Electrochemical Ring-Opening and -Closing of a Spiropyran

Chapter 4. Electrochemical Ring-Opening and -Closing of a Spiropyran

Abstract

The bistability of molecular switches is an essential characteristic in their use as functional components in molecular based devices and machines. For photoswitches, light-driven switching between two stable states proceeds via short-lived changes of bond order in electronically excited states. Here, bistable switching of a ditertbutyl-substituted spiropyran photoswitch is instead demonstrated by oxidation and subsequent reduction in an overall four-state cycle. The spiropyran structure chosen has reduced sensitivity to the effect of secondary electrochemical processes such as H⁺ production, and provides transient access to a decreased thermal Z-E isomerisation barrier in the one-electron oxidised state, akin to that achieved in the corresponding photochemical path. Thus, we show that the energy needed for switching spiropyrans to the merocyanine form on demand, typically delivered by a photon, can instead be provided electrochemically. This opens up further opportunities for the utilisation of spiropyrans in electrically controlled applications and devices.

4.1. Introduction

The bistability of molecular switches is central to their application in organic electronics and functional (smart) materials. Molecular photoswitches, for which light is used to toggle molecular structure and hence molecular properties, have dominated the field of molecular switching for over a half century.¹ As an alternative, or even complementary, switching pathway that opens up further opportunities, electrochemical switching has been investigated in a range of photochromes, e.g., stilbenes,²,³ thiindigos,⁴,⁵ fulgides,⁶ azobenzenes,⁷–⁹ overcrowded alkenes,¹⁰,¹¹ diarylethenes,¹²–¹⁹ and, notably, imidazole dimer switches developed recently by Abe et al.²⁰ The challenge, however, in electrochemical switching of photochromes is to replicate fully the process driven by a photon using a redox cycle.

The spiropyran family of compounds shows chromic response, in addition to light, to a wide range of external stimuli.²¹–²³ Chromism can be triggered by external redox units, e.g., by oxidation of a ferrocene²⁴ or polyoxometalate moiety²⁵,²⁶ or by oxidation or reduction of an ancillary carboxamidine moiety.²⁷ Among them, electrochemical input has been shown to cause spontaneous ring-opening of spiropyrans,²⁸–³⁰ such as in the oxidative ring-opening of indolinoazolidines³¹,³² and the reductive ring-opening of nitro-substituted spiropyrans by Fujishima et al. and later Hartl et al.³³,³⁴

Switching between spiropyran and merocyanine forms electrochemically without the involvement of ancillary groups is synthetically advantageous. However, the oxidation of simple spiropyrans results in carbon-carbon bond formation via the indolino unit yielding dimers and releasing protons (Figure 4.1).³⁵,³⁶

Blocking of the para position of the indoline unit, as in a methyl-substituted spiropyran (MeNSP), disables dimerisation, and the oxidation to the spiropyran radical cation becomes reversible (Figure 4.1). Electrochemical oxidation in these cases can, however, indirectly trigger spontaneous ring-opening through the protons generated at the
4.2. Results & Discussion

Figure 4.1: Redox chemistry of a non-substituted and a methyl-substituted nitrospiropyran. *Adapted in part from Browne et al., 36 with permission from The Royal Society of Chemistry.

electrode by protonation-driven ring-opening to the merocyanine Z-MCH. 37,38

Computational studies indicate that ring-opening in the oxidised state can occur upon photo-excitation, 37 and hence when electrochemical dimerisation is avoided, formation of the spiropyran radical cation can facilitate ring-opening to the merocyanine form. Indeed, direct oxidative ring-opening of a spiropyran was recently shown by Kubo et al., where the stabilisation of the phenoxyl radical was driven by the aromatization of the acridine substituent. 39 Subsequent reduction, however, recovered the spiro compound rather than the open zwitterionic form.

Here, we show that a diterbutyl-substituted spiropyran, in which a chloro substituent prevents oxidative aryl-aryl coupling (tbSP, Scheme 4.1), has a sufficiently low oxidation potential to avoid competing acidochromism during electrochemical oxidation. The reversal in relative stability of the spiropyran and merocyanine forms in the oxidised state is observed along with a low barrier to subsequent Z-E isomerisation. The resulting thermally reversible electrocatalytic ring-opening of the spiropyran provides a new approach to bistable switching of spiropyrans.

4.2. Results & Discussion

tbSP was prepared following the standard Fischer base synthetic procedure, and characterised by 1H NMR spectroscopy and high-resolution mass spectrometry (see Experimental Details).
4.2.1. Photo- & Acidochromism

As is the case with non-substituted spiropyrans,\textsuperscript{23,40} \textit{tbSP} does not show significant photochromism in solution at room temperature due to rapid thermal reversion of the merocyanine form to the spiropyran form. At -80 °C, UV irradiation generates the characteristic absorbance of a zwitterionic \textit{E}-merocyanine (\textit{E}-\textit{tbMC}), with a distinctive vibrational structure that is more pronounced in solvents of lower polarity (Figure S4.1, \textit{vide infra}). As with other spiropyrans, \textit{tbSP} exhibits acidochromism,\textsuperscript{38} specifically, addition of near-stoichiometric amounts of strong acids, e.g., CF\textsubscript{3}SO\textsubscript{3}H, results in protonation-driven ring-opening to the protonated \textit{Z}-merocyanine isomer (\textit{Z}-\textit{tbMCH}\textsuperscript{+}), which undergoes both thermal and (reversible) photochemical conversion to the \textit{E}-isomer (\textit{E}-\textit{tbMCH}\textsuperscript{+}), manifested in a bathochromic shift of the UV-Vis absorption band (Figures 4.2, S4.2 and S4.3). Addition of base at room temperature to either form results in complete recovery of the original spectrum of \textit{tbSP}, while at -40 °C intermediate formation of the deprotonated \textit{E}-merocyanine (\textit{E}-\textit{tbMC}) is observed.

