Redox and pH-Induced Switching in Solution and on Surfaces
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Redox Switching of a Spiropyran on Gold
**Chapter 5. Redox Switching of a Spiropyran on Gold**

**Abstract**

Immobilisation on a surface allows for instantaneous electrochemical switching of compounds. Non-destructive read-out of the state of the compound requires surface-sensitive techniques that provide structural information. Surface-enhanced Raman scattering (SERS) spectroscopy is an ideal tool, however, sufficient reference data is required for interpretation of spectra. In this chapter, the redox chemistry of a ditertbutyl-substituted spiropyran (MetbSPSS) was investigated both in solution and self-assembled on gold surfaces. Redox switching in its immobilised state was confirmed by electrochemical measurements at various temperatures. The relevant isomers involved in the oxidation-reduction switching cycle, both neutral and oxidised states, were characterised by Raman spectroscopy. These data provide a reference set for future measurements with which electrochemical switching on surfaces can be characterised by SERS spectroscopy.

**5.1. Introduction**

Redox-driven switching of molecules immobilised on a surface is a logical second step after establishing functionality in solution, as exemplified in studies on surfaces functionalised with well-known molecular switches, e.g., overcrowded alkenes,\(^1\) even aiming towards unidirectional motion,\(^2\) and dithienylethenes.\(^3,4\) When immobilised on a surface, the response to electrochemical switching is instantaneous due to the removal of diffusion-controlled contributions from the system. Electrochemically triggered degradation pathways observed in solution can potentially be avoided.

In this chapter, we build upon the redox switching of a ditertbutyl-substituted spiropyran (CltbSP) in solution discussed in Chapter 4.\(^5\) We investigate the electrochemical behaviour of an alkyldithiolane-substituted analogue (MetbSPSS, see Scheme 5.1) on smooth gold electrode surfaces and colloids, and compare it with cyclic voltammetry in solution of both CltbSP and MetbSPSS. Immobilisation on roughened gold would enable characterisation of the changes occurring during oxidation-reduction cycles by surface-enhanced Raman scattering (SERS) spectroscopy. However, obtaining spectral data of the expected species formed is a prerequisite.

The methyl-substituted, rather than the chloro-substituted analogue, was prepared for two reasons: Firstly, the methyl-substituted spiropyran is expected to have a less positive oxidation potential than the chloro-substituted analogue, due to the electron-donating properties of the methyl group. This should aid in preventing the protonation encountered during voltammetry for CltbSP, due to the less positive potentials required for oxidation.\(^5\) Secondly, a methyl group is less likely to undergo electrochemical reactions, compared to a chloro group, especially when the spiropyran is in a self-assembled monolayer (see also Chapter 3).\(^6\)
5.2. Results & discussion

Scheme 5.1: Redox chemistry of the methyl- and ditertbutyl-substituted spiropyran with a 1,2-dithiolane chain MetbSPSS reported here, and the name used for its self-assembled monolayers on gold (MetbSPSS-Au). tbSP = ditertbutyl-spiropyran; tbMC = ditertbutyl-merocyanine.

5.2. Results & discussion

5.2.1. Synthesis and Characterisation in Solid State

MetbSPSS was synthesised using previously reported procedures (see Experimental Details).

The solid-state ATR-FTIR and Raman spectra of MetbSPSS (λexc 785 nm) and CltbSP (λexc 1064 nm) are similar but with notable differences (Figures 5.1 and S5.1). As expected, MetbSPSS shows an additional band at 1735 cm⁻¹ due to the carbonyl of the ester of the dithiolane linker, which is pronounced in its FTIR spectrum, and small shifts in the position of the C=C stretching bands at ca. 1610 cm⁻¹. Similarly, the Raman spectra of the two compounds are largely the same with the Raman band at 1618 cm⁻¹ for MetbSPSS shifted to 1600 cm⁻¹ in the spectrum of CltbSP. Further differences between the solid-state Raman spectra appear as minor shifts of the bands at, among others, 1360 to 1346 cm⁻¹, and 1222 to 1232 cm⁻¹, for MetbSPSS and CltbSP, respectively.

