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Effect of Immobilization on Gold on the Temperature Dependence of Photochromic Switching of Dithienylethenes

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S *Supporting Information*

ABSTRACT: We report the properties and switching characteristics of a series of dithienylethene photochromic switches immobilized on gold. Self-assembled monolayers (SAMs) of three structurally related dithienylethenes were formed on roughened gold bead substrates and studied by surface-enhanced Raman spectroscopy (SERS). These data were compared to SERS spectra obtained by aggregation of colloidal gold, solid state Raman spectra, and Raman spectra calculated using density functional theory (DFT). Two of the dithienylethenes studied have an "asymmetric" design, which was demonstrated earlier to lower the thermal barrier for photochemical ring opening in solution. Herein, we show that, when immobilized on a gold surface, the asymmetric dithienylethenes in fact display a higher thermal barrier than that of their symmetric counterparts. In addition, we show that photochemical ring closing of asymmetric dithienylethenes is inhibited when immobilized on gold.
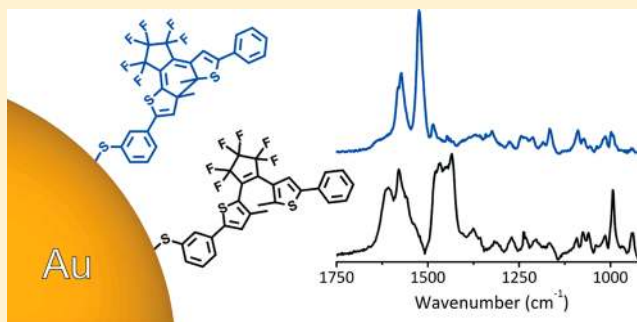
INTRODUCTION

Over the past decades, photochromic molecular switches[1] have received considerable attention due to their potential in applications as diverse as organic electronic devices,[2–4] optical data storage,[5,6] and switchable fluorescent markers in biology.[7–10] Several classes of photochromic switches have been reported, where each class has its own distinct properties and is appropriate to certain applications.[1] Examples of prominent classes of photochromic switches include spiropyrans,[11,12] fulgides,[13] azobenzenes,[14–17] hemithioindigos,[18–21] overcrowded alkenes,[22,23] and diarylethenes.[24–26] Studies on these switches generally focus on their behavior in solution; however, many of the potential applications for photochromic switches require that the switch is immobilized at an interface, and hence it is important to understand how immobilization affects their switching behavior.

Herein, we report the properties and switching characteristics of self-assembled monolayers (SAMs) of dithienylethenes on gold investigated by surface-enhanced Raman spectroscopy (SERS). Dithienylethenes[1,24–26] are a class of diarylethenes that consists of two thiophene units attached to a central olefin (Scheme 1a). They can undergo an electrocyclic ring closure upon irradiation with UV light in which the π-system rearranges to form a bond directly between the two thiophene moieties. The product of this cyclization, the closed form isomer, absorbs light in the visible region. Irradiation with visible light causes the electrocyclic reaction to be reversed, whereby the molecule changes back to its initial open form isomer. The large

Scheme 1. (a) Photochemical Switching of a Simplified Dithienylethene and (b) Structures of the Three Dithienylethenes That Were Investigated
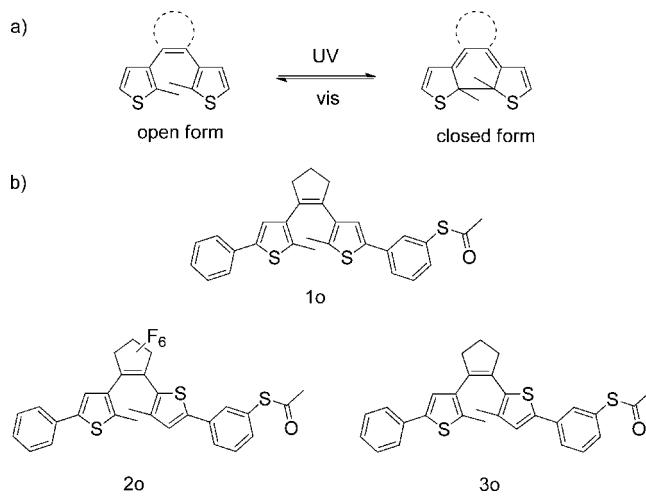
difference in the UV/vis absorption spectra of the open and closed form and the differences in the quantum yield for each process make it possible to address each form individually. In

addition, both forms are thermally stable, and the switching action can, in some instances, be triggered electrochemically also.[27,28]

