Position and Orientation Control of a Photo- and Electrochromic Dithienylethene Using a Tripodal Anchor on Gold Surfaces

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ABSTRACT: A tripodal system for anchoring photochromic dithienylethenes on gold surfaces is reported. The self-assembled monolayers of a tripod-functionalized dithienylethene were characterized by cyclic voltammetry, surface-enhanced Raman spectroscopy (SERS), and X-ray photoelectron spectroscopy (XPS). These data are compared with solution studies, solid state Raman spectroscopy, and density functional theory (DFT) calculations. We show 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 photochemical fatigue observed in solution.

INTRODUCTION

The design of solid-state molecular electronic and photonic devices incorporating photochromic or redox-active molecules is a topic of continuing interest.1−4 Several aspects pertaining to the photochromic or redox-switchable component in the material present challenges in the design of such devices. First, the switchable component should be incorporated with maximum control over its position and its orientation with respect to the surface it is interfaced with. Second, 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 toward (or can react with) the substrate on which the self-assembly is desired.5,6

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.5,6 Such an anchoring strategy has been used widely for the tethering of photochromic units to a range of substrates, such as gold,7−10 SiO2,11,12 and ITO.13 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 molecules in the self-assembled monolayer to lie flat on the surface, which can result in a disorganized SAM.14 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.15 Such unfavorable interactions with the surface were recently also observed in our study on the photochemical behavior of asymmetric dithienylethenes tethered to gold through a short thiol linker,16 and with surface bound light-driven molecular rotary motors.17

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.18,19 This anchoring unit consists of three thiol-substituted diphenyl ethyne units attached to a silicon atom (Scheme 2). This design was chosen over other tripodal structures reported previously,20−26 because the silicon atom should reduce potential long distance through-bond interactions with the gold substrate.27,28 In addition, the relatively large structure increases the separation of the switching unit from the surface by an estimated 7 Å (based on density

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functional theory calculations, vide infra), thus minimizing through-space interactions with the substrate. In contrast to the design by Tour and co-workers,29 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.

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 1).30−32 Important characteristics are that the two isomers can be addressed independently due to differences in their UV/vis absorption spectra, they are thermally stable,30 and display distinct electronic properties because of differences in their π-systems.7,33,34 In addition, it has been shown that switching can for certain systems also be induced electrochemically.35−41 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.30,42 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 1).42 In the present study, the importance of this process will be addressed as well.

Herein, we report the synthesis and characterization, and the electro- and photochemical properties of dithienylethene 1 (Scheme 2) in solution and as SAMs on gold substrates. We demonstrate that the tripod structure of 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 1 displays reversible photochemical and electrochemical switching, both in solution and on gold substrates. Finally, although 1 displays photochemical switching fatigue in solution, this is not observed during photochemical switching of SAMs of 1 on gold surfaces.

### RESULTS AND DISCUSSION

#### Synthesis of Dithienylethene 1

Dithienylethene 1 was synthesized using a convergent synthetic route (Scheme S1). The synthesis of the tripod started with the synthesis of thioether 4, which was prepared by first converting 1,3-diiodobenzene to thioether 2 by treatment with t-butylthiol and Pd(PPh₃)₄ (Scheme S1). A Sonogashira cross-coupling of 2 with trimethylsilylacetylene (TMS-acetylene) was then used to obtain thioether 3 in 85% yield. Removal of the TMS group of 3 by treatment with TBAF provided 4 in 85% 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.

The tripod was prepared starting with lithiation of 1,4-diiodobenzene followed by treatment with tetraethoxysilane, providing triiodide 5. A Sonogashira cross-coupling of 5 with thioether 4 was used to prepare trithioether 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 6, which provided trithioether 7 in 68% yield (Scheme S1).

The dithienylethene moiety was synthesized starting from a dichloro-substituted dithienylethene precursor.44 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 8. After conversion of 8 to the corresponding boronic ester as above, a Suzuki cross-coupling reaction with trithioether 7 afforded dithienylethene 9 in 87%
yield. Finally, conversion of the thioether groups to thioester groups by treatment with BBr₃ and acetyl chloride provided dithienylethene 1₀ in 45% yield (Scheme S1). For details of spectroscopic characterization, see ESI.

**Photochemical Switching of 1 in Solution.** The photochemical behavior of dithienylethene 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 1 (1₀) in toluene displayed several strong absorption bands <370 nm and no absorption >370 nm (Figure 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 1₁c. 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 1b).