5.2.2. Photochromism and Acidochromism in Solution

5.2.2.1. Photochromism

Irradiation of MetbSPSS at 300 nm at both -30 °C and -80 °C results in the generation of the ring-opened merocyanine form (MetbMCSS) (Figure 5.2). Photochemical switching is inefficient due to the low photo-stationary state that can be reached as well as competing photo-degradation ascribed to the presence of the dithiolane functional group (Figure S5.2). pH jumping experiments (vide infra) indicate that the conversion reached photochemically is ca. 10%.
Figure 5.1: (left) ATR-FTIR spectra of MetbSPSS (black) and CltbSP (red), and (right) solid-state Raman spectra of MetbSPSS ($\lambda_{\text{exc}}$ 785 nm, black) and CltbSP ($\lambda_{\text{exc}}$ 1064 nm, red). The FTIR spectra were offset for clarity. The Raman spectra were baseline corrected, normalised, and offset for clarity.

5.2.2.2. Acidochromism
The protonation-induced ring-opening to the protonated Z-merocyanine form and subsequent photochemical Z-E isomerisation are analogous to the behaviour described previously for the chloro-substituted analogue CltbSP (Figure 5.3).\(^5\) Likewise, thermally induced Z-E isomerisation is observed even at -30 °C, since addition of base to a mixture of MetbSPSS and TfOH, without irradiation at 365 nm, produces the E-merocyanine isomer, which is only formed from deprotonation of E-MetbMCSSH\(^+\). At -30 °C, the open form is stable for at least an hour (Figure 5.3), but at 20 °C, any MetbMCSS generated from the addition of base to a mixture of Z- and E-MetbMCSSH\(^+\) (PSS\(_{365}\)) undergoes rapid ring-closing within the mixing time (vide infra).

It is of note that the protonated merocyanine isomers of CltbSP and MetbSPSS have absorption maxima at longer wavelengths than those of nitro-substituted spiropyrans (NSP),\(^8\) for both the Z- and E-isomers. The opposite would be expected, considering the electron-withdrawing nitro-group on NSP that stabilises the merocyanine HOMO.
5.2.2. Photochromism and Acidochromism in Solution

Figure 5.2: UV-Vis absorption spectra of in CH$_3$CN at -30 °C of (left) MetbSPSS (60 µM) before (black) and after irradiation at 300 nm (magenta), and (right) MetbSPSS (20 µM) in butyronitrile at -80 °C before (black) and after irradiation at 300 nm (magenta). In both cases, the PSS$_{300\text{nm}}$ was not reached due to (left) photodegradation related to the dithiolane functional group, and (right) formation of ice crystals at -80 °C resulting in scatter affecting the baseline.

Figure 5.3: UV-Vis absorption spectra of MetbSPSS (60 µM) in CH$_3$CN (black) at (left) 20 °C after addition of TfOH (3 eq., yellow solid), and after subsequent sequential irradiation at 365 nm (orange) and 455 nm (yellow, dashed), and (right) -30 °C after addition of TfOH (2 eq., yellow), immediately after subsequent addition of NaOAc (10 eq., magenta, solid), and after 13 minutes (magenta, dashed). The latter spectrum is evidence for thermal ring-closing.
5.2.2.3. Thermal Relaxation of Merocyanine to Spiropyran Form

As discussed above for MetbSPSS, and previously for CltbSP, the addition of base to the E-protonated merocyanine isomer generates the neutral merocyanine isomer, which is present only transiently at room temperature, undergoing rapid ring-closing to the spiropyran isomer within the time taken for mixing with the added base (Figure 5.3). An accurate determination of the kinetics of this process for CltbMC was made by pH jumping using stopped-flow with rapid mixing of the base and the protonated merocyanine (Figure 5.4), which yielded a 1.00 s lifetime of CltbMC at room temperature. Laser flash photolysis experiments showed that the ring-closing of the E-merocyanine isomer to the spiropyran from, followed by UV-Vis transient absorption (TA) spectroscopy (Figure 5.5), proceeded with a lifetime of ca. 0.5 s, corresponding well with that determined from stopped-flow measurements.

Figure 5.4: UV-Vis absorption spectra after rapid mixing of equal volumes of a mixture of Z- and E-CltbMCH+ in CH3CN (generated from CltbSP (120 µM) with TfOH (1 eq.) at PSS365nm) and NaOAc (10 eq.) in CH3CN/H2O (9:1) showing the thermal ring-closing of E-CltbMC (magenta to black). (inset) Single-exponential fit of the decrease in area of the wavelength range where E-CltbMC absorbs.

Figure 5.5: UV-Vis transient absorption spectra of CltbSP in CH3CN with ns-pulsed excitation (0.5 Hz) at 355 nm. The experiment was performed without stirring since this can have a pronounced effect on measured lifetimes of around this value.