With respect to photochemically induced switching, it has been shown for some systems that the ring-opening process has a thermal barrier, causing the rate of ring opening to be decreased significantly when operating in a temperature range of 100−200 K.[29] This complicates switching experiments performed at low temperatures, such as experiments using low-temperature mechanically controlled break junctions (MCBJs)[30] and low-temperature ultrahigh-vacuum scanning tunneling microscopy (UHV-STM).[31] Earlier, it was found that the thermal barrier can be lowered by the introduction of asymmetry in the π-system by altering the connectivity of one of the thiophene moieties.[32] These modified dithienylethene switches were studied in solution. However, the introduction of anchoring units as well as immobilization on a surface could have a significant effect on their photochemical properties. Empirical data relating switching behavior in solution to that in the solid state as SAMs on surfaces would provide more insight into the effect of immobilization on diarylethene switching.[24−26]

Herein, we report the study of three dithienylethenes (Scheme 1b), each carrying a thioacetate functionality that allows for spontaneous absorption upon contact with a gold surface without need for prior deprotection by an exogenous base.[33] Dithienylethene 1 is "symmetric"[34] (the two thiophene units are oriented in the same way) and has been investigated previously on gold nanoparticles by UV/vis spectroscopy,[35] on smooth gold bead electrodes by electrochemistry,[36] and on atomically flat gold by STM at room temperature.[37,38] In addition, 1 has been studied in the solution phase by UV/vis spectroscopy where the rate of photochemical ring opening was found to be temperature dependent.[29] Dithienylethenes 2 and 3 have an "asymmetric" design where the two thiophene units are connected at different positions with respect to each other. This change in design compared to 1 has been shown to be effective in lowering the thermal barrier to the ring-opening process in solution for a nonfunctionalized system.[32] Herein, we demonstrate that the switching properties of 2 and 3 when immobilized on gold are different from those observed in solution. Specifically, immobilization of 2 and 3 on gold results in quenching of the excited state of the closed form isomer and inhibits photochemical ring-opening, an effect that was not observed for 1 on gold. In addition, we show that, for 2 and 3, immobilization on gold influences the thermal barrier for photochemical ring-opening.

■ EXPERIMENTAL SECTION

General. NMR spectra were recorded on a Varian Unity AS 400, operating at 399.93 MHz for ^{1}H NMR spectroscopy. Chemical shifts are relative to the residual solvent signal of CD_2Cl_2 (5.30 ppm). Raman and SERS spectra were recorded with a PerkinElmer RamanStation 400F spectrometer at 785 nm. UV/vis absorption spectra were recorded using a JASCO V-630 spectrophotometer and quartz cuvettes (1 cm path length). UV irradiation was performed with a Spectroline ENB-280C/FE UV lamp, emitting at 365 nm (range: 310−390 nm, maximum at 365 nm) or 312 nm (range: 290−370 nm, maximum at 312 nm). Visible irradiation was carried out with a Thorlabs OSL1-EC fiber-optic illuminator in combination with a > 420 nm long-pass filter. Solvents used for spectroscopic measurements and SAM formation were of UVASOL grade

(Merck). Water was doubly distilled before use. Experimental details for the preparation of dithienylethenes 2 and 3 and their precursors are provided as Supporting Information.

