Optically responsive switches
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Chapter 5

Position and orientation control of a photo- and electrochromic dithienylethene using a tripodal anchor on gold surfaces

In this chapter, a tripodal system for anchoring photochromic dithienylethenes on gold surfaces is reported. The self-assembled monolayers of the tripod functionalized dithienylethene were characterized by cyclic voltammetry and surface-enhanced Raman spectroscopy (SERS). These data are compared with solution studies, solid state Raman spectroscopy, and density functional theory (DFT) calculations. It is shown that the tripod functionalized dithienylethene forms stable monolayers on gold in which all three legs of the tripod are adsorbed via the thiol units, thus providing a fixed position and orientation of the dithienylethene moiety with respect to the surface. Importantly, immobilization in this way allows for retention of both the photochemical and electrochemical functionality of the dithienylethene unit and reduces the photochemical fatigue observed in solution.*

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5.1 Introduction
The design of solid-state molecular electronic and photonic devices incorporating photochromic or redox-active molecules is a topic of continuing interest. Several aspects pertaining to the photochromic or redox-switchable material present challenges in the design of such devices. Firstly, the switchable material should be incorporated with maximum control over its position and its orientation with respect to the surface it is interfaced with. Secondly, undesirable interactions between the photo/electro-switchable molecules and the bulk substrate should be minimized so that the responses to external stimuli observed in solution are retained when immobilized. An important method for incorporating organic molecules into devices is through the formation of self-assembled monolayers (SAMs). Responsive compounds can undergo self-assembly by introducing functional groups that show affinity towards (or can react with) the substrate on which the self-assembly is desired.

The self-assembly of compounds on a solid surface typically involves the use of a linker that provides a single anchoring point to the substrate. Such an anchoring strategy has been used widely for the tethering of photochromic units to a wide range of substrates, such as gold, SiOx, and ITO. However, while effective in anchoring the compound to the substrate, such an approach does not meet the first requirement outlined above as it does not dictate the orientation of the switchable molecule with respect to the surface. This may allow a substantial part of the self-assembled monolayer to lie flat on the surface, which can result in a disorganized SAM. Furthermore, proximity to a surface can result in loss of functionality through interactions between the surface and the monolayer, in which case the second requirement is not met. One example of such interactions is the quenching of the electronic excited states of a photochromic compound reducing or even blocking completely its photochemical responsiveness.

Our earlier findings prompted us to consider alternative strategies for tethering a photochromic switching unit to a gold surface that meet the requirements outlined above. Here, we utilize a tripodal structure reminiscent to that employed by Tour and co-workers. This anchoring unit consists of three thiol-substituted diphenylethyne units attached to a silicon atom (Scheme 5.1). This design was chosen over other tripodal structures reported previously, because the silicon atom should reduce potential long distance interactions.
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through-bond interactions with the gold substrate. In addition, the relatively large structure increases the separation of the switching unit from the surface by an estimated 7 Å (based on density functional theory calculations, vide infra), thus minimizing through-space interactions with the substrate. In contrast to the design by Tour and co-workers, which has methylene spacers connecting the thiol functionalities to the phenyl groups, we have chosen to attach the thiol functionalities directly to the phenyl groups. The rationale for this design choice is that aryl thiols adsorb on gold much more readily, without the need for an exogenous base to cleave the acetate protecting group prior to self-assembly.

Scheme 5.1 Structure and photochemical switching between open and closed forms of dithienylethene 5.1 when immobilised on a gold surface.

The switching unit chosen for attachment to the tripodal anchoring unit is a diphenyl substituted dithienyl-perhydrocyclopentene. Dithienylethenes are a popular class of photochromic molecules that can switch reversibly between an closed and open isomer by irradiation with UV and visible light, respectively (Scheme 5.2). Important characteristics are that the two isomers can be addressed independently due to differences in their UV/vis absorption spectra, they are thermally stable, and display distinct electronic properties because of differences in their π systems. In addition, it has been shown that switching can for certain systems also be induced electrochemically. A drawback of dithienylethenes however is that, as has been reported for a few specific designs, they can display a small amount of switching fatigue that becomes noticeable
upon repeated switching. Irie and co-workers have shown that, for a related system, switching fatigue was the result of the conversion of the closed form isomer to a photoinactive isomer (Scheme 5.2). In the present study, the importance of this process will be addressed as well.

Scheme 5.2  Photochemical switching of a dithienylethene and the irreversible formation of a photochemically inert isomer.

Herein, we report the synthesis and characterization, and the electro- and photochemical properties of dithienylethene 5.1 in solution and as SAMs on gold substrates (Scheme 5.1). We demonstrate that the tripod structure of 5.1 enables the formation of SAMs on gold surfaces in which all three thiol functionalities are adsorbed. The SAMs formed were found to be stable under the conditions applied for photochemical switching and, to a lesser extent, electrochemical switching. Furthermore, we demonstrate that 5.1 displays reversible photochemical and electrochemical switching, both in solution and on gold substrates. Finally, although 5.1 displays photochemical switching fatigue in solution, this is not observed during photochemical switching of SAMs of 5.1 on gold surfaces.

5.2 Results and discussion

5.2.1 Synthesis of dithienylethene 5.1

Dithienylethene 5.1 was synthesized using a convergent synthetic route (Scheme 5.3). The synthesis of the tripod started with the synthesis of thioether 5.4, which was prepared by first converting 1,3-diiodobenzene to thioether 5.2 by treatment with tert-butylthiol and Pd(PPh₃)₄. A Sonogashira cross-coupling of 5.2 with trimethylsilylacetylene (TMS-acetylene) was then used to obtain thioether 5.3 in 85 % yield. Removal of the TMS group of 5.3 by treatment with TBAF provided 5.4 in good yield. It should be noted that introduction of the TMS-protected acetylene group first was attempted, however, subsequent introduction of the thioether group was found to result in undesirable reaction of the acetylene.
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Scheme 5.3 Synthesis of dithienylethene 5.1.

