecules in the SAM is not sufficient to force desorption. The irreversible oxidation wave observed at 1.2 V in the first positive scan corresponds to the oxidation of the anti-folded form (3A, 4A) to the dicationic state (3^{2+}, 4^{2+}), as observed for 2A in solution (vide supra). On the return sweep towards negative potentials, a reduction wave is observed at 0.36 V, corresponding to the two electron reduction of the dicationic form, again as observed for 2A and 2^{2+} in solution. The relative intensity of each redox wave is independent of scan rate and shows the expected linear dependence of current on scan rate for a SAM (Figure 3.11). Remarkably on subsequent cycles the electrochemical behaviour of 3 (and 4) on surfaces shows profound differences to that of 2 in solution.

![Cyclic voltammogram of 3-Au (a) and 4-ITO (b) in CH2Cl2 (0.1 M TBAPF6) at 0.1 V s^{-1}.](image)

**Figure 3.10** Cyclic voltammogram of 3-Au (a) and 4-ITO (b) in CH2Cl2 (0.1 M TBAPF6) at 0.1 V s^{-1}.
Figure 3.11 Scan-rate dependence of the cyclic voltammetry of the SAM 3-Au, (a) first cycle at each scan rate shown only, and (b) second cycle at each scan rate. Scan rate varied from 0.1 to 5 V s\(^{-1}\), 0.1 M TBAPF\(_6\) in CH\(_2\)Cl\(_2\). After each cycle the bead was allowed to rest in electrolyte for 10 min.

Figure 3.12 Cyclic voltammogram of a SAM of 3A on a Au bead in (a) CH\(_3\)CN (0.1 M TBAPF\(_6\)), (b) CH\(_2\)Cl\(_2\) (0.1 M TBAPF\(_6\)) and (c) CH\(_3\)CN (0.1 M LiClO\(_4\)) (I\(_f\) = 1*10\(^{-10}\) mol cm\(^{-2}\)).

In solution for both 1 and 2, the reduction of the dication (e.g., 2\(^{2+}\)) is irreversible at room temperature with thermal reversion of the product - 2C (the twisted conformational state; see Figure 3.1), to 2A being much faster than the electrochemical timescale (Figure 3.1). In contrast for both 3-Au and 4-ITO the reversibility of the reduction of the dication to the neutral C form (Figure 3.11b, see twisted state, Figure 3.1, also) is substantial, as seen from the oxidation wave at ca. 0.4 V on the second cycle. It is possible that the increased reversibility of the reduction of the dication on surfaces is related to ion pairing effects; however, essentially the same behaviour is observed (for the same SAM-coated bead electrode) in dichloromethane and in acetonitrile with several electrolytes (see Figure 3.12). In the case of the 3-Au SAMs and 4-ITO monolayers, restoration of the anti-folded isomer is a thermally activated process and takes several minutes to achieve after one oxidation and reduction cycle of the SAM (Figure 3.13) in contrast to that observed in solution, where the thermal reversion is essentially instantaneous.
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Figure 3.13 Recovery of the twisted neutral state 3C generated by reduction of 32+. The initial cycle, shown in blue, oxidizes 3A to form 32+, which is reduced on the return cycle. The potential was then held at 0.0 V for two (left) and three (right) min before a second cycle commenced (red). As follows from oxidation at 1.2 V, the recovery of the anti-folded 3A is found to be incomplete with ca. 50% of the twisted form 3C still present. (left: 3-Au bead working electrode, right: 3-Au/mica working electrode, scan rate 0.1 V s⁻¹, in CH₂Cl₂ with 0.1 M TBAPF₆).

The electrochemical behaviour of 3-Au and of 4-ITO are essentially the same, despite the difference in surface density and chemical nature of the surface attachment. Hence the discussion focuses on 3-Au but is applicable to both systems. The separation (ca. 0.85 V) between the oxidation and reduction waves reported previously for 1, and in the present study for 2, in solution is observed for 4-ITO and 3-Au also.