5.2.2.4. SERS Spectroscopy with Aggregated Au Colloid

SERS spectra (λexc 785 nm) of MetbSPSS obtained by aggregation of citrate-stabilised colloidal gold were only observed after addition of aq. H2SO4, with the appearance of several bands, including an intense band at 1585 cm⁻¹ (Figure 5.6). During acquisition of Raman spectra at 785 nm, a band at 1525 cm⁻¹ appeared, hinting at Z-E isomerisation...
induced by the laser as seen before for MeNSPSS (see Chapter 3). Irradiation at 365 nm (ex situ) of the sample at pH = 0 did not induce further changes. Subsequent addition of concentrated KOH (aq.), to generate the deprotonated merocyanine isomer $E$-MetbMCSS, resulted in the appearance of a number of new bands, with notable ones at 1610, 1365, 1285, and 980 cm$^{-1}$. These marker bands will be useful as reference material for SERS data obtained of redox switching measurements on gold.

![SERS with Au colloid](image)

**Figure 5.6:** SERS spectra ($\lambda_{\text{exc}}$ 785 nm) of MetbSPSS on Au colloid in H$_2$O after addition of conc. H$_2$SO$_4$ (aq.) (yellow), after subsequent acquisition of spectra at 785 nm (orange), and after subsequent addition of conc. KOH (aq) (magenta). *Raman bands of plastic cuvette.

### 5.2.2.5. Resonance Raman Spectroscopy of Protonated and Deprotonated Merocyanine Isomers

The tbMC isomer of both MetbMCSS and CltbMC was generated by the sequential addition of acid, irradiation at 365 nm, and addition of base, at -30 °C. Taking this approach allows for generation of higher concentrations of the merocyanine form than possible by irradiation alone at -30 °C (Figure 5.2). Raman spectra recorded at 633 nm are obscured by emission from the tbMC isomer, with ring-closing evident from the concomitant decrease in absorbance and emission intensity. Excitation at 405 nm revealed several (resonantly-enhanced) Raman bands of the merocyanine isomer.
Initially, with acid present, solutions of CltbSP show several resonantly-enhanced Raman bands at 1595, 1540, 1245, 1125, 1000, and 980 cm$^{-1}$, which do not change significantly in intensity upon irradiation at 365 nm, due to $Z$-$E$ isomerisation of $Z$-CltbMCH$^+$ induced by the 405 nm laser within the confocal volume already (Figure 5.7). Addition of base (NaOAc) results in the disappearance of bands assigned to CltbMCH$^+$, and the appearance of new, relatively weak, bands at 1617 and 1580 cm$^{-1}$.

For MetbSPSS, a few differences are apparent in the resonantly-enhanced Raman spectra at 405 nm of the protonated merocyanine isomer, notably the bands at 1530 (instead of at 1540), 1485, 1195, and 1106 cm$^{-1}$. Again, irradiation at 365 nm did not induce any further changes to the spectrum. After subsequent addition of base to the solution, several strong Raman bands appeared, that we assign to the neutral merocyanine isomer (MetbMCSS), at 1620, 1585, 1540, 1190, 1140, and 1000 cm$^{-1}$.
The extra Raman bands observed for the measurement with MetbSPSS are likely partly due to the approximately four times higher concentration of MetbMCSS generated by the acid-base cycle (Figure 5.7). However, the difference in substitution on the indolino unit plays a role too, evidenced by the differences in the Raman spectra obtained at 405 nm of CltbMCH\(^+\) and MetbMCSSH\(^+\). These data indicate that solely MetbSPSS can provide reliable reference spectra of the protonated diterbutyl-merocyanine isomers for comparison with SERS spectra of MetbSPSS-Au.

A comparison of the Raman spectra at 405 nm after an acid-base cycle with those on Au colloid reveals a common Raman band at 1530 cm\(^{-1}\) that we accordingly assign to \(E\)-MetbMCSSH\(^+\), as well as several to MetbMCSS: 1615, 1500, and 1140 cm\(^{-1}\).