The tripod was further constructed with 1,4-diiodobenzene, which was lithiated and then treated with tetraethoxysilane, providing triiodide 5.5. A Sonogashira cross-coupling of 5.5 with thioether 5.4 was used to prepare trithioether 5.6 in 87 % yield. The phenyl spacer connecting the dithienylethene moiety to the tripod was introduced by the lithiation of 1,4-diiodobenzene and subsequent treatment with 5.6, which provided trithioether 5.7 in 68 % yield.

The dithienylethene moiety was synthesized starting from a dichloro-substituted dithienylethene precursor.38 Successive treatment with n-BuLi and tributylborate provided the crude boronic ester, which was used in a Suzuki cross-coupling reaction with 4-bromotoluene in order to obtain the tolyl-substituted dithienylethene 5.8. After conversion of 5.8 to the corresponding boronic ester as above, a Suzuki cross-coupling reaction with trithioether 5.7 afforded dithienylethene 5.9 in 87 % yield. Finally, conversion of the thioether groups to
thioester groups by treatment with BBr₃ and acetyl chloride provided dithienylethene 5.1 in 45 % yield.

5.2.2 Photochemical switching of 5.1 in solution
The photochemical behavior of dithienylethene 5.1 in solution was studied by UV/vis absorption and ¹H NMR spectroscopy, and cyclic voltammetry. The UV/vis spectrum of the open form isomer of 5.1 (5.1ₒ) in toluene displayed several strong absorption bands < 370 nm and no absorption > 370 nm (Figure 5.1a). Irradiation of the sample at 365 nm resulted in the appearance of a broad absorption with a maximum at 542 nm as well as a weaker absorption with a maximum at 373 nm. These spectral changes are characteristic of the formation of the closed isomer 5.1_c.[28] Irradiation at > 440 nm reversed these spectral changes although the broad absorption in the visible region did not disappear fully. Repeated switching of the sample by alternating between irradiation at 365 nm and > 440 nm showed an increase in the intensity of this residual absorption with each cycle (Figure 5.1b).

Figure 5.1 Photochemical switching of dithienylethene 5.1 in toluene monitored by UV/vis absorption spectroscopy. a) Absorption spectra of 5.1ₒ (solid) and 5.1ₚₜ₅₅₆₆₅ (dashed) in toluene. b) Absorbance at 542 nm measured over 5 switching cycles. Irradiation at 365 nm was carried out such that 99 % of the absorbance at PSS₃₆₅ₙ₅₆₆₅ was reached in the first cycle.

The photochemical switching fatigue observed for 5.1 is attributed to the conversion of 5.1_c into its isomer 5.1_byprod (Scheme 5.4). The visible absorption band of 5.1_byprod was found to have its maximum 527 nm; a minor hypsochromic shift compared to the absorption spectrum of 5.1_c. This is in agreement with dithienylethene switching fatigue reported by Irie and co-workers, previously.[36]
Scheme 5.4 Conversion of dithienylethene 5.1c into the photochemical byproduct 5.1byprod. The structure shown is inferred by comparison with the 1H NMR and UV/Vis absorption spectra of an analogous compound reported by Irie and coworkers.36

The photochemical switching was also monitored by 1H NMR spectroscopy (Figure 5.2). Irradiation of 5.1o in CD2Cl2 at 365 nm resulted in the formation of a second isomer identified as 5.1c. The most significant spectral changes observed upon UV irradiation were the shifts in the signals of the hydrogens of the thiophene groups from 7.13 and 7.01 ppm to 6.54 and 6.42 ppm (due to loss of aromaticity of the thiophenes) and the shifts of the hydrogens of the central cyclopentene group from 2.84 and 2.13–2.05 ppm to 2.51–2.46 and 1.93–1.85 ppm (due to the rearrangement of the compound’s π system).

Figure 5.2 Photochemical switching of 5.1 in CD2Cl2 monitored with 1H NMR spectroscopy. 1H NMR spectra of a) 5.1o before irradiation, b) after irradiation at 365 nm, and c) after subsequent irradiation at > 440 nm.
Continued irradiation at 365 nm resulted in the appearance of a second isomer identified as 5.1byprod. Compared to the spectrum of 5.1c, 5.1byprod exhibited the signals of the hydrogens of the thiophenes shifted slightly, from 6.54 and 6.42 ppm to 6.56 and 6.43 nm, indicating that the thiophenes in this species have not regained their aromaticity (which is consistent with the expected molecular structure). Furthermore, the signals from the two central methyl groups displayed a shift from 2.00 ppm to 2.55 and 2.50 ppm. This downfield shift of the methyls for 5.1byprod is in agreement with findings by Irie and co-workers. Subsequent irradiation at > 440 nm resulted in the disappearance of 5.1c and reappearance of 5.1o but did not change the intensity of the signals of 5.1byprod in the sample.

It has been shown previously that dithienylethenes can undergo opening and closing both photochemically and electrochemically. This was found to be the case for dithienylethene 5.1 also (Figure 5.3). As with structurally related dithienylethenes, an irreversible oxidation of the open form, 5.1o, was observed at 1.1–1.2 V (Figure 5.3b) and is assigned to a two-electron oxidation that is followed by cyclisation of the dithienylethene unit to the closed form (Figure 5.3a). Two reduction waves at 0.72 and 0.38 V were observed on the return cycling from 1.1 to 0.0 V, which are assigned to the reduction of 5.1c to 5.1c¬ and, finally, to 5.1c. The two corresponding oxidation waves (5.1c to 5.1c+) were observed in the second and subsequent cycles, at 0.44 and 0.78 V. Repeated cycling caused the intensity of the redox waves of 5.1c to increase until diffusion to and from the electrode was equilibrated.