4.2.2. Cyclic Voltammetry

The cyclic voltammogram of \textit{tbSP} at 0.1 V s\textsuperscript{-1} shows an irreversible oxidation at \textit{E}_{1/2} = 1.0 V vs Ag/AgCl and a subsequent irreversible reduction at \textit{E}_{1/2} = 0.45 V vs Ag/AgCl (Figures 4.3 and S4.4). At higher scan rates, both the redox wave at 1.0 V and the redox wave of the product at 0.45 V are electrochemically reversible (\textit{E}_{p,a}-\textit{E}_{p,c} is ca. 70 mV). Note that the 2\textsuperscript{nd} cycles are depicted, instead of the 1\textsuperscript{st}, due to the appearance of the oxidation wave at 0.45 V only after the recording of an initial cycle. At -84 °C, the homogeneous reaction that follows oxidation of \textit{tbSP} at 1.0 V is evidently inhibited as the chemical reversibility of the oxidation increases at 0.1 V s\textsuperscript{-1} (Figure S4.5). Thus, it seems that oxidation of the spiropyran to its radical cation \textit{tbSP}\textsuperscript{+\textsuperscript{+}} at 1.0 V, though electrochemically reversible, is followed by a chemically irreversible change to the open form radical cation \textit{tbMC}\textsuperscript{+\textsuperscript{+}}. The \textit{tbMC}\textsuperscript{+\textsuperscript{+}} then undergoes an electrochemically
reversible reduction to its neutral form \textit{tbMC} (at 0.45 V), followed by thermal reversion to \textit{tbSP} to complete the redox cycle (Scheme 4.1).

Figure 4.2: UV-Vis absorption spectra of \textit{tbSP} (45 \textmu M) in acetonitrile at -40 °C (black) after addition of 2.5 eq. CF$_3$SO$_3$H (yellow), subsequent irradiation with 365 nm (orange), and deprotonation with 25 eq. NaOAc to yield \( E^-\textit{tbMC} \) (blue).

Figure 4.3: Cyclic voltammetry (2$^{\text{nd}}$ cycles) of \textit{tbSP} (1 mM) in acetonitrile (0.1 M TBAPF$_6$) at 20 °C at 0.1 (solid), 10 (dashed) and 100 V s$^{-1}$ (dotted). The corresponding redox and chemical reactions are indicated. 2$^{\text{nd}}$ cycles are shown for clarity to show also the reversibility of the redox process at 0.45 V. The 1$^{\text{st}}$ cycle in each case is identical except that the forward process at 0.45 V is absent (since the species responsible is not yet generated, see Appendix).
4.2.3. DENSITY FUNCTIONAL THEORY

DFT calculations (see Appendix for computational details) are in good qualitative agreement with our proposed kinetic model and predict that, in the neutral state, ring-opening is uphill, while in the oxidised state the process is downhill with a barrier of 6.0 kcal mol\(^{-1}\) for the breaking of the C-O bond and 15.8 kcal mol\(^{-1}\) for the Z-E isomerisation (Figure 4.4). This low Z-E isomerisation barrier implies that the E-tbMC species is obtained upon subsequent reduction. The total energy barrier for tbSP\(^{**}\) ring-opening estimated from cyclic voltammetry by simulation is 15.4 kcal mol\(^{-1}\), corresponding to a lifetime of approximately 50 ms (see Appendix), which matches the value obtained by DFT. Finally, the difference in computed adiabatic ionisation energies for tbSP and E-tbMC of 0.50 eV (Figure 4.4) is also in good agreement with the experimentally observed difference in redox potential of 0.55 V between the two species (Figure 4.3).

![Reaction Coordinate Diagrams](image_url)

**Figure 4.4:** Reaction coordinate diagrams of tbSP ring-opening in neutral (bottom) and oxidised (top) states including each corresponding ionisation potential (IP). The depicted mechanism describes a simplified model since there are multiple isomers of both Z- and E- open forms (see Appendix). Relative free energies are given in kcal mol\(^{-1}\) taking the SP isomer as reference for both structures.
4.2.4. Electrochemistry of Photochemically Generated E-Merocyanine

The DFT calculations support that the merocyanine isomer Z-tbMC plays a role in the mechanism of ring-opening. Indeed, breaking the C\textsubscript{spiro}-O bond yields Z-tbMC that is a true minimum (stable isomer) according to the calculation. In the neutral state, Z-tbMC is close in energy to the opening/closing transition state (TS Opening), so that it is a transient species in the experimental conditions. In contrast, the energy of Z-tbMC\textsuperscript{**} is calculated to be lower than that of tbSP\textsuperscript{**} and it should have a longer lifetime experimentally. Nevertheless, the E-isomer is substantially lower in energy with a rather small isomerisation barrier (vide supra) and hence its rapid formation upon oxidation of tbSP is expected even at low temperature. It should be noted that the Z- and E- isomers are in fact a manifold of isomers (see Appendix),\textsuperscript{23} however, the energy difference between these isomers is small and only the lowest energy conformers are presented in Figure 4.4. The low barriers for each step raise a question as to the detailed pathway for the electrochemical processes as rapid equilibria prior or after electron-transfer steps will lead to essentially identical cyclic voltammograms.