Determination of Open/Closed Form Ratios at PSS. A 2×10^{-5} M solution of dithienylethene in ethanol in a quartz cuvette was irradiated at 365 or 312 nm. When the PSS was reached (as confirmed by UV/vis absorption spectroscopy), the sample was concentrated *in vacuo*, redissolved in a 99:1 mixture of heptane and isopropanol, and submitted for HPLC analysis.[39]

Determination of Photochemical Quantum Yields. Quantum yields were determined using a Jasco FP-6200 spectrofluorometer (5 nm bandwidth) as the irradiation source. An aqueous solution of potassium ferrioxalate was used as actinometer. A 6.0 mM solution of the actinometer was used at 365 nm and a 0.30 M solution at 436 nm. Irradiated samples were analyzed using a Analytik Jena Specord S 600 UV/vis absorption spectrophotometer.

Quantum Chemical Calculation of Raman Spectra. Quantum chemical calculations were performed with the Firefly 7.1.G and 8.0.0 beta QC programs,[40] which are based partially on GAMESS (US) source code.[41] Basis sets were obtained from the EMSL basis set exchange (https://bse.pnl.gov/bse/portal). Calculated Raman activities were converted to Raman intensities using the formula[42,43]

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i(1 - e^{-hc\nu_i/kT})}$$

where I_i is the Raman intensity, S_i is the Raman activity (Å^4 amu^{-1}), and ν_i is the wavenumber (cm^{-1}) of the ith vibration, ν_0 is the wavenumber (cm^{-1}) of the excitation laser, h is the Planck constant (J s), c is the speed of light (m s^{-1}), k is the Boltzmann constant (J K^{-1}), T is the temperature (K), and f is an optional normalization factor that is applied to all peaks.[42,43] Calculated Raman spectra were plotted with GaussSum 2.2.5 using Lorentzian curves with the full width at half-maximum (fwmh) set to 10 cm^{-1}.[44]

SERS Experiments Using Colloidal Gold. Colloidal gold in water was prepared from $HAuCl_4$ by reduction with trisodium citrate using the procedure of Frens,[45] resulting in the formation of gold particles with an average diameter of 18 nm as determined by transmission electron microscopy (TEM). 1 mL of the aqueous gold colloid was added to a quartz cuvette, and 5−10 μL of an approximately 10^{-4} M solution of a dithienylethene in acetonitrile was added and mixed by shaking. 5−10 μL of 0.2 M NaCl(aq) was added, aggregating the gold colloid as manifested in the appearance of a dark blue color, and the enhanced Raman spectrum was recorded.