Figure 5.3 a) Electrochemical and photochemical switching processes typically observed for dithienylethenes. b) Cyclic voltammogram of dithienylethene 5.1o in DCM/0.1 M TBAPF6, recorded at 0.5 V s⁻¹ with a glassy carbon working, Pt counter, and SCE reference electrode.
5.2.3 Solid state Raman spectra of 5.1

Raman spectra (Figure 5.4) were recorded of dithienylethene 5.1o in the solid state as well as for a sample of 5.1o that was irradiated at 365 nm in solution to its photostationary state (PSS) and subsequently concentrated in vacuo to a solid (denoted 5.1PSS365). The spectrum of 5.1c was obtained by a scaled subtraction of the spectrum of 5.1o from the spectrum of 5.1PSS365. Comparing the spectra of 5.1o and 5.1c, it was found that the bands at 2224, 1586, and 1152 cm⁻¹ are present in both spectra and that their relative intensities remain constant. As such, these are attributed to the non-photoactive part of the molecule, i.e. the tripod moiety. The region 1520–1200 cm⁻¹ of the spectra of 5.1o and 5.1c shows several differences. Bands in this region are thus attributed to the dithienylethene moiety. The most pronounced of these bands is a band at 1506 cm⁻¹ in the spectrum of 5.1c. This intense band was observed in earlier Raman studies of dithienylethenes and is assigned as a stretching vibration of the molecule’s conjugated polyene backbone.

![Figure 5.4 Raman spectra of dithienylethenes 5.1o (top), 5.1PSS365 (middle), and 5.1c (bottom, obtained by subtraction of the top and middle spectra).](image)

In order to confirm that the recorded spectra correspond to isomers of 5.1 as well as to elucidate their spectral features, Raman spectra of 5.1o and 5.1c were calculated using density functional theory (Figure 5.5). The B97-D3 functional and def2-SVP basis set were used for the calculation of the geometry and the vibrational modes. Raman activities were calculated using the B3LYP hybrid functional (using VWN formula 1 RPA correlation) and def2-SVPD basis set. A scaling factor of 0.998 was applied to the calculated wavenumbers in order to improve correspondence between the theoretical and
experimental spectra. It was found that the calculated spectra of $1_0$ and $1_c$ resemble the experimental spectra closely. Analysis of the calculated vibrational modes supports the assignment of modes present in the recorded spectra. The Raman spectrum of $5.1_{byprod}$ was also calculated (Figure 5.5, bottom spectrum). This isomer is predicted to show Raman scattering at 1559 and 1518 cm$^{-1}$, both originating from the dithienylethene moiety.\textsuperscript{47}

\textbf{Figure 5.5} Experimentally obtained (red) and calculated (blue) Raman spectra of dithienylethenes $5.1_0$ (top), $5.1_c$ (middle), and $5.1_{byprod}$ (bottom).

\textbf{5.3.4 Surface-enhanced Raman spectroscopy}

Surface enhanced Raman (SERS) spectra of $5.1_0$ or $5.1_{PSS65}$ obtained by mixing with aggregated colloidal gold were recorded at 785 nm (Figure 5.6). The recorded spectra were found to display significant differences compared to the Raman spectra of the solid compounds (Figure 5.4). In particular, the alkyne stretching band at 2224 cm$^{-1}$ was broadened substantially and shifted to a lower wavenumber, while the band at 1152 cm$^{-1}$ (identified as an acetylene–Ph stretching mode) was reduced in relative intensity. These spectral changes suggest a chemical reaction of the acetylene groups with the gold, which has been observed previously.\textsuperscript{48} Notably, the spectra of $5.1_0$ and $5.1_{PSS65}$ showed significant differences in the region 1000 to 1650 cm$^{-1}$, however given that it is
clear that the acetylene units have reacted with gold from the colloid a detailed further analysis of the spectra is not warranted.

![SERS spectra of dithienylethenes](image)

**Figure 5.6** SERS spectra of dithienylethenes 5.1\textsubscript{o} (top) and 5.1\textsubscript{pss365} (bottom) mixed with aggregated colloidal gold.

SERS spectra of SAMs of 5.1 on electrochemically roughened gold surfaces were more informative and indicated that under these conditions the acetylene units did not react with gold. SERS spectra of SAMs of 5.1\textsubscript{o} on roughened gold beads (Figure 5.7) were found to match the Raman spectra obtained from bulk solid samples closely. Bands originating from the acetylene groups (ca. 2000 cm\textsuperscript{-1}) were essentially identical to those of the solid samples, confirming that they did not react with the surface. Irradiation of the SAM of 5.1\textsubscript{o} at 365 nm resulted in the appearance of an intense band at 1508 cm\textsuperscript{-1} as well as several additional bands in the region 1400–1200 cm\textsuperscript{-1}, which is attributed to the presence of 5.1\textsubscript{c}. As was found in our earlier study on dithienylethene based SAMs on gold,\textsuperscript{15} the observation of 5.1\textsubscript{c} was complicated by the fact that the laser (785 nm) used to obtain Raman spectra also induced ring opening, even when employing low intensities and short exposure times (< 1 s). Ring opening of the SAM could be achieved by irradiation at > 440 nm also.
Figure 5.7 SERS spectra of a SAM of dithienylethene 5.1o on a roughened gold bead before irradiation (top), after irradiation at 365 nm (middle), and after subsequent irradiation at 785 nm (bottom).