The photochemical switching fatigue observed for 1 is attributed to the conversion of 1₁c into its isomer 1₁byprod (Scheme 3). The visible absorption band of 1₁byprod has a maximum at 527 nm, which is shifted hypsochromically compared to the visible absorption of 1₁c. This is in agreement with dithienylethene switching fatigue reported by Irie and co-workers. The photochemical switching was also monitored by ¹H NMR spectroscopy (Figure 2). Irradiation of 1₀ in CD₂Cl₂ at 365 nm resulted in the formation of a second isomer identified as 1₁c. 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).

Continued irradiation at 365 nm resulted in the appearance of a second isomer identified as 1₁byprod. Compared to the spectrum of 1₁c, 1₁byprod exhibited the signals of the hydrogens of the thiophenes shifted slightly, from 6.54 and 6.42 ppm to 6.56 and 6.43 ppm, 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 1₁byprod is in agreement with findings by Irie and co-workers. Subsequent irradiation at >440 nm resulted in the disappear-ance of 1₁c and reappearance of 1₀ but did not change the intensity of the signals of 1₁byprod in the spectrum.

It has been shown previously that dithienylethenes can undergo opening and closing both photochemically and electrochemically. As with structurally related dithienylethenes, an irreversible oxidation of the open form, 1₀, was observed at 1.1–1.2 V (Figure 3b), and is assigned to a two-electron oxidation that is followed by cyclization of the dithienylethene unit to the closed form (Figure 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 1₁c⁺ to 1₁c and, finally, to 1₁c. The two corresponding oxidation

![Figure 1](image1.png)

**Scheme 3. Conversion of Dithienylethene 1₁c into the Photochemical Byproduct 1₁byprod**

The structure shown is inferred by comparison with the ¹H NMR and UV/Vis absorption spectrum of an analogous compound reported by Irie and co-workers.
waves \((1c^+ \text{ to } 1c^2+)\) 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 \(1c\) to increase until diffusion to and from the electrode was equilibrated.

**Solid State Raman Spectra of 1.** Raman spectra (Figure 4) were recorded of dithienylethene \(1o\) in the solid state as well as for a sample of \(1o\) that was irradiated at 365 nm in solution to its photostationary state (PSS) and subsequently concentrated in vacuo to a solid (denoted \(1PSS365\)). The spectrum of \(1c\) was obtained by a scaled subtraction of the spectrum of \(1o\) from the spectrum of \(1PSS365\). Comparing the spectra of \(1o\) and \(1c\), 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 nonphotoactive part of the molecule, i.e., the tripod moiety. The region 1520–1200 cm\(^{-1}\) of the spectra of \(1o\) and \(1c\) 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 \(1c\). This intense band was observed in earlier Raman studies of dithienylethenes\(^{16,46}\) and is assigned as a stretching vibration of the molecule’s conjugated polyyne backbone.

In order to confirm that the recorded spectra correspond to isomers of 1 as well as to elucidate their spectral features, Raman spectra of \(1o\) and \(1c\) were calculated using density functional theory (Figure 5). The B97-D3 functional\(^{47,48}\) and def2-SVP basis set\(^{49}\) were used for the calculation of the geometry and the vibrational modes. Raman activities were calculated using the B3LYP hybrid functional\(^{50-52}\) (using VWN...
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 \(1_o\) 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 \(1_{byprod}\) was also calculated (Figure 5, bottom spectrum). This isomer is predicted to show Raman scattering at 1559 and 1518 cm\(^{-1}\), both originating from the dithienylethene moiety. \(^{54}\)

**X-ray Photoelectron Spectroscopy of \(1_o\) in a SAM.** SAMs of \(1_o\) on gold were prepared by immersing a freshly prepared gold on mica substrate into a solution of \(1_o\) (0.5 mM) in dichloromethane for 16 h and analyzed by X-ray photoelectron spectroscopy (XPS) to determine the elemental composition after SAM formation. In the overview spectra of \(1_o\) on gold/mica (see electronic Supporting Information) contributions from carbon (90.0 \(\pm\) 0.3 atomic percent (at. %)), sulfur (6.0 \(\pm\) 0.2 at. %), oxygen (4.5 \(\pm\) 0.5 at. %), and Au were detected. The high resolution sulfur 2p XPS spectrum (Figure 6a) was fitted with two doublet components, centered at 162.0 eV (32%) and at 163.7 eV (68%). Contributions from oxidized species (i.e., SO\(_x\)), typically observed above 167 eV,\(^{55}\) were not apparent. The absence of oxidized sulfur species indicates that deprotection of the thiols occurs via cleavage of the S–Ac bond with subsequent formation of a bond with the gold surface as opposed to undergoing oxidation. The doublet peak at 162.0 eV is characteristic for chemisorbed thiolates and its apparent intensity is consistent with a monolayer thickness. The components at 163.7 eV originate from the thiophene groups of \(1_o\).\(^{57}\)

