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Chromism of spiopyrans

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Chapter 7

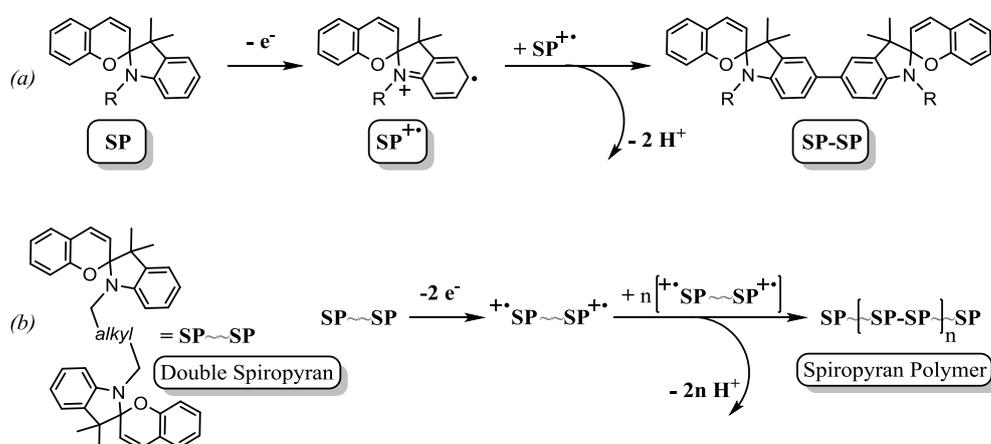
Redox-Chemistry of Bispiropyrans

Abstract Bispiropyrans discussed in chapter 6 are potential monomers for electropolymerization as described in chapter 4. Although the oxidative aryl-aryl coupling observed for spiropyrans would be expected to occur in the bispiropyrans, it is not observed due to ring opening of the spiropyran. The lack of electropolymerization is due to coupling through the phenol moiety, which results in intercomponent communication in the double photochrome and an increase in the thermal stability of the protonated open forms. Electrochemical oxidation is centered on indoline oxidation as for the other spiropyrans but appears as a reversible redox-process in bispiropyrans, consistent with a lack of oxidative C-C coupling between the indoline moieties. The competing process is shown to be related to the redox response of 4,4'-biphenol, indicating redox mediated ring-opening to the bimerocyanine form. At higher than conventional scan rates, i.e. 1 V s^{-1} , however, the coupling pathway is able to partially outcompete the quenching redox-chemistry of biphenol, yielding moderate polymerization in compound **1**. The non-polymerizable analogue, **2**, in which the para position of the indoline units is blocked from engaging in C-C coupling by a chloro substituent, provides insight into the observed spectral changes during oxidation. The results described in this chapter highlight how a delicate balance of processes (C-C coupling vs ring opening) dictates the observed behavior of a spiropyran.

Introduction

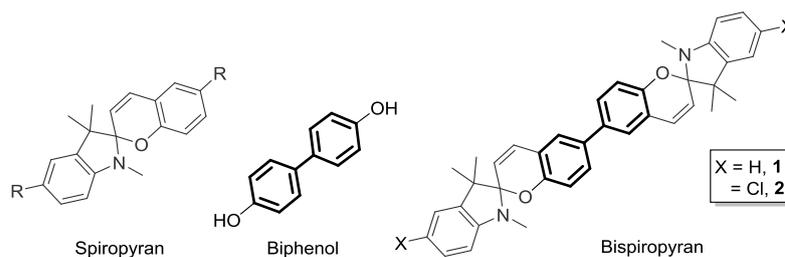
Reversible responsivity at the molecular (subnano) scale enables control over interactions between entities at that scale. Translation of changes at the molecular level to micro and macro dimensions requires cooperative or ensemble responses and/or interfacing with macroscale materials and systems.^{1,2} Stimuli such as light,³ pH (Chapter 5),⁴ electricity,⁵ and heat,^{6,7} can trigger reversible changes in molecular properties, e.g., dipole moments, proton release or uptake and color, and this functionality can be realized easily in solution.^{3,4} However, when interfaced with surfaces and macroscopically addressable materials these changes can be used to effect control at the macroscale. Incorporation of responsive functional units into polymerizable materials is an attractive approach to 'upscale' molecular responsivity and engineer so called smart materials.^{1,2,8} Incorporating molecular switches into the building block of the polymers themselves provides an added advantage of a predetermined structuring, and thereby a relatively uniform response from a material achieved without exceedingly specific conditions in a select few blended materials, where in general phase separation can create heterogeneously distributed domains.⁹⁻¹¹