Preparation of SAMs on Roughened Gold Beads. Electrochemical cleaning and roughening of gold beads was performed using a CHI760 bipotentiostat (CH Instruments). Gold beads were prepared by melting the end of a 0.5 mm diameter gold wire (99.995%) with a butane torch until a 1−2 mm diameter bead formed. The bead was cleaned electrochemically by cycling between −0.6 and 1.2 V in 0.5 M H_2SO_4 with a platinum wire counter electrode and a Hg/HgSO$_4$ reference electrode, until a stable cyclic voltammogram was obtained. Roughening of the bead was performed subsequently using a sweep step function: in 0.1 M aqueous KCl, with a platinum wire counter electrode and a SCE reference electrode, the potential was increased from −0.3 to 1.2 V at 1 V/s, held at
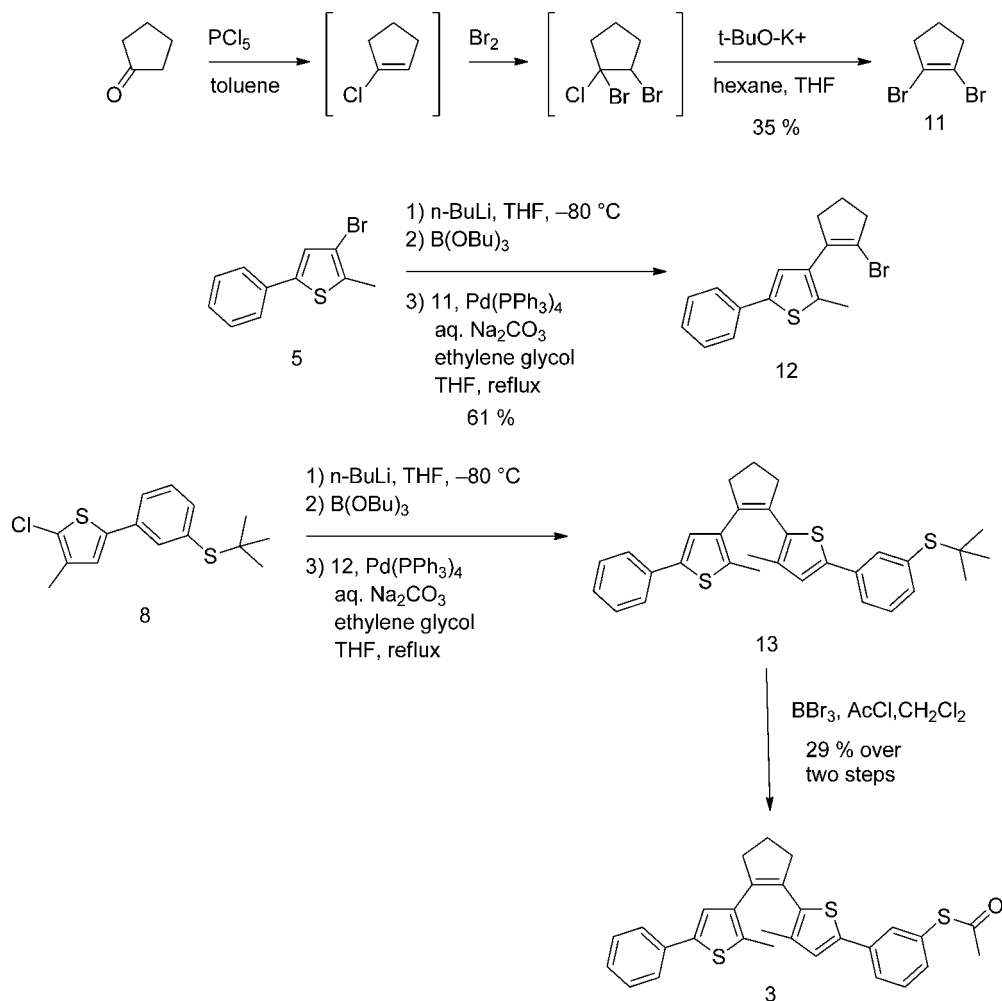
Scheme 2. Synthesis of Dithienylethene 2
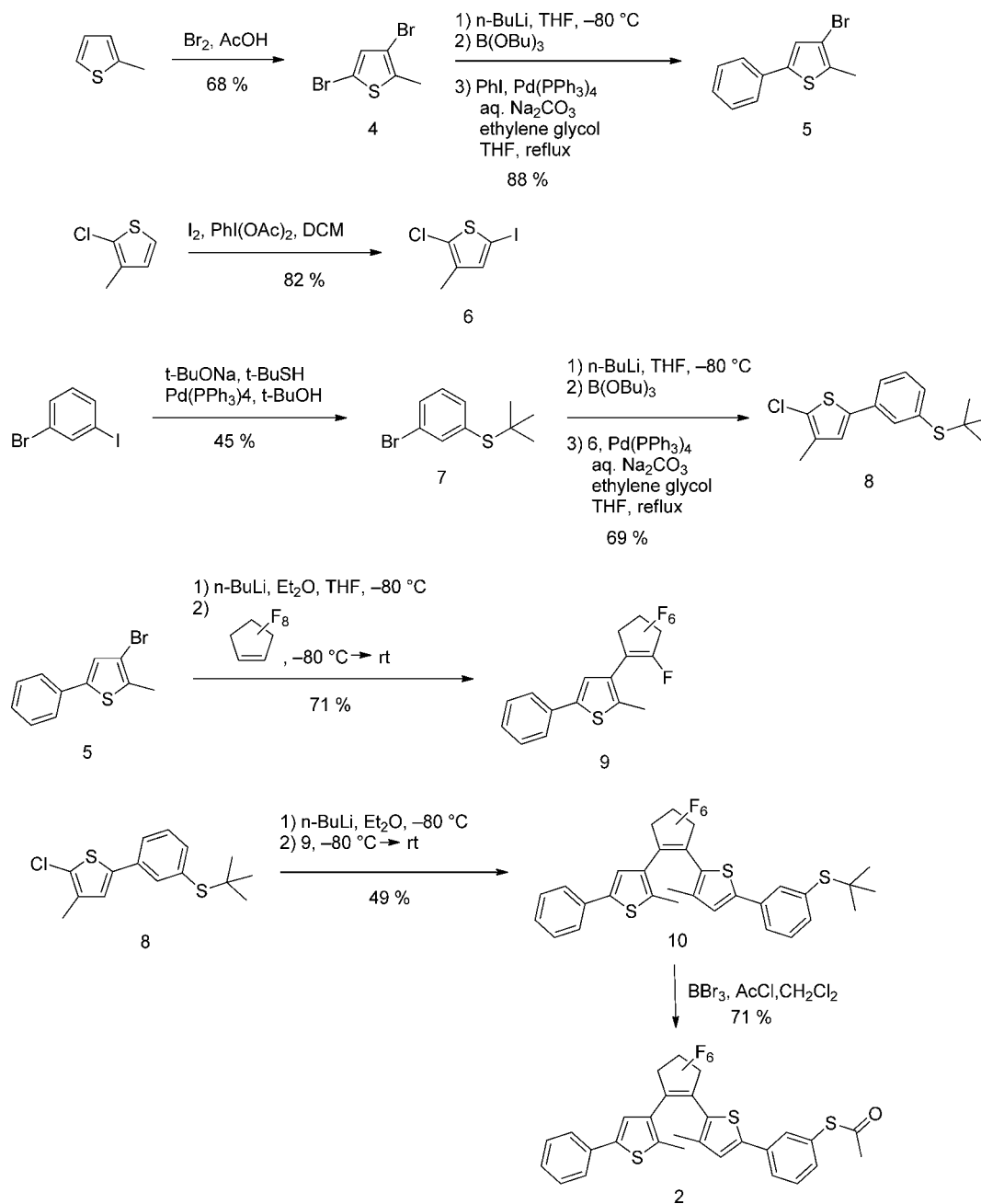
1.2 V for 30 s, and then cycled from 1.2 V back to −0.3 at 0.5 V/s. This cycle was repeated at least 24 times and caused the bead to become grayish in color. After rinsing with ethanol, the bead was transferred directly into a 0.5 mM solution of the dithienylethene of interest in ethanol and left for 16 h. The bead was then rinsed thoroughly with ethanol and dried under a flow of dry nitrogen gas.

