Chapter 5

Redox Switching of Di- and Tetra-Substituted Bisthiaxanthylidene Overcrowded Alkenes

In this chapter the electrochemical properties of di- and tetra-substituted bisthiaxanthylidenes are investigated using cyclic voltammetry. The effect of a variety of substituents and substitution patterns on the redox switching of these bisthiaxanthylidenes, which undergo geometric changes between anti-folded and dicationic orthogonal twisted states, is discussed. It is shown that this electrochemical induced geometric switching is a general and reliable feature for these type of compounds, although the effect of the substituents on the oxidation and reduction potentials is relatively small. It is anticipated that these robust molecular switches have great potential in the design of new electrochemical responsive systems.

Parts of this chapter have been published as:

5.1 Introduction

The design and integration of molecular switches and motors in hierarchical architectures, while retaining their stimuli-responsive characteristics, allowing for controlled macroscopic functionality, remains challenging. Overcrowded alkenes can function as both molecular switches and motors by undergoing geometric changes induced by light and have potential in responsive and dynamic switching systems such as soft materials. However, most of the integrated systems incorporating molecular motors are based on light responsive molecules and for instance assemblies or frameworks showing electrochemical induced rotation in “single” molecules are underexploited.

The molecules discussed in this chapter are bistricyclic aromatic enes (BAEs), a class of overcrowded alkenes, that have been studied extensively over the years. Especially their stereochemistry in combination with their photo-, electro-, and mechanochromic properties is fascinating. The origin of these properties lies in the non-planarity of the two halves of the BAE which are separated by a double bond. This non-planarity is induced by overcrowding in the fjord region and results in two deformation modes: twisting around the central double bond axis and folding of the tricyclic units. The geometric constraints associated with folding results in pyramidalization of the carbons constituting the double bond (the hybridization changes from pure sp² towards partly sp³ character). These deformations lead to the observation of four main geometries: anti-folded, syn-folded, twisted, and orthogonally twisted (Fig. 1a). BAEs are classified in homomerous (X = Y) and heteromerous (X ≠ Y) compounds and the nature of X and Y translates into the preferred geometry (Fig. 1b).

![Figure 1](image_url)

**Figure 1.** a) The four main geometries observed for BAEs, b) the general structure of a BAE, and c) the reversible switching of bisthiaxanthylidenes.
We have previously shown in our group that bisthiaxanthylidenes (an BAE where $X = Y = S$) can behave as three-state luminescent switches (Fig. 1b and 1c).\cite{21} Interconversion between multiple individually addressable states is possible by the interplay of multiple stimuli (photo- and electrochemical, and thermal steps). Here the electrochemical oxidation of a folded conformer leads to a dicationic orthogonally twisted conformer (with a single bond separating the individual thioxanthyl units), which was confirmed by X-ray crystallography. Due to this geometric change hysteresis is observed in the cyclic voltammogram and the reduction of the dicationic compound occurs at a peak potential $> 0.8$ V relative to the oxidation peak potential.

In this chapter we investigate the tolerance of the electrochemical switching of bisthiaxanthylidenes towards changing the substituents at the 2,2'-, 3,3'-, and the 4,4'-positions. We anticipate that in this way more insight into the molecular parameters affecting the electrochemical properties can be acquired, which could assist in the increased application of these molecules. Electron withdrawing substituents (-Br, also a functional handle) and electron donating substituents (-OCH$_3$, -CH$_3$) were examined. It is shown that these compounds are generally reliable and robust redox switches which provides possibilities for their application in responsive materials.

### 5.2 Results and discussion

Multiple substituted bisthiaxanthylidenes were synthesized following a new synthetic and fast procedure (Fig. 2). For a detailed discussion about the synthesis, characterization and chemical redox behavior the reader is referred to ref \cite{25} and \cite{26}. These compounds were obtained as $E/Z$ mixtures with ratios ranging from 50:50 to 72:28 and used as such in cyclic voltammetry (CV) experiments. A CV of 2 in dichloromethane (DCM) shows oxidation and reduction features typical of bisthiaxanthylidenes (Fig. 3).\cite{21} Initially the anti-folded 1 is oxidized in a two-electron step at $E_{p,a} = +1.28$ V (vs. SCE) to form a dicationic orthogonally twisted species. The dicationic compound is then reduced at $E_{p,c} = +0.38$ V. The observed hysteresis (0.90 V) is caused by the geometric change from the neutral anti-folded state to the dicationic orthogonally twisted state. A small oxidation wave appeared at $+0.47$ V during the subsequent sweep back to increasingly positive potentials, which is ascribed to the oxidation of a twisted species.\cite{27} The lack of chemical reversibility between the dicationic and twisted redox couple is the result of the relatively fast (within the time frame of the electrochemical experiment) thermal conversion of the twisted state towards the syn-folded- and succeeding anti-folded conformations. Similar CVs, with geometrical switching (hysteresis in the CV), were also observed for most of the other compounds with exception of compound 8 (\textit{vide infra}). Electrochemical induced geometrical switching has not only been observed for bisthiaxanthylidenes but is also reported for bianthrone.\cite{15} All oxidation and reduction peak potentials as well as the hysteresis for the library of compounds shown in figure 2 are reported in Table 1.
Figure 2. Scope of the bisthiaxanthylidienes of which the electrochemical properties were determined by cyclic voltammetry. Only the $E$ isomer is shown for clarity.