4.2.4. Electrochemistry of Photochemically Generated E-Merocyanine

The redox chemistry of tbMC was investigated by making use of its initial photochemical generation from tbSP at -80 °C (with an absorbance of 0.9 at 590 nm and hence a concentration of 0.05 mM) followed by a cyclic voltammogram within the potential window of 0.0-0.7 V vs Ag/AgCl (Figures 4.5 and S4.6). Indeed, the observed reversible oxidation at 0.45 V supports its assignment to tbMC, and the generation of this merocyanine isomer via sequential oxidation and reduction of closed form tbSP as observed with cyclic voltammetry at higher scan rates (Figure 4.3).

\textbf{Figure 4.5:} UV-Vis absorption spectra of tbSP (2 mM) in butyronitrile (0.1 M TBAPF\textsubscript{6}) at -80 °C before (black) and after irradiation at 340 nm to form tbMC (blue). Inset shows cyclic voltammogram of the irradiated solution at -80 °C. Estimated concentration of tbMC is 0.05 mM (using the average molar absorptivity obtained from repeated photoswitching measurements).
4.2.5. UV-Vis-NIR SPECTROELECTROCHEMISTRY

The UV-Vis and NIR absorption spectrum of \( \text{tbMC}^{\bullet\bullet} \) at 1.0 V obtained spectroelectrochemically at room temperature shows strong absorption bands at 355 nm and 505 nm, and weaker bands in the NIR region (777 nm, 877 nm, and 1008 nm, Figures 4.6 and S4.7). Subsequent reduction at 0.40 V resulted in a disappearance of the visible and NIR bands and the reappearance of the absorption band of \( \text{tbSP} \) at 310 nm together with a new absorption band at ca. 435 nm, assigned to \( E^-\text{tbMCH}^{\bullet\bullet} \) (Figure S4.8). These assignments are consistent with time-dependent DFT (TD-DFT) calculations performed on these species (see Appendix for details). These changes contrast with those observed in the reversible one-electron oxidation of \( \text{MeNSP} \), substituted with a nitro- instead of tertbutyl-groups, in which an absorption band at 457 nm of the radical cation of the closed form (i.e. \( \text{MeNSP}^{\bullet\bullet} \)) appears and is relatively stable. On the other hand, the NIR bands are comparable to those observed for the radical cation of a spiropyran dimer, but the respective visible absorption bands (443 nm and 478 nm) do not match those observed for \( \text{tbMC}^{\bullet\bullet} \) (355 nm and 505 nm). Furthermore, dimerisation by indoline C-C coupling is not expected to occur upon oxidation of \( \text{tbSP} \) since the reactive para-carbon position of the indoline unit is blocked by a chloro substituent (Figure S4.9). Nevertheless, the absorption spectrum of \( \text{tbMC}^{\bullet\bullet} \) indicates that it is a similar type of radical cation with the radical delocalised over an extended conjugated system, and its reversible electrochemical generation shows that, at room temperature, \( \text{tbSP} \) essentially exhibits reversible switching of oxidation state between the neutral closed form \( \text{tbSP} \), and the radical cation open form \( \text{tbMC}^{\bullet\bullet} \).

![Figure 4.6: UV-Vis and FT-NIR absorption spectra of \( \text{tbSP} \) (4 mM) in acetonitrile (0.1 M TBAPF$_6$) at room temperature before oxidation (black) and at 1.0 V generating \( \text{tbMC}^{\bullet\bullet} \) (violet). Inset shows the cyclic voltammogram at 0.01 V s$^{-1}$, the NIR spectra are re-scaled to show progression of 1008 nm band.

The thermally unstable species \( \text{tbSP}^{\bullet\bullet} \) and \( E^-\text{tbMC} \) were generated as a demonstra-
tion of the full redox switching cycle by the preparative oxidation and reduction of \textbf{tbSP} at low temperature monitored by UV-Vis absorption spectroscopy. At -80 °C, initially, a band at 466 nm appeared (Figure S4.10), after which it decreased in absorbance concomitant with an increase at 510 nm together with several NIR absorption bands (i.e., \textbf{tbMC^{**}}). Notably, the band at 466 nm corresponds to that of the closed form radical cation \textbf{MeNSP^{**}}, thus we assigned this absorption band to \textbf{tbSP^{**}} (Figure S4.11). These data indicate that ring-opening in the oxidised state (from \textbf{tbSP^{**}} to \textbf{tbMC^{**}}) occurs with a significant driving force and low barrier, consistent with the DFT results of Figure 4.4.