A SERS spectrum of 5.1PSS365 self-assembled on gold (Figure 5.8, top spectrum) was found to differ from the SERS spectrum obtained from a SAM of 5.1o irradiated at 365 nm, the largest difference being the presence of two intense signals at 1508 and 1478 cm⁻¹. These signals did not reduce in intensity upon irradiation at > 440 nm and are assigned to the presence of 5.1byprod, which is formed to a small extent during irradiation to the PSS365nm in solution (vide supra). A sample of 5.1byprod generated in solution (by irradiation at 365 nm for extended periods and subsequently irradiated at > 400 nm to revert any remaining 5.1c to 5.1o) and then self-assembled on gold (Figure 5.8, bottom spectrum) was found to give the same spectrum. It should be noted that 5.1byprod is not observed after 5.1o on gold is irradiated successively at 365 and > 440 nm (Figure 5.7), which indicates that the photochemical switching fatigue observed in solution is absent when the molecules were self-assembled on gold. This was corroborated by the observation that irradiation of 5.1o on gold at 355 nm (10 mW) for 1 h did not result in the appearance of Raman bands corresponding to 5.1byprod.
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Figure 5.8 SERS spectra of a SAM of 5.1_{pss365} (top) and a mixture of 5.1_{o} and 5.1_{byprod} (bottom, prepared by extended irradiation of a solution of 5.1_{o} at 365 nm followed by irradiation with visible light to revert any remaining 5.1_{c} to 5.1_{o}) on a roughened gold bead.

5.3.5 Cyclic voltammetry of SAMs of 5.1_{o} on gold electrodes
As observed for 5.1_{o} in solution (vide supra), oxidatively induced switching was observed for a SAM of 5.1_{o} on gold. Cycling between 0.0 and 1.1 V at 2 V s⁻¹ effected the formation of 5.1_{c} manifested in the appearance of reversible redox waves at 0.46 and 0.73 V (Figure 5.9a). The peak-to-peak separation (after compensation for solution resistance) for the first and second redox process were found to be 11 mV and 14 mV, respectively, which is close to ideal behavior for a surface bound redox couple and indicates that the rate of heterogeneous electron transfer is fast on the cyclic voltammetry time scale (> 0.05 s⁻¹). Similarly, a linear relation between current and scan rate was observed, consistent with surface confinement of the redox active species (Figure 5.9b). A surface coverage \( \Gamma \) of ca. \( 5 \times 10^{-11} \) mol cm⁻², calculated from the first redox wave of the closed form, corresponds to that typically observed for a monolayer of a small molecule.³⁵
Figure 5.9  a) Cyclic voltammograms of a SAM of dithienylethene 5.1c on a gold bead electrode, recorded at 2 V s\(^{-1}\) in DCM/0.1 M TBAPF\(_6\) with a Pt counter electrode and SCE reference electrode. Repeated cycling results in the formation of 5.1c. b) The scan rate dependence of the non-Faradaic (0.125 V vs SCE, squares) and Faradaic (0.70 V vs SCE, circles) currents of dithienylethene 5.1c. \(R^2\) for the linear fits is > 0.99.

Cycling between 0.0 and 0.8 V at 0.25 V s\(^{-1}\) effected the depletion of the redox response of 5.1c (Figure 5.10) with a complete loss of current after ca. 100 cycles. Subsequent cycling between 0.0 and 1.1 V resulted in the reappearance of the redox waves of 5.1c, albeit with peak areas approximately 90% less than those observed initially.
Figure 5.10 Cyclic voltammograms of a SAM of dithienylethene 5.1c on a gold bead electrode, recorded at 0.25 V s⁻¹ in DCM/0.1 M TBAPF₆ with a Pt counter electrode and an SCE reference electrode. Repeated cycling results in the depletion of the redox waves of 5.1c. Only every 10th cyclic is shown.

Cyclic voltammetry of SAMs of 5.1o recorded on a roughened gold bead allowed for SERS spectra of the SAM to be obtained between cycles. It was found that upon full depletion of 5.1c, the SAM consisted mainly of 5.1o with a minor amount of 5.1byprod observable (Figure 5.11). As such, the lower amount of detectable 5.1c upon the second electrochemical closing/opening cycle is attributed primarily to the partial desorption of the SAM. Such desorption has been observed in other instances where slow scan rates were used and is attributed to oxidation of the gold substrate.35

Figure 5.11 SERS spectrum of a SAM of dithienylethene 5.1o on a roughened gold bead after electrochemically induced ring closing followed by electrochemically induced ring opening.

Photochemically induced switching of 5.1 on smooth gold beads was monitored by cycling between 0.0 and 0.8 V at 0.5 V s⁻¹ (Figure 5.12). The number of cycles was limited in order to minimize electrochemical switching. It was found that
irradiation of the bead at 365 nm resulted in the formation of 5.1c. Subsequent irradiation at > 440 nm resulted in the depletion of the signal of 5.1c.

![Cyclic voltammogram of a SAM of dithienylethene 5.1o on a smooth gold bead electrode before irradiation (thin line), after irradiation at 365 nm (thick line), and after subsequent irradiation at > 440 nm (dashed line). Recorded at 0.5 V s⁻¹ in DCM/0.1 M TBAPF₆ with a Pt counter electrode and an SCE reference electrode.](image)

**Figure 5.12**

### 5.3 Conclusions

The photochemical behavior of dithienylethene 5.1 was studied in solution as well as on gold substrates. In solution, 5.1 was shown to display reversible photochemical switching albeit with switching fatigue that was observed over multiple photochemical switching cycles due to irreversible isomerization. Self-assembly of 5.1 on gold substrates was confirmed by cyclic voltammetry to result in the formation of monolayers. SERS confirmed adsorption of the tripod and the stability of the monolayer upon irradiation with UV and visible light. The desorption of the monolayer that was observed upon electrochemical cycling between 0 and 0.8 V is attributed to the oxidation of underlying gold surface.