SERS Spectroelectrochemistry. Spectroelectrochemistry was performed with a CHI1210B potentiostat (CH Instruments), using a roughened gold bead carrying a SAM of dithienylethene **1** (prepared as described above) as working electrode, a platinum wire as counter electrode, and a silver/silver(I) chloride wire as pseudoreference electrode. The electrodes were placed in a quartz cuvette containing 2 mL of 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane. The cuvette was placed in the Raman

spectrometer, after which SERS spectra were recorded with a laser power at sample of 10 mW.

Low-Temperature SERS Experiments. Experiments were performed using a MicrostatN2 nitrogen cooled cryostat, a VC41 gas flow controller, and a ITC503 temperature controller (Oxford Instruments). Measurements were performed with an Olympus BX51 M microscope attached to the Raman spectrometer, using 5× and 20× magnifications. The laser power at sample was set to 9.0 mW (5×) or 7.0 mW (20×) depending on the magnification used. Acquisition times used were less than 1 s. The laser power was determined using a hand-held LaserCheck calibrated power meter (Coherent Inc., model No. 54−018).

Scheme 3. Synthesis of Dithienylethene 3

■ RESULTS AND DISCUSSION

Synthesis of Dithienylethenes 2 and 3. The synthesis of the perfluorodithienylethene **2** is described in Scheme 2. Thiophene **4** was synthesized in 68% yield through the double bromination of 2-methylthiophene with bromine. The bromine at the 5-position was then substituted for a phenyl group by lithiation and boration, followed by a Suzuki–Miyaura cross-coupling reaction with iodobenzene. This provided the substituted thiophene **5** in 88% yield. NOESY NMR spectroscopy was used to confirm that the substitution pattern was as expected (see Supporting Information). Thiophene **6** was synthesized by the iodination of 2-chloro-3-methylthiophene by *N*-iodosuccinimide which provided the expected product in good yield. Thioether **7** was synthesized by reaction of 3-bromoiodobenzene with 2-methyl-2-propanethiol in the presence of sodium *tert*-butoxide and tetrakis-(triphenylphosphine)palladium(0). Subsequent lithiation and boration of thioether **7**, followed by coupling to thiophene **6**, provided thiophene **8** in 69% yield. The coupling of thiophenes **5** and **8** to octafluorocyclopentene was achieved in moderate to good yields: the addition of **5** provided compound **9** in 71% yield, whereas the subsequent coupling of **8** provided dithienylethene **10** in a somewhat lower yield (49%). Finally, the thioether group of **10** was converted into a thioacetate group, providing the target dithienylethene **2** in 71% yield.

The synthetic pathway described above could also be employed for the synthesis of the perhydro analogue, dithienylethene **3**, by the use of dibromocyclopentene **15** instead of octafluorocyclopentene (Scheme 3). In this case, the couplings between the two thiophene precursors and the central cyclopentene were achieved by a Suzuki–Miyaura cross-coupling reaction instead of an addition–elimination reaction. Dibromocyclopentene **11** was prepared in a three-step, one-pot procedure beginning with cyclopentanone. Thiophene **5** was then coupled to **11**, which provided olefin **12** in 61% yield. It was found that **12** decomposed completely within one day of its preparation. Therefore, **12** was used in the next synthetic step immediately after purification. Coupling of thiophene **8** and olefin **12** provided dithienylethene **13**, although it was found that, after column chromatography, **13** still contained a small amount of unidentified impurities that could not be removed by repeating column chromatography or by recrystallization. It was therefore decided to convert the slightly impure dithienylethene **13** into the acetate-protected dithienylethene **3**, which was obtained and purified without further complications.

Photochemical Switching of 2 and 3 in Solution. The switching behavior of dithienylethenes **2** and **3** in solution was studied by UV/vis absorption (Figure 1) and ^{1}H NMR spectroscopy (Figure 2), and their photochemical and spectroscopic properties are detailed in Table 1. Irradiation of the open form of **2** (**2$_o$**) at 365 nm caused the appearance of a
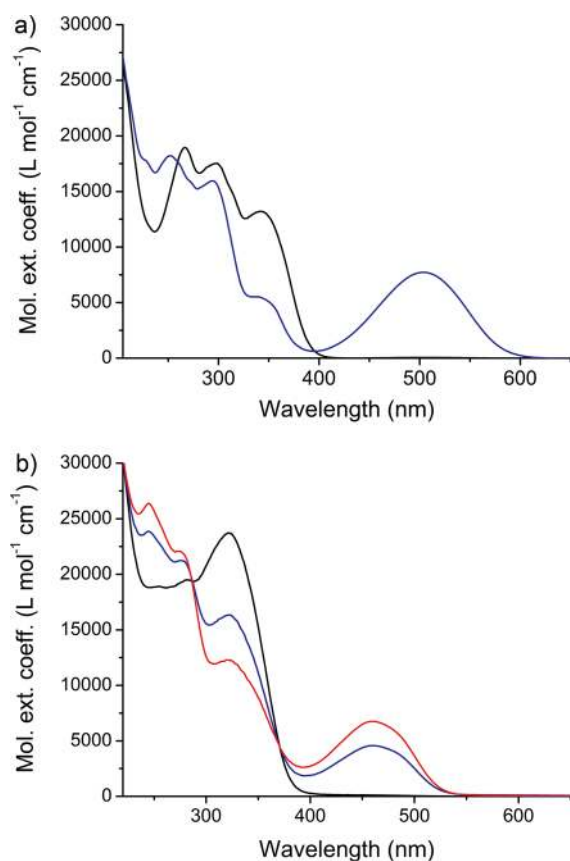
a)

b)