The C 1s spectrum of \(1_o\) on gold/mica was fitted with two singlet components at 284.6 eV from C–C, C=Si, and at 285.7 eV from C–S and possibly C–O. (c) O 1s core level photoelectron spectrum of \(1_o\) on gold/mica showing contributions from C=O–C and/or C=O at 532.5 eV due to contamination from air during sample transfer. Notably, signals assignable to C=O groups (531.0–531.5) are absent.

The stoichiometric ratio of C/S leads to the conclusion that \(1_o\) adsorbs on the surface without loss of molecular integrity. The attenuation of the S–Au component in the S 2p spectrum of \(1_o\) is close to the stoichiometrically expected value of 14 and the mismatch is similarly rationalized by attenuation.

The carbon 1s core level region of the XPS spectrum (Figure 6b) was fitted with two components: one at 284.6 eV accounting for C–C aromatic and aliphatic bonds and C–Si with a total 91% of the overall C intensity; and the second one at 285.7 eV originating from C–S and possibly C–O. Contributions from the carbonyl of the acetate protecting groups, which are observed typically around 287 eV, were not apparent in the C 1s spectrum of the SAM. This suggests that successful deprotection and the subsequent removal of the acetate group from the surface occurs upon SAM formation. In the oxygen 1s core level XPS spectrum (Figure 6c), a component at 532.5 eV was observed related to C=OH or C=O–C, and again contributions assignable to C=O (expected typically at 531.0–531.5 eV)\(^{59}\) were absent, which is in agreement with the C 1s XPS spectrum.
and the absence of contributions from C==O groups in the C 1s and O 1s spectral regions testify that chemisorption of 1 rather than physisorption (i.e., in the protected form, \(I_{\text{SAM}}\)) occurs upon self-assembly and confirm that binding of all three “legs” to the surface occurs. Exposure to UV light for 2 h within the XPS vacuum chamber did not result in detectable changes in S 2p core level spectrum, which suggests that the S–Au bond is stable toward UV irradiation.

**Surface-Enhanced Raman Spectroscopy.** Surface-enhanced Raman (SERS) spectra of \(I_0\) or \(I_{\text{PSS365}}\) obtained by mixing with aggregated colloidal gold were recorded at 785 nm (Figure 7). The recorded spectra were found to display significant differences compared to the Raman spectra of the solid compounds (Figure 4). In particular, the alkylene 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.\(^{58}\) Notably, the spectra of \(I_0\) and \(I_{\text{PSS365}}\) 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 SAMs of 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 \(I_0\) on roughened gold beads (Figure 8) were found to match the Raman spectra obtained from bulk solid samples closely. Bands originating from the acetylene groups (ca. 2000 cm\(^{-1}\)) were essentially identical to those of the solid samples, confirming that they did not react with the surface. Irradiation of the SAM of \(I_0\) at 365 nm resulted in the appearance of an intense band at 1508 cm\(^{-1}\) as well as several additional bands in the region 1400–1200 cm\(^{-1}\), which is attributed to the presence of \(I_{1c}\). As was found in our earlier study on dithienylethene based SAMs on gold,\(^{10}\) the observation of \(I_{1c}\) 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.

A SERS spectrum of \(I_{\text{PSS365}}\) self-assembled on gold (Figure 9, top spectrum) was found to differ from the SERS spectrum obtained from a SAM of \(I_0\) 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 \(I_{1\text{byprod}}\) which is formed to a small extent during irradiation to the PSS365 nm in solution (vide supra). A sample of \(I_{1\text{byprod}}\) generated in solution (by irradiation at 365 nm for extended periods and subsequently irradiated at >400 nm to revert any remaining \(I_0\) to \(I_{1c}\)) and then self-assembled on gold (Figure 9, bottom spectrum) was found to give the same spectrum. It should be noted that \(I_{1\text{byprod}}\) was not observed after \(I_0\) on gold is irradiated successively at 365 and >440 nm (Figure 8), 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 \(I_0\) on gold at 355 nm (10 mW) for 1 h did not result in the appearance of Raman bands corresponding to \(I_{1\text{byprod}}\).