SAMs of 5.1 on gold were shown by SERS spectroscopy and cyclic voltammetry to display reversible photochemical switching. Importantly, self-assembly of the fatigue product (5.1byprod), generated by prolonged irradiation of 5.1o in solution, a

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a Adsorption of the three legs of the tripod on the surface, monolayer thickness, and monolayer stability were also confirmed by XPS experiments, see: Pijper, T. C.; Ivashenko, O.; Walko, M.; Rudolf, P.; Browne, W. R.; Feringa, B. L. *J Phys. Chem. C* 2015, 119, 3648–3657.
onto a gold surface allowed for observation of the SERS spectrum of 5.1byprod (Figure 9). In contrast to 5.1c, 5.1byprod is not subject to photoreversion upon irradiation at 785 nm and. Together with its visible absorption which leads to pre-resonant enhancement of the spectrum, this means that if present even in minor amounts in a SAM, it can be observed readily. Hence, the absence of bands from 5.1byprod in the spectra of SAMs of 5.1c, even after extended irradiation at 355 nm, confirms that this fatigue process is suppressed substantially when immobilized. The origin of the quenching of one chemical pathway and not another is unclear at present but given that the orientation of the switch is relatively well-controlled, it may be that there is a difference between the dipole moments of the transitions that access the states leading to irreversible isomerization and reversible cyclization. As such, we conclude that, despite the design of the tripodal anchoring unit, there remains sufficient interaction between the switching unit and the gold surface to quench, albeit in this case usefully, certain photochemical processes (i.e. the irreversible rearrangement, Scheme 5.2).

In conclusion, the tripod structure has been shown to successfully link a photoswitchable unit to a gold surface while retaining the photochemical and redox switching properties. As the tripod structure has all of its thiols adsorbed, there is full control over position and orientation of the photoswitchable unit with respect to the gold surface. This provides a substantial improvement over the use of linkers that offer only a single point of attachment and is an important step forward in the ongoing design of switchable SAM based organic light responsive devices.

5.4 Experimental section
General experimental
General experimental details can be found in chapter 3.

Quantum chemical calculation of Raman spectra
Quantum chemical calculations were performed with the Firefly 8.0.0 release candidate QC program,50 which is based partially on GAMESS (US) source code.51 The basis sets was obtained from the EMSL basis set exchange (https://bse.pnl.gov/bse/portal). Calculated Raman activities were converted to Raman intensities using the method described in chapter 3.
Chapter 5

SERS experiments using colloidal gold
Experimental details describing the preparation of colloidal gold and its use in SERS experiments can be found in chapter 3.

Preparation of SAMs on roughened gold beads
Experimental details describing the formation of SAMs of dithienylethene 5.1 on gold beads can be found in chapter 3.

Cyclic voltammetry
Solution experiments were performed using a Teflon-shrouded glassy carbon working electrode (CH Instruments), a Pt wire counter electrode, and a saturated calomel electrode (SCE) reference in DCM/0.1 M TBAPF₆. The concentration of the analyte was 0.50 mM. Experiments with SAMs of dithienylethene 5.1 on gold beads employed the gold bead as the working electrode, a Pt counter electrode, and an SCE reference electrode in DCM/0.1 M TBAPF₆. iR compensation was employed with scan rates > 0.25 V s⁻¹ in order to correct for solution resistance. The surface coverage of 5.1c on the gold beads was calculated using the cathodic and anodic parts of both redox waves displayed by 5.1c.

tert-Butyl(3-iodophenyl)sulfane (5.2). A mixture of 1,3-diiodobenzene (33.9 g, 103 mmol), 2-methyl-2-propanethiol (11.1 g, 123 mmol), sodium tert-butoxide (23.7 g, 246 mmol), tetrakis(triphenyl phosphine)palladium(0) (4.27 g, 3.69 mmol), and tert-butanol (1.3 L) was stirred at 65 °C for 16 h. The mixture was concentrated in vacuo and pentane (600 mL) was added. The resulting mixture was washed with water (2 × 300 mL), dried over Na₂SO₄, and concentrated in vacuo. Column chromatography (silica gel, heptane + 0.2 % EtOAc, Rf = 0.55) yielded thioether 5.2 as a colorless solid (12.6 g, 42 %); mp 45–46 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (t, J = 1.7 Hz, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.07 (t, J = 7.8 Hz, 1H), 1.29 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 145.7 (d), 137.7 (d), 136.6 (d), 135.2 (s), 130.1 (d), 94.0 (s), 46.5 (s), 31.1 (q); IR (neat) νmax 2959, 1565, 1550, 1454, 1386, 1362, 1152, 1057, 995, 777, 741, 685, 647 cm⁻¹; Raman (neat) νmax 3054, 2960, 2921, 2895, 1566, 1167, 1102, 1058, 996, 808, 743, 648, 583, 250 cm⁻¹; m/z (EI, %): 292 (M⁺, 18), 236 (100); HRMS (APPI): calcd for C₁₀H₁₃IS: 291.9777, found: 291.9775.
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((3-(tert-Butylthio)phenyl)ethynyl)trimethylsilane (5.3). A mixture of tert-butyl(3-iodophenyl)sulfane (5.2, 14.5 g, 49.7 mmol), trimethylsilylacetylene (7.32 g, 74.5 mmol, 10.6 mL), and N,N-diisopropylethylamine (10.9 g, 84.5 mmol, 14.7 mL) in tetrahydrofuran (135 mL) was stirred for 30 min at rt. Bis(triphenylphosphine)palladium(II) dichloride (1.74 g, 2.48 mmol) and copper(I) iodide (473 mg, 2.48 mmol), both degassed in vacuo for 1 h, were added and the resulting mixture was stirred for 48 h at rt. Water (150 mL) and diethylether (150 mL) were added, after which the layers were separated and the water layer was extracted with diethylether (150 mL). The combined organic layers were washed with water (150 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification by column chromatography (silica gel, heptane/toluene 10:1, Rf = 0.50) provided thioether 5.3 as a slightly yellow liquid (11.06 g, 85 %); ¹H NMR (300 MHz, CDCl₃) δ 7.64 (t, J = 1.5 Hz, 1H), 7.50–7.43 (m, 2H), 7.26 (t, J = 7.8 Hz, 1H), 1.29 (s, 9H), 0.25 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 140.6 (d), 137.6 (d), 133.1 (s), 132.3 (d), 128.4 (d), 123.7 (s), 104.5 (s), 94.9 (s), 46.2 (s), 31.1 (q), 0.1 (q); IR (neat) νmax 2961, 2162, 1466, 1364, 1250, 1161, 888, 843, 793, 760, 691 cm⁻¹; Raman (neat) νmax 3060, 2961, 2922, 2898, 2163, 1582, 1217, 997, 646, 604, 593, 572 cm⁻¹; m/z (EI, %): 262 (M⁺, 12), 206 (53), 191 (100); HRMS (APPI): calcd for C₁₅H₂₃SSi ([M + H]+): 263.1284, found: 263.1280.