Figure 1. UV/vis absorption spectra of (a) 2_o (black) and 2_{PSS365} (blue) in *n*-hexane; (b) 3_o (black), 3_{PSS365} (blue), and 3_{PSS312} (red) in *n*-hexane.

Table 1. Photochemical and Spectroscopic Properties of Dithienylethenes 2 and 3

compd	abs λ_{max} [nm] ($\varepsilon[10^3$ L mol^{-1} cm^{-1}])	open/closed ratio at PSS	Φ_c	Φ_o
2	open: 342 (13.2), 298 (17.5), 267 (19.0)	9:91 (365 nm)	0.65 (365 nm)	0.07 (436 nm)
	closed^a: 293 (10.1), 503 (8.47)			
3	open: 312 (23.7)	59:41 (365 nm)	0.16 (365 nm)	0.43 (436 nm)
	closed^a: 459 (11.0), 245 (31.2)	39:61 (312 nm)		

^{a}Obtained by a scaled subtraction of the absorption spectrum of the open form from the absorption spectrum of the PSS mixture.

broad absorption with a maximum at 503 nm, which is characteristic of the formation of the closed form (2_c). Irradiation with visible light (>420 nm) reversed these changes (Figure 1a). Similarly, irradiation of 2_o at 365 nm in CD$_2$Cl$_2$ resulted in a large change to the ^{1}H NMR spectrum that was reversed by irradiation with visible light (Figure 2a). The most apparent shifts where those of the signals of the hydrogens of the two thiophene moieties (from 7.31 and 7.15 ppm to 6.73 and 6.15 ppm, respectively) and of the two central methyl groups attached to the thiophene moieties (from 2.03 and 1.80 ppm to 1.87 and 1.81 ppm, respectively). The ratio of open/closed form at the photostationary state at 365 nm (PSS$_{365\ nm}$) was determined by HPLC and found to be 9:91. The quantum yields for the ring-closing and ring-opening processes (Φ_c and Φ_o) were determined to be 0.65 (measured at 365 nm) and 0.07 (436 nm), respectively. These values were expected since the equilibrium at PSS$_{365\ nm}$ favors the closed form.
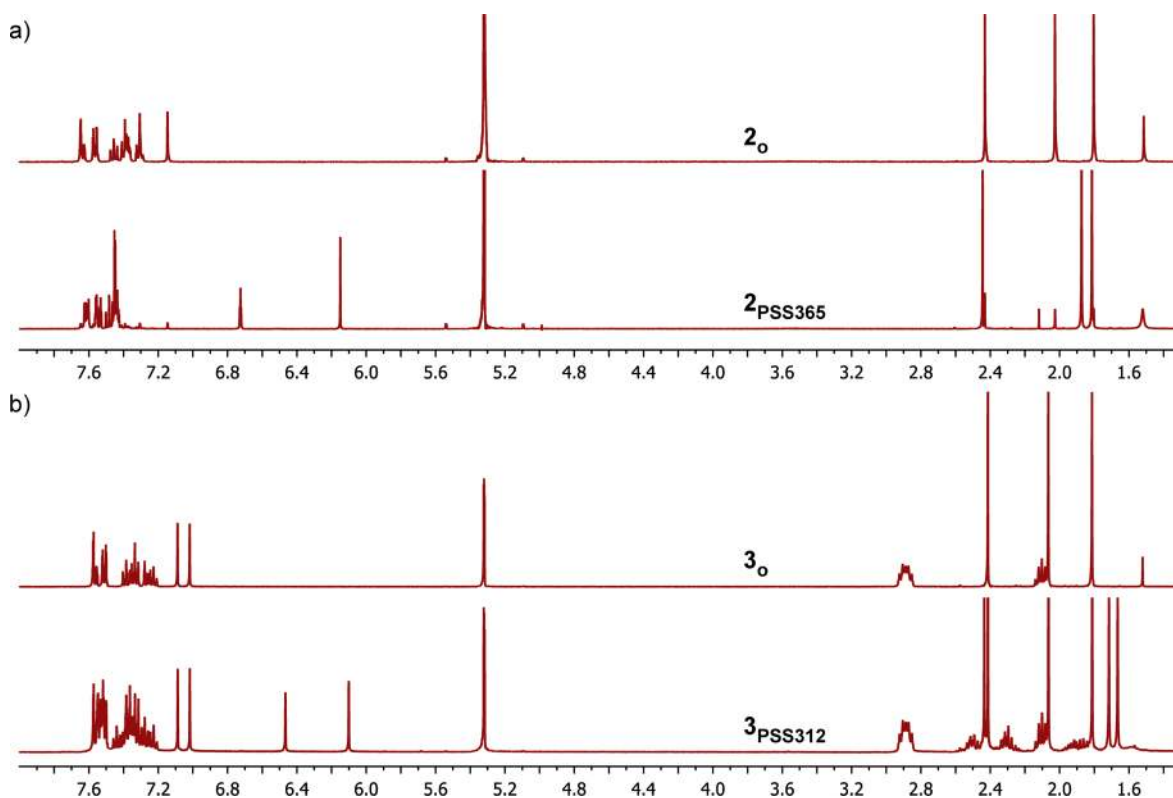
a)