The temperature dependence of the cyclic voltammetry of a 3-Au SAM is shown in Figure 3.14. At all temperatures the initial cycle shows oxidation of 3A to 32+ at 1.2 V, followed by reduction of 32+ at ca. 0.4 V. At 20 °C the redox wave associated with 3A on the second cycle is 15 % of the intensity observed on the initial scan. As the temperature is increased the recovery of 3A on the timescale of the experiment (ca. 20 s between reduction of 32+ at below 0.4 V and the reoxidation at 1.2 V) increases and at 60 °C the intensity in the second cycle reaches 90% that of the initial cycle. On returning the electrode to 0 °C, again 3A does not recover on the time scale of the cyclic voltammetry and the compound remains in the twisted and syn-folded states after reduction of 32+ Au.

Figure 3.14 Temperature dependence of the cyclic voltammetry of 3-Au. CVs at (a) 20 °C, (b) 30°C, (c) 50°C, (d) 60 °C, (e) 0°C. 0.1 M LiClO₄ in CH₂CN at 0.1 V s⁻¹.
Importantly, although at elevated temperatures some desorption of 3-Au occurs with repeated cycling, manifested in a decrease in charge of the reduction wave of $3^{2+}$-Au; this decrease is only moderate and allows for extensive repeated measurements on each SAM modified electrode. The percentage in Figure 3.14 (a-e) indicates the area of the oxidation wave (of 3A) on the second cycle with respect to the initial cycle.

**UV/Vis absorption and Surface enhanced Raman spectroelectrochemistry**

UV/Vis absorption spectroelectrochemistry was performed on SAMs of 3 on semitransparent Au slide electrodes (with a 20 nm thick layer of gold on glass). The absorption spectrum of 3-Au is characterized by a shoulder at ca. 300 nm ($\Gamma=1.1\times10^{-10} \text{ mol cm}^{-2}$) and a maximum at 330 nm (Figure 3.15a). Oxidation at 1.2 V leads to substantial changes in the absorption spectrum consistent with the formation of $3^{2+}$-Au. Intense absorption bands appear at 314 nm and 398 nm, and a decrease in absorption is observed at 337 nm. The original spectrum can be recovered completely by reduction at 0.36 V and the oxidation and reduction could be repeated for several cycles, indicating that the SAM is stable in both oxidation states with respect to desorption (Figure 3.15b). The cyclic voltammogram of 3-Au on a transparent gold slide is shown in Figure 3.15c.

![Figure 3.15](image-url) (a) UV/Vis spectrum of the monolayer of 3 on a surface of 20 nm thin Au film on glass electrode during spectroelectrochemical oxidation (1.2 V) and reduction (0.0 V). The difference between the spectra of the initial and oxidized state is shown with an offset of +0.03. (b) Potential dependence of the intensities of individual absorption bands over several oxidation/reduction cycles. (c) Cyclic voltammetry in acetonitrile (0.1 M TBAPF$_6$) of the SAM of 3 on gold (on glass) measured during spectroelectrochemistry (a), scan rate is 0.1 V s$^{-1}$. 

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**Figure 3.15** (a) UV/Vis spectrum of the monolayer of 3 on a surface of 20 nm thin Au film on glass electrode during spectroelectrochemical oxidation (1.2 V) and reduction (0.0 V). The difference between the spectra of the initial and oxidized state is shown with an offset of +0.03. (b) Potential dependence of the intensities of individual absorption bands over several oxidation/reduction cycles. (c) Cyclic voltammetry in acetonitrile (0.1 M TBAPF$_6$) of the SAM of 3 on gold (on glass) measured during spectroelectrochemistry (a), scan rate is 0.1 V s$^{-1}$. 