### 5.2.3. Electrochemistry and Spectroelectrochemistry in Solution

#### 5.2.3.1. Cyclic Voltammetry

The cyclic voltammetry of MetbSPSS is similar to that of CltbSP (Figure 5.8). Electrochemically reversible oxidation of the closed form occurs at 0.9 V which, at lower scan rates such as 1.0 V/s, is out-competed by ring-opening to the merocyanine radical cation. The subsequent reduction of MetbMCSS\(^{++}\) at 0.5 V is accompanied by a corresponding oxidation that is not readily apparent, due to the low concentration of the generated MetbMCSS. At -20 °C, the rate of ring-opening in the oxidised state has reduced sufficiently to see essentially fully reversible oxidation of MetbSPSS at 0.9 V at a relatively low scan rate, 1.0 V/s. Overall, the redox behaviour of MetbSPSS in solution corresponds well to that of CltbSP, apart from the relatively greater sensitivity to protonation during cyclic voltammetry for MetbSPSS.

![Figure 5.8](image-url)

**Figure 5.8:** Cyclic voltammograms of MetbSPSS (1 mM) in solution at (left) 20 °C in CH\(_3\)CN (0.1 M TBAPF\(_6\)) and (right) -20 °C in DCM (0.1 M TBAPF\(_6\)). The CVs were not corrected for uncompensated resistance (iR drop), except for that at 100 V/s.
5.2.3.2. UV-Vis Absorption Spectroelectrochemistry

UV-Vis spectroelectrochemistry of MetbSPSS was carried out using a porous carbon (reticulated vitreous carbon, or rvc) working electrode, since the use of a platinum working electrode resulted in mainly the appearance of an absorption band at 435 nm due to solution acidification and formation of E-MetbMCSSH\(^+\) (Figure 5.9). With the carbon working electrode, electrolysis at 1.0 V vs Ag/AgCl initially resulted in the appearance of an absorption band at 515 nm, as well as several NIR bands at 800, 900, and 1000 nm, assigned to the merocyanine radical cation. Concomitantly, the absorption band at 435 nm of E-MetbMCSSH\(^+\) appears also and persists even after holding the potential at 0.2 V to reduce the merocyanine radical cation.

At -20 °C, the initial formation of MetbMCSS\(^{**}\) is apparent, with again the eventual generation of E-MetbMCSSH\(^+\), evidenced by its residual absorption at 435 nm after an oxidation-reduction cycle (Figure 5.9). The changes in UV-Vis absorption of MetbSPSS upon oxidation and subsequent reduction indicate similar redox behaviour to that reported for CltbSP, i.e. oxidation followed by ring-opening; reduction followed by ring-closing, but with one notable difference: the increased propensity for protonation of MetbSPSS compared to CltbSP.

![UV-Vis absorption spectra](image)

Figure 5.9: UV-Vis absorption spectra in a 5 mm pathlength cuvette of (left) MetbSPSS (1 mM) in CH\(_3\)CN (0.1 M TBAPF\(_6\)) at 20 °C before (black), during bulk electrolysis with a porous carbon electrode at 1.0 V (light blue-cyan), and subsequently at 0.2 V (beige-orange), and (right) MetbSPSS (130 μM) in DCM (0.1 M TBAPF\(_6\)) before (black), at 0.9 V (cyan), and after subsequent application of 0.2 V vs Ag/AgCl (orange).

5.2.3.3. Resonance Raman Spectroscopy of Oxidised Species

Chemical oxidation of CltbSP with Magic Blue (MB) yields CltbMC\(^{**}\).\(^5\) Raman spectra recorded at 785 nm were dominated by intense background fluorescence, possibly originating from the merocyanine form. At 1064 nm, which is resonant with the long
wavelength absorption bands, interference from fluorescence was avoided and Raman spectra of both CltbSP and MetbSPSS after addition of 1 equivalent of Magic Blue (Figure 5.10), i.e. of the merocyanine radical cations CltbMC\(^+\) and MetbMCSS\(^+\), respectively, showed resonantly-enhanced bands at 1595, 1569, 1410, 1325, 1212, 1180, and 1110 cm\(^{-1}\).

**Figure 5.10:** Raman spectra (\(\lambda_{\text{exc}}\) 1064 nm) of MetbMCSS\(^+\) (cyan) and CltbMC\(^+\) (light blue), generated upon addition of MB (1 eq.) to MetbSPSS (1 mM, dark gray) and CltbSP (1 mM, light gray), respectively, in CH\(_3\)CN at -25 °C. See Figure 5.9 and Chapter 4 for corresponding UV-Vis absorption spectra.