At higher temperature (-60 °C), oxidation of \textbf{tbSP} resulted in the immediate appearance of the 466 nm band assigned to \textbf{tbSP^{**}} as well as the characteristic absorption bands of \textbf{tbMC^{**}} at 510 nm and several in the NIR (Figures 4.7 and S4.12). EPR spectroscopy at 77 K of this oxidised merocyanine species shows a single line at \( g = 2.004 \) and a linewidth of 1.2 mT indicating significant broadening due to unresolved hyperfine coupling (Figure S4.13). In contrast, the EPR spectrum of the oxidised open form of the acridine spiropyran reported by Kubo et al. did exhibit hyperfine splitting.\(^{39}\) This suggests that the radical in \textbf{tbMC^{**}} is delocalised over an extensive part of the molecule including the indoline unit. The DFT-computed spin density supports this analysis (see Appendix).

![Figure 4.7: UV-Vis absorption spectrum of \textbf{tbSP} (1 mM) in butyronitrile (0.1 M TBAPF\(_6\)) at -60 °C (black) after preparative oxidation to form \textbf{tbMC^{**}} (violet) and after its subsequent reduction to \textbf{tbMC} (blue). The difference in applied potential for oxidation and that required for reduction was 1.2 V, consistent with cyclic voltammetry (Figure 4.3). Inset shows EPR spectrum of \textbf{tbMC^{**}} at 77 K.](image)

Subsequent reduction at -60 °C resulted in the loss of absorbance from \textbf{tbMC^{**}} and the appearance of a band at 590 nm with a vibrational progression characteristic of \textbf{tbMC}, which provides strong evidence of our proposed ring-opening of \textbf{tbSP} driven by a redox cycle, as well as an additional broad band at 455 nm assigned to the protonated species \( E\text{-}tbMCH^+ \) (Figures 4.7 and 4.8). It should be noted, however, that
the data do not exclude formation of Z-tbMC also after reduction since this isomer will immediately ring-close to reform tbSP. The formation of the E-isomer through preparative oxidative and then reductive electrolysis indicates that Z-E isomerisation is facile in the monocationic state (tbMC**) with > 25% yield. The yield is less than complete, partly due to the generation of protons at the working electrode “trapping” some of the E-tbMC in the thermally favoured E-tbMCH+ form (absorption band at 450 nm).37,38 This effect limits the extent of oxidation that can be realised under the conditions employed. A second aspect to consider is the rapid equilibrium (low barriers) between tbSP** and tbMC**, and hence upon switching to a reducing potential, under diffusion-controlled conditions, the ring-closing to tbSP** followed by its subsequent reduction to tbSP competes with the desired reduction of tbMC** to E-tbMC. In the case of dithienylperhydrocyclopentene photochromes, this limit to efficiency was shown to be overcome when immobilised as monolayers on a surface15 or incorporation in thin polymer films.17

Figure 4.8: Normalised UV-Vis absorption spectra of electrochemically generated tbMC (blue, solid) and photochemically generated tbMC at -80 °C (blue, dashed), and a mixture of Z- and E-tbMCH+ (orange) at PSS365nm (prepared by protonation and irradiation of tbSP).

4.3. Conclusions

The redox driven ring-opening of a photochromic spiropyran is facilitated by adding electron-donating tert-butyl substituents ortho- and para- to the phenolic oxygen of the benzopyran. The importance of the tert-butyl groups in achieving electrocatalytic ring-opening was evident in the work of Kubo et al. also,39 thus we expect the formation of a thermodynamically stable phenoxy radical to drive the merocyanine formation. Additionally, next to preventing dimerisation, the chloro substituent on the indoline unit is expected to destabilise the indoline-based radical cation that is formed initially also.
Although its redox potential is close to that of analogous spiropyrans,\textsuperscript{23} \textit{tbSP} shows much less interference from protonation during electrochemical measurements, enabling ring-opening and \textit{Z}-\textit{E} isomerisation of the zwitterion. Therefore, ring-opening and -closing of spiropyrans can be achieved by redox cycling in a manner analogous to the well-known photochemical pathway and with similar conversion efficiencies.

Ultimately, this approach to molecular switching opens up opportunities in controlling interfacial properties by transient electrochemical as well as photochemical stimuli, and is especially of relevance to molecular based devices in which optical access is limited.

\textbf{Acknowledgements}

For this work we used computational resources of the CCIPL center installed in Nantes.

\textbf{Bibliography}

\begin{itemize}
\item[(1)] \textit{Molecular Switches}; Feringa, B. L., Browne, W. R., Eds.; Wiley-VCH, Weinheim: 2011, p 792.
\end{itemize}


Chapter 4. Electrochemical Ring-Opening and -Closing of a Spiropyran


**EXPERIMENTAL DETAILS**

**MATERIALS AND METHODS**

All chemicals for electrochemical and spectroscopic measurements and for the synthesis of tbSP were purchased from Sigma-Aldrich or TCI and were used without further purification. NMR spectra were obtained on a Bruker 400 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) with respect to tetramethylsilane and referenced to residual solvent (CHD₂CN), and coupling constants are reported in Hertz. Multiplicities are denoted as s = singlet, d = doublet, m = multiplet. Electrospray ionisation mass spectrometry (ESI-MS) was recorded on an LTQ Orbitrap XL spectrometer.