One approach is to append molecular switches to the backbone of well-established polymerizable systems or to absorb them into the polymer matrix.^{12,13} The benefit to this approach is that with a sufficiently flexible alkyl spacer unit, the photochromic units are undisturbed by electronic intramolecular communication.^{14,15} This electronic interaction becomes more probable when the switching functionality is incorporated within the polymer backbone, resulting in cross-talk between the components which may affect adversely the properties of the individual components, but can also result in additional unexpected behaviour.¹⁶⁻¹⁸ Areephong *et al.*, for example, reported that a dithienylethene based double terthiophene exhibited cross-talk between the polymerizable and photoswitchable components resulting in electropolymerization proceeding only when the ring open form of the dithienylethene was used.¹⁹ The difference in reactivity of open and closed forms provided for photocontrol over its polymerization and hence photopatterning. In chapter 4 another of the well-established class of photochromes, the spiropyrans, are shown to undergo electrochemical sequential dimerization to form redox polymers by taking advantage of their propensity to undergo oxidative C-C bond formation at their indoline unit (Scheme 1).^{18,20}



Scheme 1. (a) Oxidative (electrochemical) indoline-indoline coupling of spiropyrans as first described by Ivashenko *et al.*²⁰ and (b) the approach to polymerizable double spiropyrans coupled by a diester alkyl spacer through the modular N-alkyl sidechain described in chapter 4.¹⁸

In Chapter 6 an alternative approach to tethering two spiropyrans together, i.e., through their chromene unit, yields novel photochemical properties. In this chapter, the propensity to undergo electropolymerization analogous to the approach described in chapter 4 is investigated,¹⁸ as the point of tethering should not impede, sterically, oxidative dimerization of the indoline units.²⁰ Interestingly, this approach shifts the balance in reactivity between C-C coupling and ring-opening to the bimerocyanine. When, however, cyclic voltammetry is performed at scan rates above 1 V s^{-1} , the oxidation of the indoline seems to occur in tandem with the alternative biphenol oxidation process, yielding partly the response which resembles that of the previously observed electropolymerization of double spiropyrans.¹⁸



Scheme 2. Structure of spiropyran, 4,4'-biphenol and, with a fused motif of the latter two, the bispiropyrans (X = H and X = Cl) studied in this chapter.

Double spiropyrans linked through an N-alkyl spacer (**Scheme 1**) show cyclic voltammetry, as with all unmodified spiropyrans (at least in their indoline unit), irreversible in nature.¹⁸ Concomitantly, as shown in earlier work, compound **2** was expected to preclude electrochemical coupling altogether as the position at which the dimerization occurs is blocked by chloro-substituents.²⁰ Remarkably, compound **1**, though sterically unhindered in its indoline fragment, also exhibits chemical reversibility (**Figure 1**). Furthermore, the redox behavior is predominantly diffusion controlled as the current output relates almost linearly to the square root of the scan rate. These properties of compounds **1** and **2**, due to tethering of the two photochromic units via their phenol moiety, arise from the cross-talk such a connection causes and prompted further examination of the basic properties of spiropyrans (chapter 5). The pronounced tendency of bispiropyrans to undergo ring-opening at an electrode results in ring opening outcompeting aryl-aryl coupling observed in monospiropyrans. Indeed the effect of crosstalk and acid sensitivity is to render the redox chemistry chemically reversible overall and resemble that of the biphenol core, while simultaneously providing insight to some of the spiropyran electrochemistry observed before. It demonstrates that protons produced at the electrode are not necessarily innocent and should be considered as a factor in understanding the kinetics of the processes that lead to polymer formation.