tert-Butyl(3-ethynylphenyl)sulfane (5.4). A stirred solution of ((3-(tert-butylthio)phenyl)ethynyl)trimethylsilane (5.3, 11.1 g, 42.1 mmol) in tetrahydrofuran (540 mL) and methanol (8 mL) was cooled to 0 °C. Tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 20.6 mmol, 20.6 mL) was added dropwise over 5 min, after which the mixture was stirred for 2 h at 0 °C. The mixture was poured onto a saturated aqueous solution of NH₄Cl (500 mL) and extracted with dichloromethane (2 × 300 mL). The combined organic layers were washed with water (2 × 300 mL), dried over Na₂SO₄, and concentrated in vacuo. The resulting oil was filtered over a short column of silica gel (pentane), providing thioether 5.4 as a slightly yellow liquid (7.35 g, 85 %); ¹H NMR (400 MHz, CDCl₃) δ 7.67 (s, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 3.10 (s, 1H), 1.29 (s, 9H); ¹³C NMR (75 MHz,
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CDCl₃) δ 140.8 (d), 137.9 (d), 133.3 (s), 132.4 (d), 128.5 (d), 122.6 (s), 83.1 (s), 77.9 (d), 46.2 (s), 31.1 (q); IR (neat) νmax 3291, 2960, 1585, 1560, 1466, 1457, 1394, 1363, 1158, 1079, 900, 843, 792, 691, 652 cm⁻¹; Raman (neat) νmax 3060, 2962, 2922, 2898, 2112, 1585, 1198, 999, 682, 599, 570, 466, 361 cm⁻¹; m/z (EI, %): 190 (M⁺, 11), 134 (100).

Ethoxytris(4-iodophenyl)silane (5.5). A stirred suspension of 1,4-diiodobenzene (50.0 g, 152 mmol) in diethylether (750 mL) was cooled to –78 °C and n-BuLi (1.6 M in hexane, 113.5 mmol, 70.9 mL) was added dropwise over 15 min. The resulting mixture was stirred for 1 h, after which tetraexthoxysilane (7.90 g, 37.9 mmol, 8.5 mL) was added at once and stirring was continued for 1 h. The mixture was allowed to warm to rt and stirred for an additional 4 h. Aqueous HCl (1 M, 125 mL) was added and the layers were separated after which the organic layer was washed with water (2 × 250 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification was performed by column chromatography (silica gel, heptane/toluene 9:1, Rf = 0.45), which provided silane 5.5 as a white solid (14.20 g, 55 %); m.p. 177–178 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 8.2 Hz, 6H), 7.28 (d, J = 8.2 Hz, 6H), 3.83 (q, J = 7.0 Hz, 2H, 1.22 (t, J = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 137.4 (d), 136.8 (d), 132.9 (s), 98.1 (s), 60.1 (t), 18.5 (q); IR (neat) νmax 2967, 1565, 1474, 1373, 1116, 1104, 1077, 1055, 1002, 951, 802, 761, 724 cm⁻¹; Raman (neat) νmax 3042, 1567, 1190, 1106, 1056, 694, 628, 329, 288, 252, 230 cm⁻¹; HRMS (APPI): calcd for C₂₀H₁₈I₃O₃Si ([M + H]⁺): 682.8256, found: 682.8242.

Tris(4-(3-(tert-butythio)phenyl)ethynyl)phenyl)(ethoxy)silane (5.6). A mixture of ethoxytris(4-iodophenyl)silane (5.5, 8.00 g, 11.7 mmol), tert-butyl(3-ethynylphenyl)sulfane (5.4, 13.3 g, 70.1 mmol), bis(dibenzylideneacetone)palladium(0) (1.01 g, 1.76 mmol), triphenylphosphine (1.54 g, 5.87 mmol), copper(I) iodide (302 mg, 1.58 mmol), N,N-diisopropylethylamine (267 mL), and tetrahydrofuran (800 mL) was stirred at rt for 48 h. Water (600 mL) was added, after which the mixture was extracted with
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diethylether (3 × 750 mL). The combined organic layers were washed with water (2 × 500 mL), dried over Na₂SO₄, and concentrated in vacuo. Column chromatography (silica gel, heptane/toluene 4:3, Rₛ = 0.45) provided thioether 5.6 as a yellow sticky oil (5.35 g, 87 %); ¹H NMR (300 MHz, CDCl₃) δ 7.72 (s, 3H), 7.63–7.49 (m, 18H), 7.32 (t, J = 7.7 Hz, 3H), 3.89 (q, J = 6.9 Hz, 2H), 1.31 (s, 27H), 1.26 (t, J = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 140.3 (d), 137.6 (d), 135.3 (d), 134.4 (s), 133.3 (s), 131.9 (d), 131.1 (d), 128.5 (d), 125.0 (s), 123.6 (s), 90.2 (s), 89.9 (s), 60.1 (t), 46.2 (s), 31.1 (q), 18.5 (q); IR (neat) νₘₐₓ 2959, 1594, 1362, 1159, 1106, 1075, 790, 766, 687, 642 cm⁻¹; Raman (neat) νₘₐₓ 2223, 2189, 1595, 1584, 1150, 1094, 998, 600, 570 cm⁻¹.