**Cyclic Voltammetry of SAMs of 1 on Gold Electrodes.** As observed for \(I_0\) in solution (vide supra), oxidatively induced switching was observed for a SAM of \(I_0\) on gold. Cycling between 0.0 and 1.1 V\(^{36}\) at 2 V s\(^{-1}\) affected the formation of \(I_{1c}\) manifested in the appearance of reversible redox waves at 0.46 and 0.73 V (Figure 10). 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 10, inset). A surface coverage Γ of ca. 5 × 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.⁴¹

Cycling between 0.0 and 0.8 at 0.25 V s⁻¹ effected the depletion of the redox response of 1c (Figure 11) 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 1c, albeit with peak areas approximately 90% less than those observed initially, which indicates desorption of the monolayer occurs predominantly rather than electrochemically driven ring-opening.

Cyclic voltammetry of SAMs of 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 1o, the SAM consisted mainly of 1c with a minor amount of 1byprod observable (Figure 12). As such, the lower amount of detectable 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.⁴¹

Photochemically induced switching of 1 on smooth gold beads was monitored by cycling between 0.0 and 0.8 at 0.5 V s⁻¹ (Figure 13). 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 1c. Subsequent irradiation at >440 nm resulted in the depletion of the signal of 1c.

**CONCLUSIONS**

The photochemical behavior of dithienylethene 1 was studied in solution as well as on gold substrates. In solution, 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-

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**Figure 10.** Cyclic voltammograms of a SAM of dithienylethene 1o on a gold bead electrode, recorded at 2 V s⁻¹ in DCM/0.1 M (TBA)PF₆ with a Pt counter electrode and SCE reference electrode. Repeated cycling results in the formation of 1c. The inset shows 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 1c. R² for the linear fits is >0.99.

**Figure 11.** Cyclic voltammograms of a SAM of dithienylethene 1c on a gold bead electrode, recorded at 0.25 V s⁻¹ in DCM/0.1 M (TBA)PF₆ with a Pt counter electrode and an SCE reference electrode. Repeated cycling results in the depletion of the redox waves of 1c. Only every 10th cycle is shown.

**Figure 12.** SERS spectrum of a SAM of dithienylethene 1o on a roughened gold bead after electrochemically induced ring-closing followed by electrochemically induced ring-opening.

**Figure 13.** Cyclic voltammogram of a SAM of dithienylethene 1c 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 (TBA)PF₆ with a Pt counter electrode and an SCE reference electrode.
assembly of 1 on gold substrates was confirmed by XPS and cyclic voltammetry to result in the formation of monolayers. XPS indicates that the three thiol groups of 1 are chemisorbed to the surface, which suggests that the orientation of 1 on the surface is as anticipated (Scheme 2). Furthermore, spectral characteristics of the acetate protecting groups were not detected by XPS. XPS and SERS confirmed adsorption of the tripod and the stability of the monolayer upon irradiation with UV and visible light.

SAMs of 1 on gold are shown by SERS spectroscopy and cyclic voltammetry to display reversible photochemical switching. Importantly, self-assembly of the fatigue product (1 byprod), generated by prolonged irradiation of 1 on solution, onto a gold surface allowed for observation of the SERS spectrum of 1 byprod (Figure 9). In contrast to 1c, 1 byprod is not subject to photoreversion upon irradiation at 785 nm and, together with its visible absorption which leads to resonant enhancement of the spectrum, means that even if present in minor amounts in a SAM, it can be observed readily. Hence, the absence of bands from 1 byprod in the spectra of SAMs of 1 even after extended irradiation at 365 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 gives that the orientation of the switch is relatively well controlled, it may be that the dipole moments of the transitions that access the state leading to irreversible isomerization and reversible cyclization. As such, we conclude that, despite the design of the tripod 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 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 surface attachment units 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.

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45) For additional spectroscopic data, see the Supporting Information.


54) 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. A resonance Raman spectrum was obtained at 532 nm as a dilute solution in DCM. See SOI section 7 for details.


(59) The potential applied was limited to 1.1 V as higher potentials are known to result in desorption of the SAM. See ref 41.