Experimental section

Materials

Tetrabutylammonium hexafluorophosphate (TBAPF₆), 4,4'-dimethoxybiphenyl and 4,4'-biphenol were purchased from Aldrich or TCI and were used without further purification. HPLC grade acetonitrile was used without additional purification. 4-chloro-N,N-dimethylaniline was purchased from SynQuest Labs. Inc. and used without further purification. Compounds **1** and **2** were available from earlier studies (Chapter 6).

Physical methods

Electrochemical data were obtained using a 406E electrochemical workstation (CH Instruments). The working electrodes used were a Teflon-shrouded glassy carbon electrode (3 mm diameter) or indium tin oxide (ITO) on glass slides (1 cm × 3 cm).⁴² A platinum wire auxiliary electrode, and a Ag/AgCl electrode or a saturated calomel electrode (SCE) reference electrode were used. Cyclic voltammograms were, unless stated otherwise, obtained at a sweep rate of 100 mV s⁻¹ in acetonitrile containing 0.1 M TBAPF₆ with analyte concentrations of 0.5 to 2 mM. All potentials are quoted with respect to SCE. Redox potential ($E_{p,a}$, anodic peak potential; $E_{p,c}$, cathodic peak potential; $E_{1/2} = (E_{p,a} + E_{p,c})/2$) values are ±10 mV. UV/vis absorption spectroelectrochemistry of **2**, 4,4'-dimethoxybiphenyl, and 4,4'-biphenol was carried out using an optically transparent thin-layer electrochemical (OTTLE) cell (a liquid IR cell modified with Infrasil windows, platinum mesh working and counter electrodes, and a Ag/AgCl reference electrode; University of Reading) mounted in a Specord600 UV/vis absorption spectrometer with the potential controlled by a CHI406E potentiostat. The Ag/AgCl reference electrode of the OTTLE cell was prepared by anodization at 9 V with a platinum wire cathode in 3 M KCl(aq). In situ UV/vis absorption spectroelectrochemistry of poly-**2** was carried out by initial modification of an ITO electrode by cyclic voltammetry followed by transfer to a quartz cuvette as an electrochemical cell. Irradiation at 300 nm (370 μW) and 455 nm (3200 mW) was provided by M300F2 and M455L3-C5 Thorlabs laser diodes.

Results and Discussion

Cyclic Voltammetry of **1** and **2**

The cyclic voltammetry of compound **1** and **2** indicates that the oxidations are overall chemically reversible (**Figure 1**), with no evidence for formation of polymer at the electrode over multiple cycles. Such behavior could be considered expected for **2** since dimerization at the indoline unit is blocked by the presence of chloro-substituents, however for **1** the lack of electrochemical reversibility (i.e. that its voltammetry is similar to **2**) is surprising compared to the analogous methyl blocked and unblocked mono (nitro)spiropyran reported earlier.²⁰ This suggests that the changes in chemical structure that gives rise to the irreversibility are common to both **1** and **2** and unrelated to oxidative C-C coupling (vide infra) The scan rate dependence of the cyclic voltammetry (up to 5 V s⁻¹) however, shows an additional redox response at 0.95 and 0.75 V at higher scan rates. Indeed, when cycling repeatedly at 1 V s⁻¹ the response of this additional redox-response increases with each cycle (**Figure 2**). The scan rate dependence will be discussed further below.