Figure 3. Cyclic voltammogram of compound 2 in DCM (0.1 M TBAPF$_6$) with a GC (WE), Pt wire (CE), and SCE (RE) at a scan rate of 10 mV s$^{-1}$. The abbreviations af and t stand for antifolded and twisted, respectively. Assignment of oxidation/reduction waves based on ref$^{[21]}$. 

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When comparing the linear conjugated to the cross conjugated (with respect to the central C=C double bond) compounds for each electron donating group (-Me, and -OMe) a significant effect on the redox potentials is not observed. Moreover, one would expect that substitutions with the –OMe group, compared to the –Me group, would lead to a higher electron density on the bisthiaxanthylidene and therefore a lower oxidation potential (as well as a lower reduction potential of the formed dicationic species), but the effect is minimal. The introduction of the –Br group at the 2,2’- and the 3,3’-positions (compounds 7 and 8) results in higher oxidation potentials due to the increased electron withdrawing nature of –Br as compared to both the –OMe and –Me groups rendering a more electron poor bisthiaxanthylidene motif. Compound 8 shows two small reduction waves (relative to the oxidation wave) and it is anticipated that after the first oxidation step the formed dicationic state undergoes a chemical reaction (EC mechanism) possibly due to the higher reactivity of the –Br substituent at the para position (relative to the central double bond) as compared to compound 7 (which has the –Br substituent at the meta position). By fourfold substitutions with –Me or –OMe groups at the 4,4’-position (compounds 9 and 10, respectively) we expected to see less positive redox potentials (compared to the twofold substituted compounds at the 4,4’-position) but the effects were minimal. Finally, adding phenyl substituents (compound 11) or extending the aromatic core (compound 12) again revealed similar CVs with geometrical switching deduced from the observed hysteresis.

<table>
<thead>
<tr>
<th></th>
<th>$E_{p,a}$ (V)</th>
<th>$E_{p,c}$ (V)</th>
<th>Hysteresis (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.22</td>
<td>0.34</td>
<td>0.88</td>
</tr>
<tr>
<td>2</td>
<td>1.28</td>
<td>0.38</td>
<td>0.90</td>
</tr>
<tr>
<td>3</td>
<td>1.28</td>
<td>0.38</td>
<td>0.90</td>
</tr>
<tr>
<td>4</td>
<td>1.17</td>
<td>0.33</td>
<td>0.84</td>
</tr>
<tr>
<td>5</td>
<td>1.15</td>
<td>0.25</td>
<td>0.90</td>
</tr>
<tr>
<td>6</td>
<td>1.24</td>
<td>0.40</td>
<td>0.84</td>
</tr>
<tr>
<td>7</td>
<td>1.40</td>
<td>0.56</td>
<td>0.84</td>
</tr>
<tr>
<td>8</td>
<td>1.39</td>
<td>0.47</td>
<td>0.92</td>
</tr>
<tr>
<td>9$^b$</td>
<td>1.25</td>
<td>0.34</td>
<td>0.89</td>
</tr>
<tr>
<td>10$^b$</td>
<td>1.16</td>
<td>0.31</td>
<td>0.85</td>
</tr>
<tr>
<td>11</td>
<td>1.26</td>
<td>0.45</td>
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</tr>
<tr>
<td>12</td>
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<td>0.46</td>
<td>0.83</td>
</tr>
</tbody>
</table>

$^a$ CVs of all compounds (1 mM) were measured in DCM with 0.1 M TBAPF$_6$ using a GC as WE, Pt coil as CE, and SCE as RE at room temperature under diffusion limited conditions at 10 mV s$^{-1}$. Electrochemical parameters were derived from the first full sweeping cycle. $^b$ Measured as saturated solution due to the limited solubility of 9 and 10. $^c$ The first reduction wave was selected.
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5.3 Conclusion

The library of bisthiaxanthylidenes discussed in this chapter shows that for these type of compounds the electrochemical geometrical switching between anti-folded and orthogonal twisted geometries is a general feature. Although the effect of the substituents on the oxidation and reduction potentials is relatively small, the electrochemical switching does tolerate a range of substitutions and substitution patterns. Since these type of bisthiaxanthylidenes are easily accessible, and can be considered robust functionalizable switches, it is expected that these compounds have a bright future in for example electrochromic responsive materials.

5.4 Acknowledgements

Brian P. Corbet is acknowledged for his contribution to the synthesis of the bisthiaxanthylidenes, the electrochemical characterization of a part of the bisthiaxanthylidenes library and for scientific discussions.

5.5 Experimental procedures

For compound synthesis and characterization see references\textsuperscript{[25][26]}

5.5.1 Diffusion limited cyclic voltammetry

Cyclic voltammograms were recorded using a three-electrode setup on a CHI600C electrochemical workstation (CH Instruments) or a VSP-300 Potentiostat/Galvanostat (Biologic Science Instruments) using a saturated calomel electrode (SCE) reference electrode, a glassy carbon (3 mm diameter) disc working electrode, and a platinum wire as counter electrode. All CVs were recorded with a scan speed of 0.010 V s\textsuperscript{-1} at room temperature with tetrabutylammonium hexafluorophosphate (TBAPF\textsubscript{6}) (0.1 M) as supporting electrolyte in DCM. The working electrode was polished with an aqueous aluminum oxide solution before every experiment. In our experimental setup, diffusion limited conditions were maintained, but could not be completely excluded.
5.5.2 Diffusion limited cyclic voltammograms
5.6 References