Tris(4-((3-(tert-butylthio)phenyl)ethynyl)phenyl)(4-iodophenyl)silane (5.7). A stirred solution of 1,4-diiodobenzene (683 mg, 2.07 mmol) in tetrahydrofuran (10 mL) and diethylether (10 mL) was cooled to –78 °C. n-Butyllithium (1.6 M in hexane, 2.28 mmol, 1.4 mL) was added dropwise over 5 min, after which the resulting mixture was stirred at –78 °C for 1 h. A precooled solution of tris(4-((3-(tert-butylthio)phenyl)ethynyl)phenyl)(ethoxy)silane (5.6, 1.50 g, 1.73 mmol) in tetrahydrofuran (20 mL) was added and the resulting mixture was stirred at –78 °C for 30 min, after which it was allowed to warm to rt overnight. Water (50 mL) and ethyl acetate (50 mL) were added and the layers were separated. The aqueous layer was extracted with ethyl acetate (50 mL), after which the combined organic layers were washed with water (50 mL), dried over Na₂SO₄, and concentrated in vacuo. Column chromatography (silica gel, heptane/toluene 4:3) provided thioether 5.7 as a sticky oil (1.21 g, 68 %); ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 8.2 Hz, 2H), 7.72 (t, J = 1.5 Hz, 3H), 7.58–7.50 (m, 18H), 7.32 (t, J = 7.7 Hz, 3H), 7.27 (d, J = 7.1 Hz, 2H), 1.32 (s, 27H); ¹³C NMR (75 MHz, CDCl₃) δ 140.4 (d), 137.9 (d), 137.6 (d), 137.4 (d), 136.3 (d), 133.6 (s), 133.4 (s), 132.7 (s), 132.0 (d), 131.3 (d), 128.6 (d), 125.0 (s), 123.6 (s), 97.8 (s), 90.4 (s), 89.8 (s), 46.3 (s), 31.2 (q); IR (neat) νₘₐₓ 2958, 1594, 1455, 1362, 1158, 1103, 1004, 822, 790, 765, 714, 687, 643 cm⁻¹; Raman (neat) νₘₐₓ 2223, 2190, 1594, 1583, 1150, 1091, 997, 599, 570 cm⁻¹; HRMS (APPI): calcd for C₆₀H₅₅I₃SiSi: 1026.2274, found: 1026.2264.
5-Chloro-2-methyl-3-(2-(2-methyl-5-(p-tolyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophene (5.8). $n$-Butyllithium (1.6 M solution in hexane, 3.19 mmol, 2.0 mL) was added dropwise to a stirred solution of 1,2-bis(5-chloro-2-methylthiophen-3-yl)cyclopent-1-ene (1.00 g, 3.04 mmol) in tetrahydrofuran (40 mL), after which stirring was continued for 1 h. Tributyl borate (978 mg, 4.25 mmol, 1.1 mL) was added dropwise and the resulting mixture was stirred for an additional 1 h. Meanwhile, in a separate flask, a stirred mixture of 4-bromotoluene (779 mg, 4.55 mmol), tetrakis(triphenylphosphine)palladium(0) (105 mg, 91.1 μmol), ethylene glycol (0.4 mL), aqueous Na$_2$CO$_3$ (2 M, 16 mL), and tetrahydrofuran (24 mL) was heated to 70 °C. The crude boronic ester was added and the resulting mixture was refluxed for 16 h. The mixture was diluted with diethyl ether (100 mL) and washed with water (2 × 50 mL). The combined aqueous layers were extracted with diethyl ether (50 mL), after which the combined organic layers were dried over Na$_2$SO$_4$ and concentrated in vacuo. Column chromatography (silica gel, heptane + 1 % ethyl acetate, $R_f = 0.5$) provided dithienylethene 5.8 as a slightly pink oil (848 mg, 73 %); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 7.9$ Hz, 2H), 6.93 (s, 1H), 6.62 (s, 1H), 2.83–2.71 (m, 4H), 2.34 (s, 3H), 2.09–2.00 (m, 2H), 1.98 (s, 3H), 1.88 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.1 (s), 137.0 (s), 136.4 (s), 135.5 (s), 135.3 (s), 134.0 (s), 133.7 (s), 133.4 (s), 131.8 (s), 129.6 (d), 127.0 (d), 125.4 (d), 125.1 (s), 123.4 (d), 38.6 (t), 38.5 (t), 23.1 (t), 21.2 (q), 14.5 (q), 14.29 (q); IR (neat) $\nu_{\text{max}}$ 2916, 2842, 1512, 1437, 1164, 1004, 828, 810, 750 cm$^{-1}$; Raman (neat) $\nu_{\text{max}}$ 2916, 2842, 1512, 1437, 1164, 1004, 828, 810, 750 cm$^{-1}$; HRMS (APPI): calcd for C$_{22}$H$_{22}$Cl$_2$S$_2$ ([M + H]$^+$): 385.0846, found: 385.0840.
Tris(4-((3-(tert-butylthio)phenyl)ethynyl)phenyl)(4-(5-methyl-4-(2-(2-methyl-5-(p-tolyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophen-2-yl)phenyl)silane (5.9). 