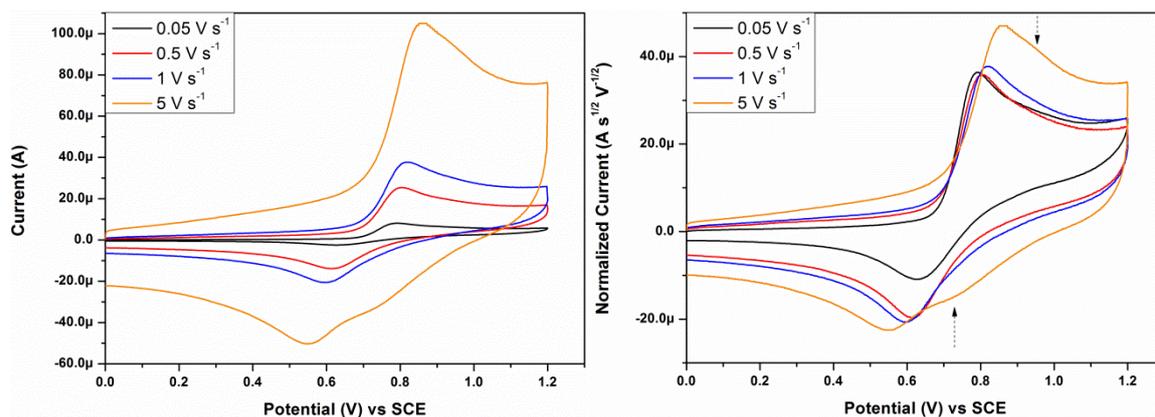


Figure 1. (Left) Scan rate dependence of 0.5 mM of **1** in acetonitrile (0.1 M TBAF, GC working, SCE reference and platinum counter electrode) and (right) with current normalized to the square root of the scan rate.

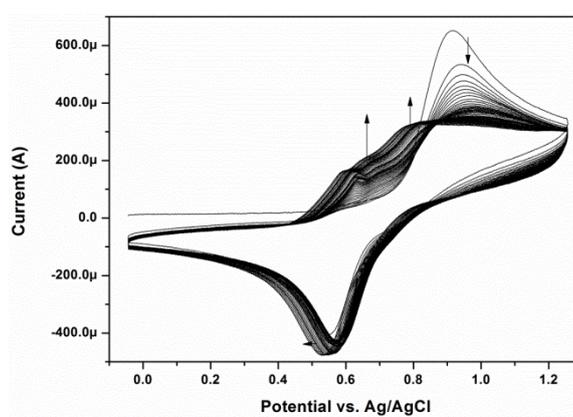


Figure 2. Cyclic voltammetry of 0.5 mM of **1** in acetonitrile (0.1 M TBAF, ITO working, Ag/AgCl reference and platinum counter electrode) at 1 V s^{-1} .

Despite that the redox chemistry at low scan rate shows chemical reversibility since the phenol part of the spiropyran system is fundamentally distinct from that of the mono-spiroprans, the possibility that the redox chemistry was essentially that of bisphenol (the core unit in **1** and **2**) was explored.

4,4'-Dimethoxybiphenyl mimics the structure of the bisphenol unit in the bispiroprans and undergoes electrochemically reversible oxidation at 1.25 V. Considerable chemical irreversibility is observed also especially upon cycling to more positive potentials with a new reversible redox wave appearing at at 0.75 V (**Figure 3**, left). The origin of the redox wave at 0.75 V is confirmed by comparison with the cyclic voltammetry of 4,4'-biphenol, which shows a quasi-reversible redox wave at 0.80 V, similar to that of the bispiropran (**Figure 4**).