The notable independence of the Raman spectra of CltbMC\(^+\) and MetbMCSS\(^+\) at 1064 nm of substitution on the indolino unit, i.e. the chloro- and methyl-groups, is opposite from that observed in solid state of the neutral closed spiropyrans (Figure 5.1), and indicates that the absorption band at 1000 nm is a transition centered on the benzopyran unit for both species. This is in agreement with the calculations previously performed for the isomers of CltbSP\(^5\) where the electron density difference plot of the low-energy vertical transition at 743 nm of CltbMC\(^+\), corresponding to the experimental absorption in the 750-1050 nm region, shows that it is localised on the benzopyran moiety with the oxygen atom serving as the donor group.

These Raman bands serve as marker bands of the ditertbutyl-merocyanine radical cation in future SERS spectroscopy measurements of MetbSPSS-Au during electrochemical oxidation on a roughened gold surface. Of the four known species involved in the redox switching of ditertbutylspiropyrans, the oxidised closed form remains to be characterised by Raman spectroscopy. The inherent instability of the ditertbutyl-
spiropyran radical cation complicates the Raman characterisation, but we have shown earlier (in Chapter 4) that the radical cation should be sufficiently long-lived at -60 °C to allow for the acquisition of Raman spectra. Since CltbSP** has electronic absorption at the same range of wavelengths as its nitro-substituted analogue MeNSP, resonance enhancement is likewise expected at 457 nm (see Chapter 3).

**5.2.4. Electrochemistry on Gold Surfaces**

**5.2.4.1. Cyclic Voltammetry on Smooth Gold**

Cyclic voltammetry of MetbSPSS-Au (SAMs) on a smooth (i.e. non-roughened) gold electrode gives us insight into the redox behaviour of this spiropyran on a gold surface (Figure 5.11). The combined cyclic voltammetric data at room temperature and lower temperatures indicate similar behaviour to that of MetbSPSS (and CltbSP) in solution (Figure 5.8). An electrochemically reversible oxidation at around 0.9 V (most clearly observed in the data at -20 °C), is followed by a chemical reaction that produces a redox-active species with a reversible reduction at around 0.6 V. The redox wave at 0.6 V is only observed in the 2nd cycle, and only at certain scan rates low enough to provide sufficient time for MetbSPSS**-Au to form. The redox switching observed in solution for MetbSPSS**-Au is relatively unperturbed when incorporated into self-assembled monolayers on roughened gold, with, notably, a greater apparent stability of the neutral merocyanine MetbMC isomer on the surface than in solution.

**Figure 5.11:** Cyclic voltammograms of MetbSPSS-Au SAMs at various scan rates (left) on a smooth gold bead in CH$_3$CN (0.1 M TBAPF$_6$) at 20 °C (1st and 2nd cycle) and (right) on a teflon-shrouded smooth gold working electrode in DCM (0.1 M TBAPF$_6$) at -20 °C (2nd cycles).
5.3. Conclusions

We have shown that the previously reported CltbSP is not the only electrochemically switchable spiropyran and that this motif of two tertbutyl-groups is a reliable strategy to obtain redox switching of a spiropyran. Furthermore, we have performed initial investigations into the electrochemically-driven switching of MetbSPSS-Au self-assembled on gold, and have shown that it indeed undergoes the oxidation-reduction switching cycle in this immobilised state as well.

The redox switching of ditertbutyl-spiropyans on roughened gold surfaces will be further investigated by SERS spectroscopy. The Raman spectral data reported in this chapter of the various relevant isomers and oxidation states of MetbSPSS and CltbSP, will aid in the elucidation of the redox and chemical reactions occurring during an electrochemically-driven oxidation-reduction cycle of MetbSPSS-Au.

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Bibliography


**Experimental Details**

**Synthesis**

1,2-dithiolane-substituted methyl-diterbutylspiropyran *MetbSPSS* was synthesised according to previously reported procedures for *CltbSP*, and *MeNSPSS* (see Chapters 3 and 4).