EPR spectroscopy (X-band, 9.5 GHz) was performed on a Bruker EMX Nano spectrometer in liquid nitrogen at 77 K. Samples were flash frozen in a capillary tube in liquid nitrogen after generation of the desired species (monitored by UV-Vis absorption spectroscopy). Fitting of EPR spectra was performed using EasySpin. UV-Vis absorption spectra at room temperature were recorded on an Analytik Jena Specord 600 spectrometer, and spectra at lower temperatures were recorded on an Agilent Technologies Cary 8454 spectrometer in a Unisoku CoolSpek USP-203-B cryostat. Irradiation at 340 nm, 365 nm, and 455 nm was provided by Thorlabs LEDs M340L4 (53 mW), M365LP1-C5 (435 mW), and M455L3-C5 (400 mW), respectively.

Electrochemical measurements were performed on a model 604E or 760B Electrochemical Analyzer (CH Instruments). Typical analyte concentrations were 1.0 mM in acetonitrile (≥99.9%) or butyronitrile (≥99%) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) and the electrodes employed were, unless stated otherwise, a 3 mm diameter Teflon-shrouded glassy carbon (GC) working electrode (CH Instruments), a Pt wire auxiliary electrode, and a Ag/AgCl wire reference electrode. Cyclic voltammetry at lower temperatures was carried out, at -84 °C, using a liquid nitrogen/ethyl acetate bath in a V-shaped tube, or, at -80 °C after irradiation, using a Unisoku temperature control cell in a 1 cm pathlength quartz cuvette. UV-Vis absorption spectroelectrochemistry at room temperature was carried out using an optically transparent thin-layer electrode (OTTLE) cell which consists of platinum mesh working and auxiliary electrodes, and a Ag/AgCl wire reference electrode in a liquid IR cell modified with quartz windows. Preparative oxidation and reduction experiments (bulk electrolysis) at lower temperatures were carried out in a Unisoku temperature control cell using a 2 mm pathlength quartz cuvette equipped with a Pt mesh working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode.

**SYNTHESIS**

tbSP was prepared according to the standard Fischer base synthetic procedure.²³
Synthesis of tbSP.

5-chloro-1,3,3-trimethyl-2-methyleneindoline (2.55 mmol, 530 mg) was added dropwise to a solution containing 3,5-ditertbutylsalicaldehyde (2.16 mmol, 507 mg) in 35 ml ethanol. The reaction mixture was heated at reflux overnight under argon. The solvent was removed in vacuo and the resulting crude was dissolved in cold ether and passed over a P4 glass filter. An obvious residue was not collected on the filter but it turned purple. The P4 filter was washed (upside down) with ethanol to remove the purple-colored species. The product 6,8-di-tert-butyl-5’-chloro-1’,3’,3’-trimethylspiro[chromene-2,2’-indoline] (tbSP) precipitated from the ethanol solution as pinkish-white crystals (290 mg, 31 % yield). $^1$H NMR spectroscopy (CD$_3$CN, 400 MHz, ): δ 7.21 (d, J = 2.5 Hz, 1H, h/i), 7.13 – 7.09 (m, 2H, k & l), 7.06 (d, J = 2.4 Hz, 1H, h/i), 6.97 (d, J = 10.2 Hz, 1H, g), 6.47 (d, J = 8.8 Hz, 1H, j), 5.76 (d, J = 10.2 Hz, 1H, f), 2.63 (s, 3H, e), 1.32 (s, 3H, c/d), 1.27 (s, 9H, a/b), 1.18 (s, 3H, c/d), 1.11 (s, 9H, a/b). HRMS (ESI/Orbitrap) m/z: [M]+ Calculated for C$_{27}$H$_{34}$ClNO: 424.2402; Found 424.2395. Elemental Analysis Calculated for C$_{27}$H$_{34}$ClNO: C, 76.48; H, 8.08; N, 3.30. Found: C, 76.69; H, 8.20; N, 3.34.
**APPENDIX**

**SUPPORTING FIGURES**

![Normalized UV-Vis absorption spectra](image1.png)

**Figure S4.1:** Normalised UV-Vis absorption spectra of E-tbMC generated from tbSP at -40 °C in acetonitrile via the protonation-deprotonation pathway (blue, solid) and photochemically at -80 °C in butyronitrile (blue, dashed).

![Absorption spectra](image2.png)

**Figure S4.2:** UV-Vis absorption spectra of tbSP (43 µM) in acetonitrile at -40 °C (black) 10 min after addition of 2.5 eq. CF$_3$SO$_3$H without irradiation (orange), and after subsequent deprotonation with 25 eq. NaOAc to yield $E$-tbMC (blue).
Figure S4.3: UV-Vis absorption spectra of tbSP (59 µM) in acetonitrile at room temperature (black) after addition of 4 eq. CF₃SO₃H (yellow, solid), irradiation with 365 nm (orange) and irradiation with 455 nm (yellow, dashed).

Figure S4.4: Cyclic voltammetry (2nd cycles) of tbSP (1 mM) in acetonitrile (0.1 M TBAPF₆) at 20 °C at various scan rates.
Figure S4.5: Cyclic voltammetry of tbSP (1 mM) in butyronitrile (0.1 M TBAPF$_6$) at -84 °C at 0.1 (solid) and 1.0 V s$^{-1}$ (dashed).