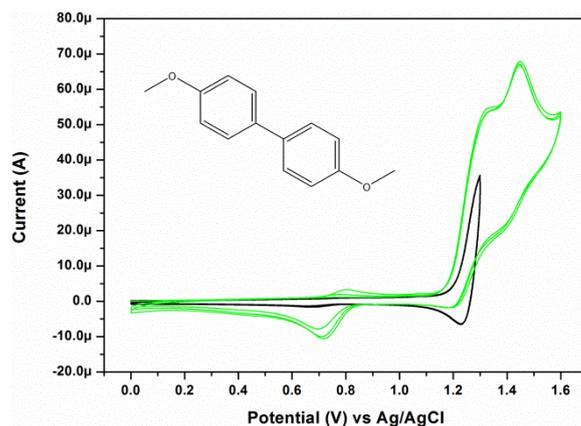


Figure 3. Cyclic voltammetry of 4,4'-dimethoxybiphenyl (1 mM) in acetonitrile (0.1 M TBAF, GC working, Ag/AgCl reference and platinum counter electrode, scan rate 0.1 V s^{-1}).

Hence, it is apparent that during oxidative cyclic voltammetry the ring-closed bispiropyran undergoes rapid ring opening to the bimerocyanine form which presents a 4,4'-biphenol motif.

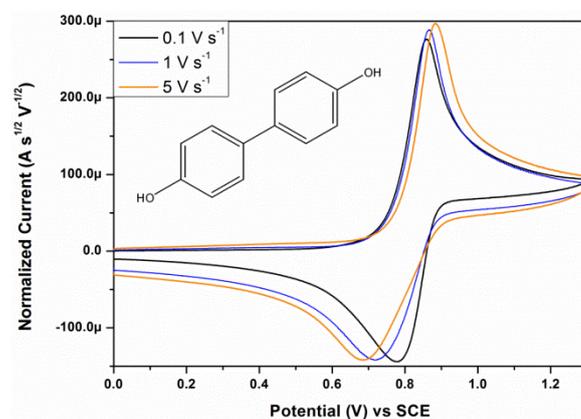


Figure 4. Scan rate dependence of 1 mM of 4,4'-biphenol in acetonitrile (0.1 M TBAF, GC working, SCE reference and platinum counter electrode) with current normalized to the square root of the scan rate.

The cyclic voltammogram of **2** at various scan rates does not show evidence for electrochemical coupling (**Figure 5**) as would be expected since the coupling position has been taken in by chloride substituents already.²⁰

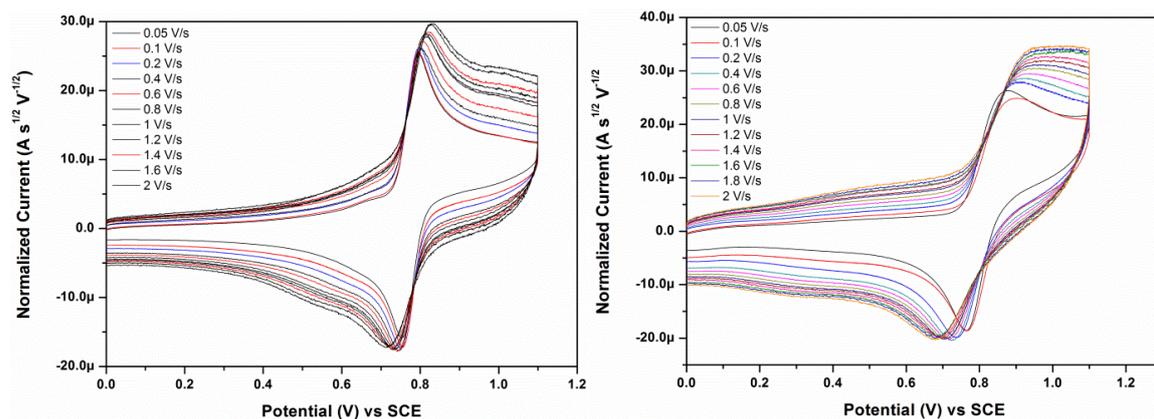


Figure 5. Scan rate dependence of the cyclic voltammograms of **2** (0.5 mM) in acetonitrile (0.1 M TBAF, GC working, SCE reference and platinum counter electrode) without (left) and with (right) 0.5 mM trifluoromethanesulfonic acid. The current is corrected for the square root of the scan rate.