![Synthesis of MetbSPSS from hydroxyethyl-substituted methyl-diterbutylspiropyran (MetbSP-EtOH) and thioctic acid.](image)

5-(1,2-dithiolan-3-yl)pentanoic acid (thioctic acid, 0.1569 g, 0.727 mmol, 1 equiv.), 2-(6,8-di-tert-butyl-3',3',5'-trimethylspiro[chromene-2,2'-indolin]-1'-yl)ethan-1-ol (MetbSP-EtOH, 0.3153 g, 0.727 mmol, 1 equiv.) and 4-dimethylaminopyridine (DMAP, 15 mg, 0.123 mmol, 0.17 equiv.) were dissolved in anhydrous dichloromethane (75 mL) under inert atmosphere (N$_2$). The mixture was cooled to 0 °C and N,N'-dicyclohexylcarbodiimide (DCC, 0.1516 g, 0.727 mmol, 1 equiv.), dissolved in anhydrous dichloromethane (50 mL), was added over 1 h using a dropping funnel. The mixture was stirred at room temperature (20 °C) for 22 h, after which it was stored at -25 °C for 3 days. The precipitated side-product N,N'-dicyclohexylurea (DCU) was filtered off using a P4 glass filter. The product was concentrated *in vacuo* and purified by column chromatography (dichloromethane/pentane 4:1), yielding a yellow sticky oil (194 mg) 43 % of 2-(6,8-di-tert-butyl-3',3',5'-trimethylspiro[chromene-2,2'-indolin]-1'-yl)ethyl 5-(1,2-
dithiolan-3-yl)pentanoate (MetbSPSS). The product was characterised by $^1$H and $^{13}$C NMR.

$^1$H NMR (400 MHz, acetonitrile-\textit{d}_3): \delta 7.21 (d, J = 2.5 Hz, 1H), 7.05 (d, J = 2.4 Hz, 1H), 7.00 - 6.90 (m, 3H), 6.51 (d, J = 7.8 Hz, 1H), 5.82 (d, J = 10.2 Hz, 1H), 4.20 - 4.08 (m, 2H), 3.55 (dq, J = 14.6, 6.1 Hz, 1H), 3.31 - 3.06 (m, 4H), 2.47 - 2.37 (m, 1H), 2.28 (s, 3H), 1.75 - 1.33 (m, 7H), 1.29 (m, 12H), 1.15 (s, 3H), 1.10 (s, 9H).

$^{13}$C NMR (101 MHz, acetonitrile-\textit{d}_3): \delta 175.7, 152.6, 148.0, 144.6, 139.5, 137.5, 133.2, 130.8, 130.1, 127.2, 125.0, 121.1, 120.1, 108.7, 107.3, 65.3, 59.0, 53.7, 45.6, 42.7, 40.9, 36.3, 33.5, 31.9, 31.1, 28.7, 27.1, 22.8, 21.6.
Physical Methods

Reagents and solvents were obtained from Sigma-Aldrich or Tokyo Chemical Industry (TCI) Europe and used as received unless stated otherwise. NMR spectra were obtained on a Bruker 400 spectrometer. Chemical shifts $\delta$ are reported in parts per million (ppm) with respect to tetramethylsilane and referenced to the residual solvent (CD$_2$CN), and coupling constants are reported in hertz. Multiplicities are denoted as $s =$ singlet, $d =$ doublet, and $m =$ multiplet.

UV-Vis absorption spectra at room temperature were recorded on an Analytik Jena Specord 600 spectrometer or an Agilent Technologies Cary 8454 spectrometer, and spectra at lower temperatures were recorded in a Quantum Northwest temperature-controlled cuvette holder or in a Unisoku Cool Spek USP-203-B cryostat. Irradiation at 300, 365 and 455 nm was provided by Thorlabs LEDs M300L4 (26 mW) mounted with a lens tube, M365LP1-C5 (435 mW), and M455L3-C5 (400 mW), respectively.

Electrode potential was controlled with either a CHI760c or CHI604E potentiostat. Cyclic voltammetry in solution was performed with a platinum wire counter electrode (CE) and a Hg/HgSO$_4$ (CHI151) or Ag/AgCl wire reference electrode (RE). For cyclic voltammetry on non-roughened gold, a teflon-shrouded gold working electrode (Au WE, CHI101) was electrochemically cleaned by 20 cyclic voltammetric cycles in 0.5 M H$_2$SO$_4$ between -0.6 V and 1.2 V vs Hg/HgSO$_4$, and gold beads were prepared by melting gold wire in a butane flame. Self-assembled monolayers (SAMs) formed upon immersion of the Au WE or gold bead in acetonitrile or dichloromethane containing MetbSPSS (1-2 mM). Cyclic voltammetry of 2-Au on non-roughened gold was performed in dichloromethane or acetonitrile (0.1 M TBAPF$_6$) with a Pt wire CE and Hg/HgSO$_4$ or Ag/AgCl wire RE. The potential of Hg/HgSO$_4$ vs SCE (saturated calomel electrode, CHI150) was measured at 0.4 V in CH$_3$CN (0.1 M TBAPF$_6$), and the potential of Ag/AgCl was defined as 0.04 V vs SCE.