Figure S4.6: Cyclic voltammograms at -80 °C in butyronitrile (0.1 M TBAPF$_6$) of a mixture of tbSP and tbMC, formed by irradiation at 340 nm, recorded first (blue, solid) between 0.0-0.7 V and subsequently over the extended potential window of tbSP (blue, dashed, 0.0-1.2 V).
**Figure S4.7:** UV-Vis and FT-NIR spectra of tbSP (4 mM) in acetonitrile (0.1 M TBAPF$_6$) at room temperature before oxidation (black) and at 1.0 V (violet). Inset cyclic voltammogram at 0.01 V s$^{-1}$. Original spectra without re-scaling. The difference in absorbance of the 1008 nm band is due to the measurements having been recorded in two separate experiments using different stock solutions.

**Figure S4.8:** UV-Vis absorption spectra of tbSP (4 mM) in acetonitrile (0.1 M TBAPF$_6$) during spectroelectrochemistry at room temperature before oxidation (black), at 1.0 V (violet) and after subsequent reduction (orange) showing the remaining absorption due to E-tbMCH$^+$. 
Figure S4.9: Cyclic voltammogram of 4-Cl-\(N,N\)-dimethylaniline (1 mM) in acetonitrile (0.1 M TBAPF\(_6\)) at 0.01 V s\(^{-1}\) showing reversible redox chemistry.

Figure S4.10: UV-Vis absorption spectrum of tbSP (1 mM) in butyronitrile (0.1 M TBAPF\(_6\)) at -80 °C after application of 1.2 V (red) showing the appearance of the 466 nm absorption band of tbSP\(^{+\bullet}\).
Figure S4.11: UV-Vis absorption spectra of $tbSP^{\bullet\bullet}$ (red) and $MeNSP^{\bullet\bullet}$ (navy) in butyronitrile at -60 °C immediately after addition of 1 eq. Magic Blue to $tbSP$ (1 mM) and $MeNSP$ (1 mM), respectively. The spectrum of Magic Blue in acetonitrile (gray) is included for comparison. The dashed vertical lines indicate the matching absorption maxima.

Figure S4.12: UV-Vis absorption spectra of $tbSP$ (1 mM) in butyronitrile (0.1 M TBAPF$_6$) at -60 °C during preparative oxidation to form initially $tbSP^{\bullet\bullet}$ (red) which gradually converted to $tbMC^{\bullet\bullet}$ (violet). Note that spectra are not at equal time intervals.
Figure S4.13: Experimental EPR spectrum of tbMC$^{••}$ at 77 K (violet, dashed) and fit (gray, solid) performed with Easyspin from which were obtained a g-factor of 2.00403 and a linewidth of 1.229 mT.
Modelling of ECEC Mechanism

The following reaction mechanism was modelled using Python 3.8:

\[
\begin{align*}
A & \rightleftharpoons k_{f,E1} A + k_{b,E1} B \\
B & \rightleftharpoons k_{1} B + k_{f,E2} C \\
C & \rightleftharpoons k_{b,E2} C + k_{f,E2} D \\
D & \rightleftharpoons k_{2} D + k_{b,E1} A
\end{align*}
\]

The code developed by Peter Mattia for an EC mechanism was adapted for use in Python with an ECEC mechanism. The electrochemical steps were modelled using the Butler-Volmer model. However, since experimentally the reactions are electrochemically reversible, even at relatively high scan rates, the electrochemical rate constants were set sufficiently large (i.e., 10 cm s\(^{-1}\)) so as to not be rate-limiting.

The concentrations are denoted by \(A[i_1,i_2]\), where the first index denotes time, and the second denotes space. Using the finite-difference method and the explicit method, the following equations are obtained for the diffusion under Fick’s laws, when all diffusion coefficients are assumed equal:

\[
\begin{align*}
A[i_1 + 1,i_2] &= A[i_1,i_2] + DM \ast (A[i_1,i_2] + A[i_1,i_2 - 1] - 2 \ast A[i_1,i_2]) + km2 \ast D[i_1,i_2] \\
B[i_1 + 1,i_2] &= B[i_1,i_2] + DM \ast (B[i_1,i_2] + B[i_1,i_2 - 1] - 2 \ast B[i_1,i_2]) - km1 \ast B[i_1,i_2] \\
C[i_1 + 1,i_2] &= C[i_1,i_2] + DM \ast (C[i_1,i_2] + C[i_1,i_2 - 1] - 2 \ast C[i_1,i_2]) + km1 \ast B[i_1,i_2] \\
D[i_1 + 1,i_2] &= D[i_1,i_2] + DM \ast (D[i_1,i_2] + D[i_1,i_2 - 1] - 2 \ast D[i_1,i_2]) - km2 \ast D[i_1,i_2]
\end{align*}
\]

Here, \(DM\) is the model diffusion coefficient (page 788 of Bard and Faulkner), set to 0.45, and \(km1\) and \(km2\) are the normalised dimensionless kinetic parameters (page 797 of Bard and Faulkner). At the surface, the concentrations need to be updated using the Butler-Volmer model. The fluxes of both redox couples are:

\[
\begin{align*}
JA[i_1 + 1] &= \frac{kJF1[i_1 + 1] \ast A[i_1 + 1,1] - kbE1[i_1 + 1] \ast B[i_1 + 1,1]}{1 + Dx/Dc \ast (kJF1[i_1 + 1] + kbE1[i_1 + 1])} \\
JC[i_1 + 1] &= \frac{kJF2[i_1 + 1] \ast C[i_1 + 1,1] - kbE2[i_1 + 1] \ast D[i_1 + 1,1]}{1 + Dx/Dc \ast (kJF2[i_1 + 1] + kbE2[i_1 + 1])}
\end{align*}
\]