The complete absence of coupling in compound **2** allows us to investigate its electrochromic properties by thin layer UV-vis absorption spectroelectrochemistry. UV/vis spectroelectrochemistry of the analogous 4-chloro-*N,N'*-dimethylaniline, and 4,4'-dihydroxybiphenyl provides comparative spectra for the indoline fragment and the bisphenol moieties, respectively (**Figure 6**).

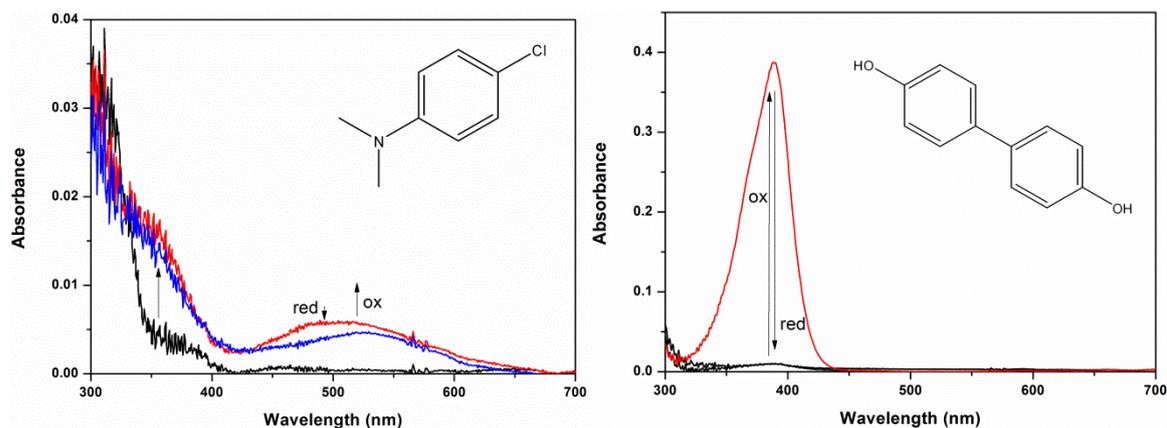


Figure 6. In situ UV/vis absorption spectra of (left) 4-chloro-*N,N'*-dimethylaniline and (right) 4,4'-dihydroxybiphenyl obtained during thin layer cyclic voltammetry by cycling between 0 and 1.2 V in an OTTE cell (0.1 M TBAF, platinum working and counter electrode, Ag/AgCl reference electrode).

Oxidation of 4-chloro-*N,N'*-dimethylaniline results in the appearance of a broad absorption at 500 nm, which persists after reduction whereas the oxidation of 4,4'-biphenol results in a reversible appearance of an absorption band at 389 nm. The reversibility in the case of **2** is also dependent on the duration at which the potential is held above 1.0 V (**Figure 7**).

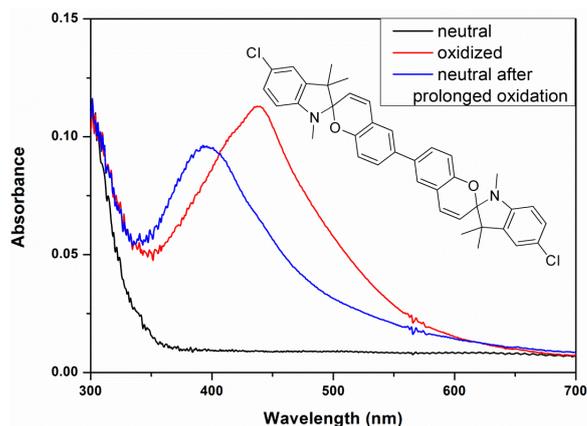


Figure 7. UV/vis absorption spectra of **2** obtained during thin layer cyclic voltammetry between 0 (black line) and 1.2 V (red line) in an OTTE cell (0.1 M TBAPF₆, platinum working and counter electrodes, Ag/AgCl reference electrode). Pausing at 1.2 V affects the reversibility, and a gradual blue shift yield a new absorption (blue line), which does not bleach upon returning to 0 V.