Raman spectra at 785 nm of samples in H$_2$O with Au colloid were recorded using an integrated laser probe (500 mW, Cobolt Lasers) fiber-coupled to an Andor Shamrock SR-163 spectrograph and Andor iVac DR-324B-FI-560 camera and 200 line/mm grating with 730 nm blaze. The gold colloid suspension in water was prepared according to the citrate method.9

Solid-state Raman spectra at 785 nm were recorded using an Olympus BX51 microscope equipped with a fibre-coupled laser (BT785, ONDAX) and a fibre-coupled Shamrock163i spectrograph and iVac-DLL CCD camera and 235 line/mm grating with 750 nm blaze. The power at the sample was varied from 1 to 300 mW and was typically 2-5 mW.

Raman spectroscopy at 1064 nm (500 mW, Cobolt Rumba) was performed using a home-built setup in a 180° backscattering arrangement with the Raman scattering collected by a 10x microscope objective (for solid samples, Olympus LMPlan N) or a plano-convex lens (for solutions, 2.5 cm diameter, $f = 3.5$ cm). The collimated light was then passed through the appropriate long-pass edge filter (Semrock) after which it was focused by a second plano-convex lens (2.5 cm diameter, $f = 40$ mm) into an Andor Kymera spectrograph with a 600 line/mm grating blazed at 830 nm. Acquisition was
Experimental Details

performed with an Andor iDus InGaAs camera.

Raman spectra in solution at 405 nm (40 mW at source, ONDA LM-405-PLR-40-1) excitation wavelength were recorded in a 180° backscattering arrangement with the Raman scattering collected by a plano-convex lens (2.5 cm diameter, \( f = 7.5 \) cm). The collimated light was then passed through the appropriate long-pass edge filter (Semrock) after which it was focused by a second plano-convex lens (2.5 cm diameter, \( f = 15 \) cm) into an Andor Shamrock 500i-D7 spectrograph with a 2400 line/mm grating blazed at 300 nm. Acquisition was performed with an Andor iDus DV420A-BU2 CCD camera.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra in solid state were recorded using a JASCO 4700 FTIR spectrometer with an ATR attachment.

Stopped flow UV-Vis absorption spectroscopy experiments were performed with an Applied Photophysics RX2000 Rapid Kinetics Spectrometer Accessory mixing unit and a fibre-coupled cuvette holder. The light was collected with an Avantes AvaSpec spectrometer, and the trigger pulses were generated by a Tektonix DPO4032 oscilloscope and the time stamps logged by a Moku GO data logger.

Nanosecond transient absorption (TA) spectroscopy was performed using a laser system consisting of an EKSPLA Nd:YAG laser with integrated optical parametric oscillator, which allows for selection of laser wavelengths from 300 to 1064 nm. A Xe flashlamp is used as probe light source. The beam is collimated and passed through a 50:50 beamsplitter. One beam is passed through the sample and overlaps with the laser pulse to the spectrograph. The other beam is passed directly into the spectrograph onto the detector (Princeton Instruments PI-MAX iCCD), with the image positioned below that of the first beam. This allows for simultaneous referencing, so that intensity fluctuations in the probe pulse can be corrected for. The change in absorbance signal, \( \Delta A \) is calculated according to the following equation:

\[
\Delta OD = -\log\left(\frac{I_{\text{probe}}I_{\text{ref}}}{I_{\text{probe+pump}}I_{\text{ref}}}ight)
\]
Figure S5.1: (left) full-width ATR-FTIR spectra of MetbSPSS and CltbSP, and (right) full-width solid-state Raman spectrum of MetbSPSS ($\lambda_{\text{exc}}$ 785 nm). The Raman spectrum of CltbSP shown in Figure 5.1 is already the full recorded spectral width. The IR and Raman spectra were baseline-corrected and off-set for clarity.

Figure S5.2: UV-Vis absorption spectra of MetbSPSS (60 µM) in CH$_3$CN at -30 ºC (black) during irradiation at 300 nm at maximum absorbance of the merocyanine isomer (purple, solid) and after 15 min (purple, dashed), after which irradiation was ceased, and 20 min later (blue) showing photo-degradation and a residual broad absorption band at 430 nm.