The values for \(kbE1, kbE2, kF1,\) and \(kJF2\) are calculated using the potential and the Butler-Volmer model, \(Dx\) is the spatial step, and \(Dc\) is the diffusion coefficient of all species. The surface concentration (at spatial point 0) is updated using:
\[ A[i1 + 1, 0] = A[i1 + 1, 1] - JA[i1 + 1] \times (Dx/Dc) + km2 \times D[i1 + 1, 0] \]
\[ B[i1 + 1, 0] = B[i1 + 1, 1] + JA[i1 + 1] \times (Dx/Dc) + km1 \times B[i1 + 1, 0] \]
\[ C[i1 + 1, 0] = C[i1 + 1, 1] - JC[i1 + 1] \times (Dx/Dc) + km1 \times B[i1 + 1, 0] \]
\[ D[i1 + 1, 0] = D[i1 + 1, 1] + JC[i1 + 1] \times (Dx/Dc) - km2 \times D[i1 + 1, 0] \]

The current density was calculated by adding both sources of current:
\[ J = -nF(J/C + JA) \]

The capacitance was then added to the calculated current density:
\[ I_{\text{withcap}} = (J - \text{capacitance} \times v) \times A \]

Where \( v \) is the scan rate, taking the direction of scanning into account (i.e., at the start \( v = 1 \text{ V s}^{-1} \) and at the vertex \( v = -1 \text{ V s}^{-1} \)), and \( A \) is the area of the electrode (a 0.3 cm diameter electrode was used).

Since one simulation takes 30 s and the experimental data is not free of imperfections, it was not feasible to perform least-squared fitting with multiple free parameters. Therefore, the data was fitted graphically, for a single scan rate. This means that the obtained parameters are a rough estimate of the true optimized value.

As mentioned before, since, experimentally, reversible electrochemistry is observed even at relatively high scan rates, the electrochemical reactions are considered diffusion limited, (i.e., the electrochemical rate constants are set sufficiently high so as never to be the limiting factor for the current).

The simulation with \( k_1 = 30 \text{ s}^{-1} \) and \( k_2 = 15 \text{ s}^{-1} \) was found to match closely with the experimental data (Figure S4.14), corresponding to a barrier (\( \Delta G^\ddagger \)) of 15.4 kcal mol\(^{-1}\) for B to C, and 15.8 kcal mol\(^{-1}\) for D to A.

\[ \text{Figure S4.14: Simulated and experimental cyclic voltammograms.} \]
Computational Details

All theoretical calculations were performed with the Gaussian16.A03 code,\textsuperscript{43} using default approaches, algorithms and thresholds, except when noted below. We have followed a computational protocol similar to the one proposed by Bieske\textsuperscript{44} and applied in our previous reports as well.\textsuperscript{38,45} We performed DFT geometry optimization and vibrational frequency calculations with the PW6B95D\textsuperscript{46} functional combined with the def2-TZVP atomic basis sets. We accounted for solvent effects systematically using the Polarisable Continuum Model,\textsuperscript{47} considering CH\textsubscript{3}CN as medium. For determining the various transition-states, we followed exactly the same protocol as in our previous works,\textsuperscript{38,45} that is, we computed the Hessian at each step; starting from scans along the target coordinate. Note that, as in our previous reports, the broken-symmetry (BS-DFT) wavefunction collapsed into the restricted solution and the latter approach is therefore followed, which should result in overestimated barriers for rotations around the double bond. TD-DFT calculations were performed with the CAM-B3LYP functional\textsuperscript{48} and the aug-cc-pVDZ, using the vertical approximation. We are well aware of the limits of the vertical approximation but we are here interested in trends between systems. We note that, with such approximation, one naturally expects the theoretical vertical values to be blue-shifted as compared to measured $\lambda_{\text{max}}$. Finally, the vertical ionisation potentials (IPs) have been obtained by Delta SCF procedure. Cartesian coordinates for the molecular structures displayed in Figure 4.4, both ground and transition states, can be found in the Supporting Information of our publication.\textsuperscript{49}

Analysis of the neutral and radical cationic SP forms

For the tbSP, TD-DFT returns the three first vertical excitations at 287 nm ($f = 0.10$), 269 nm ($f = 0.07$), and 250 nm ($f = 0.04$). The first transition corresponds to the experimental absorption band peaking at 310 nm. The difference between 287 and 310 nm (+0.32 eV) is typical of the use of the vertical approach with a range-separated hybrid. We note that the theoretical value is blue-shifted, which is the normal error sign in such vertical theory versus experimental $\lambda_{\text{max}}$ comparison.