Spectroelectrochemistry of poly-1:

Cyclic voltammetry of **1** at a scan rate of 1 V s⁻¹ at an ITO-coated glass slide working electrode yields a thin film coating on the electrode, of which the response is retained upon light washing and transferring to a solution with only electrolyte (**Figure 8**). UV/vis absorption spectroelectrochemistry of this film showed the appearance and disappearance of an absorption at 440 nm upon oxidation and reduction of the film, respectively.

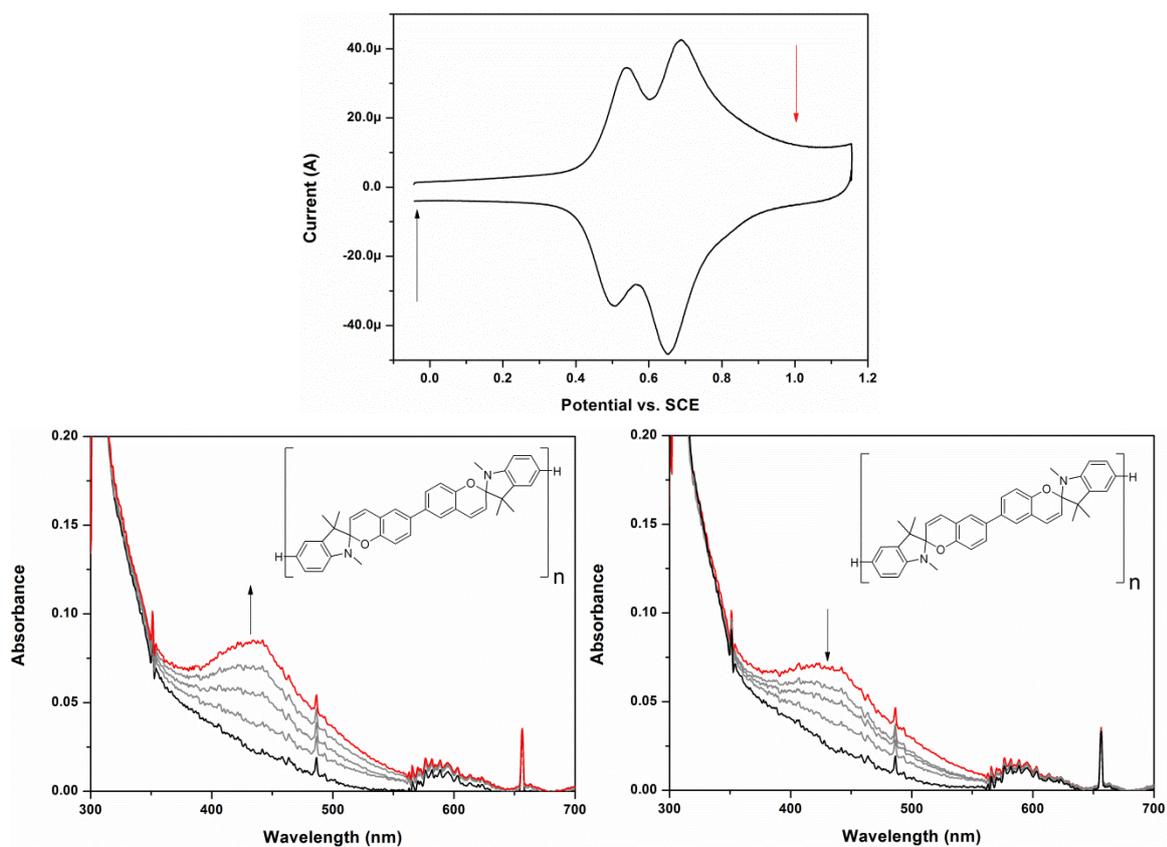


Figure 8. (Top) Cyclic voltammetry of a lightly washed and transferred ITO slide electrode after polymerization of **1** (0.5 mM in acetonitrile, 0.1 M TBAPF₆, Ag/AgCl reference and platinum counter electrode, 100 segments at 1 V s⁻¹), in acetonitrile with TBAPF₆ in the same potential window. The arrows indicate the high (red arrow) and low potential (black arrow) for the UV/vis spectroelectrochemistry shown