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**Chapter 3**

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**Figure 3.16** Surface enhanced Raman spectra of 3A-Au bead before and after oxidation and after subsequent reduction. A multipoint baseline correction has been applied to the spectra. The initial spectrum was recorded before applying a potential to the electrode. The spectrum oxidized was obtained after cycling the potential from 0 to 1.2 V and then to 0.6 V (vs. SCE), i.e. intermediate between the oxidation wave of 3A and the reduction wave of 3'. The reduced spectrum was obtained by continuing the cyclic voltammogram from 0.6 V to 0.0 V and holding the potential at 0.0 V.

Surface enhanced Raman spectroscopy (SERS) was employed to study the oxidation and reduction of 3A on roughened gold bead electrodes. The Raman spectra of solid samples of 2A and 3A are shown in Figure 3.3 and show strong modes at 1610, 1586, 1563 cm⁻¹ as expected for an aromatic system. The initial spectrum of the SAM of 3A on roughened gold bead electrodes (Figure 3.16, top) contains aromatic ring breathing modes at 1608, 1586 and 1562 cm⁻¹, consistent with the solid state spectrum of 3A. Upon oxidation at 1.2 V a large change in the SERS spectrum was observed with the appearance of four strong modes at 1557, 1453, 1388, 1328 cm⁻¹ (Figure 3.16, middle). Reduction again at 0.0 V resulted in a recovery of the initial spectrum (Figure 3.16, bottom).

**X-rays photoelectron spectroscopy and contact angles of oxidized SAMs**

The X-ray photoelectron spectroscopy (XPS) data of a SAM of 3A on a gold film (on mica) demonstrate a reversible change in the sulfur oxidation state upon electrochemical oxidation (Figure 3.17). Obtained pattern is consistent with that measured on a thin film of 2²⁺ (*vide supra*) with an additional component in the S 2p core level region due to the sulfur chemisorbed to the gold surface. As can be seen in Figure 3.17 (centre) the chemisorbed sulfur component (33%) remains unaffected by electrochemical oxidation, but the intensity of the bisthiaxanthylidene sulfur peak at 163.6 eV has decreased due to electrochemical
conversion to the dicationic state, which results in a peak shifted to 165.0 eV. Subsequent reduction of the electrochemically oxidized SAM results in a complete recovery of the original XPS spectrum of 3A-Au and a complete absence of signals from PF$_6^-$ as expected for the neutral state. In addition this indicates that the monolayer is stable in the oxidized state for at least several hours and under the vacuum conditions of the XPS instrument. The cyclic voltammogram of the 3A on gold coated mica slide used for XPS measurements is identical to that shown in Figure 3.18.

Electrochemical oxidation to the dicationic form 3$_2^+$-Au manifests itself in a change in the contact angle of water on the surface of the SAM on roughened Au (Figure 3.18). The oxidized SAM is less hydrophobic and the contact angle decreases to 53° from an initial value of 89° (78° and 46°, respectively, on SAM on Au/mica surfaces). This change is reversed upon reduction with the contact angle restored to 78°. The process was repeatable for several cycles.

The changes in contact angle are unlikely to be due to changes in molecular structure, i.e. anti-folded vs. orthogonal. It is more reasonable to ascribe the changes in contact angle to changes in polarity, especially when the differences in solubility between 2A and 2$_2^{2+}$(PF$_6$)$_2$ are considered. 2A is soluble in CH$_2$Cl$_2$ but only sparingly soluble in CH$_3$CN whilst 2$_2^{2+}$(PF$_6$)$_2$ is soluble in CH$_3$CN but only sparingly in CH$_2$Cl$_2$. Hence in the reduced state the surface should be more hydrophobic than in the oxidized state, which is observed (Figure 3.18).
High energy conformers in SAMs of a bistable electro- and photoswitchable overcrowded alkene

Figure 3.18 Change in contact angle of water on a SAM of 3 on roughened Au slide before (left image) and after electrochemical oxidation (centre image) and subsequent reduction (right image) in CH$_2$Cl$_2$ (0.1M TBAPF$_6$). The corresponding oxidation a) and reduction b) sweeps of the cyclic voltammogram are shown below the droplet images.