For tbSP\textsuperscript{**}, the spin density distribution reveals it is located on the indolino unit (Figure S4.15). For this species, PCM-TD-CAM-B3LYP calculations return the following (first five) vertical excitations: 669 nm ($f = 0.01$), 510 nm ($f = 0.01$), 476 nm ($f = 0.09$), 420 nm ($f = 0.05$), and 403 nm ($f = 0.15$). The 669 nm absorption corresponds to a charge transfer (CT) transition between the two moieties of the compound (Figure S4.15), explaining its extremely weak oscillator strength. In the experimental measurement (Figure S4.11), it is likely buried under the absorption band of Magic Blue. The stronger absorption at 403 nm is a local $\pi-\pi^*$ transition associated to the indolino unit, the local character explaining the much stronger intensity. A convolution of the theoretical excitations (with a broadening Gaussian of HWHM of 0.33 eV) yields a maximum at 420 nm, a shift of +0.34 eV from the experimental band of Figure S4.11. Interestingly this shift is rather similar to the one noted for tbSP.
Analysis of the neutral and mono-protonated E-MC forms

In Figure S4.16, we represent the four well-known possible conformers of $E$-tbMC together with their relative free energy (w.r.t. tbSP) and the computed vertical transition energies. We note that, as expected for the open merocyanine species, the lowest-lying transition is always very strongly dipole allowed. The results follow expectations, with all merocyanines being slightly less stable than the closed spiropyran forms and presenting a strongly red-shifted band as compared to tbSP.

$$
\begin{align*}
+2.61 \text{ kcal mol}^{-1} \\
502 \text{ nm (} f = 0.86) \\
+2.54 \text{ kcal mol}^{-1} \\
486 \text{ nm (} f = 0.86) \\
+4.37 \text{ kcal mol}^{-1} \\
502 \text{ nm (} f = 0.88) \\
+5.51 \text{ kcal mol}^{-1} \\
487 \text{ nm (} f = 0.84)
\end{align*}
$$

Figure S4.16: Representation of the four possible $E$-tbMC conformers, with their relative free energies as compared to tbSP in kcal mol$^{-1}$, as well as the computed vertical transition wavelength (nm) to the lowest excited state.

We have also considered the protonated forms corresponding to the ones displayed above (in which the oxygen is protonated, that is, $E$-tbMCH$^+$), as these forms are considered experimentally. This leads to vertical transitions at 408 nm ($f = 1.05$), 393 nm ($f = 1.06$), 407 nm ($f = 1.05$), and 382 nm ($f = 1.00$) for the four conformers corresponding to those displayed in Figure S4.16. The most stable protonated conformer is the first one, and its absorption at 408 nm is again blue-shifted as compared to experiment (435 nm) with a difference of $+0.18 \text{ eV}$ between the vertical TD value and the experimental $\lambda_{max}$.

Analysis of the radical cationic E-MC forms

In Figure S4.17, we display the same conformers as in Figure S4.16, but for the radical cationic forms, i.e., $E$-tbMC$^{\bullet\bullet}$. Strikingly, the MC forms are more stable than the SP forms for the radical cations, by values going from -5.77 to -2.94 kcal mol$^{-1}$. The most stable radical (leftmost in Figure S4.17) has a radical principally localised on its benzopyran unit, but with significant delocalisation on the bridge as well as on the
indolino segment. This much stronger delocalisation than in \textbf{tbSP}^+ (\textit{vide supra}) qualitatively explains the gain in stability. For the most stable \textit{E-tbMC}^+ conformer, TD-DFT calculations return two very low-lying excited states, the second one being significantly (though not strongly) dipole allowed: 743 nm with $f = 0.10$. This corresponds to the low-lying band in the 750-1050 nm domain observed experimentally (Figure 4.6 of the main text). Again, theory is blue-shifted as compared to experiment but numerical comparisons are not easy, given the complex structure of the experimental absorption band. The first strong absorption is located at 452 nm ($f = 0.48$) in the calculation, which corresponds to the strong absorption at 505 nm experimentally (blue-shift of +0.29 eV between theory and experiment).

\begin{center}
\begin{tabular}{cccc}
 & -5.77 kcal mol\(^{-1}\) & -4.90 kcal mol\(^{-1}\) & -3.50 kcal mol\(^{-1}\) & -2.94 kcal mol\(^{-1}\) \\
759 nm ($f = 0.00$) & 806 nm ($f = 0.00$) & 760 nm ($f = 0.00$) & 806 nm ($f = 0.00$) \\
743 nm ($f = 0.10$) & 751 nm ($f = 0.10$) & 706 nm ($f = 0.08$) & 702 nm ($f = 0.08$) \\
506 nm ($f = 0.14$) & 506 nm ($f = 0.10$) & 496 nm ($f = 0.14$) & 488 nm ($f = 0.09$) \\
452 nm ($f = 0.48$) & 434 nm ($f = 0.51$) & 440 nm ($f = 0.45$) & 419 nm ($f = 0.48$) \\
\end{tabular}
\end{center}

**Figure S4.17:** Representation of the spin densities for the four possible \textit{E-tbMC}^+ conformers, with their relative free energies as compared to \textbf{tbSP}^+ in kcal mol\(^{-1}\), as well as the computed four lowest vertical transition wavelengths (nm).

For the most stable conformer of \textit{E-tbMC}^+\(^{\text{**}}\), we show the density difference plots corresponding to the 759 and 452 nm transitions in Figure S4.18. As can be seen, the former is localised on one moiety with the oxygen center acting as the donor group, whereas the more intense band at 452 nm is related to a delocalised $\pi-\pi^*$ like transition.

**Figure S4.18:** Density difference plots corresponding to the vertical transitions at 759 and 452 nm of the most stable conformer of \textit{E-tbMC}^+\(^{\text{**}}\). See caption of Figure S4.17 for more details.