below it. (Bottom) UV/vis absorption spectroelectrochemistry of a *poly-1* film on an ITO slide (in acetonitrile containing 0.1 M TBAPF₆, Ag/AgCl reference and platinum counter electrode) with the potential held high (left) and subsequently low (right).

Furthermore, when the oxidized film is irradiated with visible light ($\lambda_{\text{exc}} = 440 \text{ nm}$), the blue shift in absorbance (to 390 nm) is accelerated (**Figure 9**). The redox-gated species that absorbs at 390 nm is stable to irradiation and does not bleach in the potential window of 0 to 1.2 V.

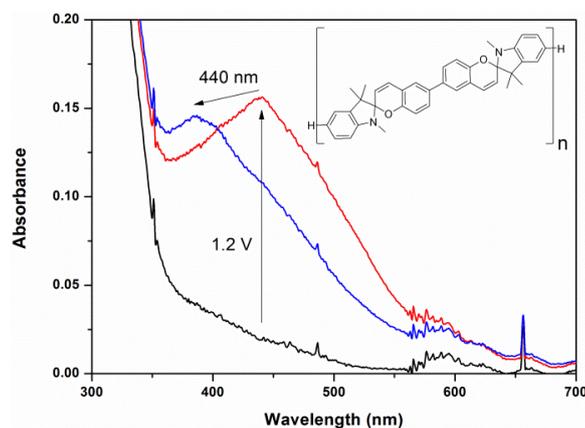


Figure 9. UV/vis absorption spectroelectrochemistry of a *poly-1* film on an ITO slide (in acetonitrile containing 0.1 M TBAPF₆, Ag/AgCl reference and Pt counter electrode) with the potential held at 1.2 V during irradiation at 440 nm.

Concluding Remarks and Future Prospects

The distinct photochromic response shown by bispiroopyrans (Chapter 6) coupled to their redox-chemistry opens many opportunities to expanding further this versatile class of photochrome. The bispiroopyrans discussed in these chapters undergo spontaneous reversible ring-opening to the bimerocyanine form upon oxidation, manifested in their cyclic voltammetry which is analogous to but distinct from the redox chemistry of both 4,4'-dimethoxybiphenyl and spiroopyran. At higher scan rates, however, the typical response of spiroopyrans, i.e. the indoline-centered oxidation followed by aryl-aryl radical coupling, was observed to partially outcompete the alternative biphenol centered redox-process of **1**. As expected, compound **2** does not show evidence for aryl-aryl coupling of the indoline units at higher scan rates, as the chloro-substituents block such processes. Spectroelectrochemistry of **2** showed that the absorption during alternating redox states indeed resembled that of 4,4'-biphenol, analogous to the ring-open bimerocyanine form. Furthermore, prolonged oxidation resulted in the appearance of an absorption band that persisted at 0 V. Finally, a polymer film of **1** was formed at a transparent electrode by repeated oxidation at high scan rate. *Poly-1* showed a similar spectroelectrochemical response to that of **2**, with an additional species generated upon irradiation at 440 nm. Future work includes more detailed characterization of the additional species formed by, e.g., Raman spectroscopy. Additionally, to investigate the role of local pH cyclic voltammetry will be conducted at varying pH and in a buffered solution. Ultimately, a grip on the polymerization process of this remarkably multifaceted species is desired.

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