5-Chloro-2-methyl-3-(2-(2-methyl-5-(p-tolyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophene (5.8, 725 mg, 1.88 mmol) was dissolved in tetrahydrofuran (20 mL). n-Butyllithium (1.6 M solution in hexane, 2.07 mmol, 1.3 mL) was added dropwise, after which stirring was continued for 45 min. Tributyl borate (476 mg, 2.07 mmol, 0.56 mL) was added dropwise and stirring was continued for 45 min. Meanwhile, in a separate flask, a stirred mixture of tris(4-((3-(tert-butylthio)phenyl)ethynyl)phenyl)(4-iodophenyl)silane (5.7, 1.45 g, 1.41 mmol), tetrakis(triphenylphosphine)palladium(0) (65.2 mg, 56.4 μmol), ethylene glycol (0.20 mL), aqueous Na₂CO₃ (2 M, 12 mL), and tetrahydrofuran (8 mL) was heated to 70 °C. The crude boronic ester was added and the resulting mixture was refluxed for 16 h. The mixture was diluted with pentane (50 mL) and washed with water (2 × 50 mL). The combined aqueous layers were extracted with pentane (50 mL), after which the combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. Column chromatography (silica gel, heptane/toluene 4:3) provided dithienylethene 5.9 as a light grey sticky oil (1.53 g, 87 %); ¹H NMR (300 MHz, CDCl₃) δ 7.72 (s, 3H), 7.57–7.49 (m, 22H), 7.39 (d, J = 8.2 Hz, 2H), 7.32 (t, J = 7.7 Hz, 3H), 7.13 (d, J = 7.9 Hz, 2H), 7.10 (s, 1H), 6.99 (s, 1H), 2.87–2.81 (m, 4H), 2.34 (s, 3H), 2.11–2.04 (m, 2H), 2.01 (s, 3H), 1.98 (s, 3H), 1.31 (s, 27H); ¹³C NMR (75 MHz, CDCl₃) δ 140.4 (d), 140.0 (s), 139.2 (s), 137.6 (d), 137.1 (s), 136.95 (d), 136.92 (s), 136.6 (s), 136.3 (d), 136.2 (s), 135.4 (s), 135.1 (s), 134.5 (s), 134.3 (s), 134.0 (s), 133.4 (s), 132.0 (d), 131.9 (s), 131.4 (s), 131.2 (d), 129.6 (d), 128.6 (d), 125.4 (d), 125.0 (d), 124.9 (d), 124.8 (s), 123.7 (s), 123.6 (d), 90.2 (s), 89.9 (s), 46.3 (s), 38.64 (t), 38.59 (t), 31.2 (q), 23.2 (t), 21.3 (q), 14.7 (q), 14.5 (q); IR (neat) νmax 2957, 1593, 1455, 1392, 1362, 1159, 1103, 821, 812, 790, 764, 737, 686, 644 cm⁻¹; Raman (neat) νmax 2223, 2189, 1594, 1583, 1502, 1465, 1149, 1091, 997 cm⁻¹; HRMS (APPI): calcd for C₈₂H₇₆S₅Si: 1271.4212, found: 1271.4224.
\[ S,S',S''-((((4-(5-methyl-4-(2-(2-methyl-5-(p-tolyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophen-2-yl)phenyl)silanetriyl)tris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))tris(benzene-3,1-diyl)) triethanethioate \] (5.1). Tris(4-((3-(tert-butylthio)phenyl)ethynyl)phenyl)(4-(5-methyl-4-(2-(2-methyl-5-(p-tolyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophen-2-yl)phenyl)silane (5.9, 1.50 g, 1.20 mmol) was dissolved in dichloromethane (60 mL) and acetyl chloride (2.83 g, 36.0 mmol, 2.6 mL) was added. Boron tribromide (1.0 M in dichloromethane, 3.96 mmol, 4.0 mL) was added dropwise over 5 min, after which the resulting mixture was stirred for 16 h. Water (50 mL) and ethyl acetate (50 mL) were added and the layers were separated. The inorganic layer was extracted with ethyl acetate (50 mL), after which the combined organic layers were washed with water (50 mL), dried over Na\(_2\)SO\(_4\), and concentrated in vacuo. Column chromatography (silica gel, heptane/ethyl acetate 67:1) provided dithienylethene 5.1 as a brown sticky oil (659 mg, 45 %); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (s, 3H), 7.59–7.49 (m, 19H), 7.43–7.37 (m, 8H), 7.13 (d, \(J = 8.0\) Hz, 2H), 7.10 (s, 1H), 6.99 (s, 1H), 2.84 (t, \(J = 7.5\) Hz, 4H), 2.44 (s, 9H), 2.34 (s, 3H), 2.13–2.04 (m, 2H), 2.01 (s, 3H), 1.98 (s, 3H); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 193.6 (s), 134.0 (s), 139.2 (s), 137.5 (d), 137.1 (s), 137.0 (d), 136.6 (s), 136.3 (d), 136.2 (s), 135.4 (s), 135.0 (s), 134.5 (d), 134.3 (s), 134.0 (s), 132.7 (d), 131.9 (s), 131.2 (d), 129.6 (d), 129.3 (d), 128.4 (s), 125.4 (d), 125.0 (d), 124.8 (d), 124.6 (s), 124.5 (s), 123.6 (d), 90.5 (s), 89.7 (s), 38.65 (t), 38.61 (t), 30.4 (q), 23.2 (t), 21.3 (q), 14.7 (q), 14.6 (q); IR (neat) \(\nu_{\text{max}}\) 2915, 1705, 1593, 1497, 1101, 1018, 946, 884, 820, 787, 765, 737, 684 cm\(^{-1}\); Raman (neat) \(\nu_{\text{max}}\) 2224, 2190, 1586, 1502, 1466, 1152, 1090, 996 cm\(^{-1}\); HRMS (APPI): calcd for C\(_{76}H_{59}O_3S_5Si ([M + H]\(^+\)): 1207.2832, found: 1207.2804.
Dithienylethene 5.1. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.61–7.54 (m, 22H), 7.46–7.39 (m, 8H), 7.15 (d, $J = 8.0$ Hz, 2H), 6.54 (s, 1H), 6.42 (s, 1H), 2.51–2.46 (m, 4H), 2.43 (s, 9H), 2.358 (s, 3H), 2.00 (s, 6H), 1.93–1.85 (m, 2H); Raman (neat) $\nu_{\text{max}}$ 2224, 1587, 1506, 1312, 1265, 1187, 1151, 1102 cm$^{-1}$.

5.5 Full IR and Raman spectra
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(obtained by scaled subtraction)
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5.6 References

47 A Raman spectrum of this isomer could not be recorded at 785 nm due to interfering fluorescence. Excitation at 1064 nm resulted in burning of the sample.
49 The potential applied was limited to 1.1 V as higher potentials are known to result in desorption of the SAM, see reference 35.