3.3 Conclusions

In this chapter the effect of immobilization of analogues of 2A on a range of surfaces was discussed. In particular we focused on the investigation of changes in electrochemical, thermal and photochemical behaviour when the molecules are anchored to surfaces. Modification of the overcrowded alkene with thiol- or alkylsiloxyl-terminated aliphatic ‘legs’ enabled the immobilization of the overcrowded alkenes (3A and 4A) on gold, quartz and ITO. The SAMs and monolayers formed were characterized by XPS, UV/Vis absorption and surface enhanced Raman spectroscopy as well as electrochemically. Overall the properties of 2A were found to be retained when immobilized on surfaces. However, whereas in solution intermolecular interactions are essentially absent, when immobilized on surfaces as SAMs, intermolecular interactions dominate the thermal and photochemical properties. With regard to photochemical activity a combination of rapid intermolecular excited state deactivation (as seen for related SAMs earlier) [37] and the tight packing within the monolayers serves to reduce the efficiency of the anti/syn- isomerization. The ability to access highly unstable states by electrochemical oxidation in the present system allows for the effect of packing on thermal relaxation to the lowest energy conformer (the anti-folded state) to be observed. Remarkably whereas in solution the twisted conformer, which lies 18 kcal mol$^{-1}$ above the anti-folded state [22], is not observable, it is stable for several minutes at room temperature after being formed by reduction of a SAM of 3$^{2+}$ on gold. The results described here underline the need to consider the increase in the contribution of intermolecular interactions in densely packed arrangements when designing functional surfaces based on SAMs of photo/electrochromic molecular systems, which undergo large structural changes in response to external stimuli, in particular
electrochemistry. The large hysteresis and volatile memory, i.e. the slow reversion of the highly unstable twisted conformation to the anti-folded conformation, opens new prospects in organic electronics and molecular memory systems.

### 3.4 Synthesis and characterization of dication $2^{2+}(\text{PF}_6)_2$

The dication of $2\text{A}$ was prepared by bulk oxidation in CH$_3$CN with 0.1 M KPF$_6$ and isolated as its PF$_6^-$ salt as described earlier for compound $1^{2+}$ [12].

### 3.5 Experimental details

Monolayers were prepared by self-assembly from a $10^{-4}$-10$^{-3}$ M solution of compounds in dichloromethane or ethanol. Freshly prepared gold surfaces were immersed in a solution overnight at room temperature in the dark. Quartz and ITO slides were functionalized with overcrowded alkene by heating at reflux in toluene overnight. After functionalization of the surface, the substrate was rinsed with ethanol and dichloromethane, thoroughly dried with an argon gas stream and introduced immediately into the measuring system.

Thin films XPS and Raman measurements were prepared by dropcasting on a gold substrate from CHCl$_3$ (or CH$_3$CN for oxidized $2^{2+}$ compounds).

ITO and quartz substrates were prepared by treatment as described earlier (see for example Markovich et al. [55]).

![Figure 3.19 1H NMR spectrum of $2^{2+}$ in CD$_3$CN.](image)

Figure 3.19 $^1$H NMR spectrum of $2^{2+}$ in CD$_3$CN.
3.6 Acknowledgments

Compounds 2 and 3 were synthesized by Dr. Anthony C. Coleman; the synthesis of compounds 1 and 4 and temperature dependent electrochemistry was conducted by Dr. Jetsuda Areephong. UV/Vis absorption and Surface enhanced Raman spectroelectrochemistry were carried out together with Dr. Hella Logtenberg. The oxidized compound $2^{2+}$ was prepared by Dr. Wesley R. Browne.

3.7 References

[38] Similar photocyclisation is observed for 1A only after prolonged irradiation.
[54] The SAMs formed result in the capacitance of the electrode changing from 20 µF cm⁻² for a non-modified Au electrode to 4 µF cm⁻² for 3-Au.