b)

Figure 2. ^{1}H NMR spectra of (a) 2_o (top) and 2_{PSS365} (bottom); (b) 3_o (top) and 3_{PSS312} (bottom), recorded at 400 MHz in CD$_2$Cl$_2$.
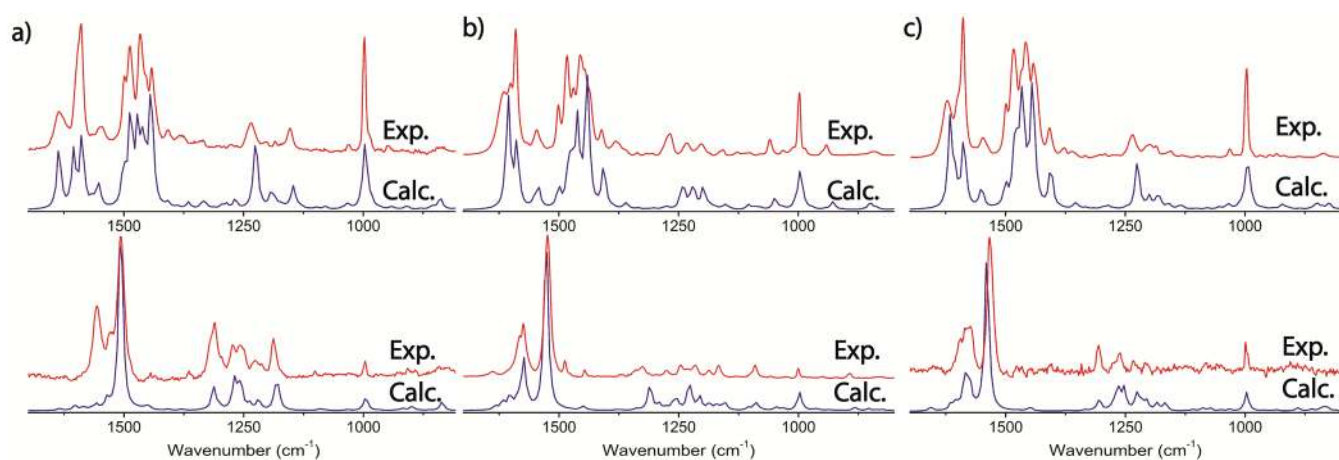
Figure 3. Experimentally obtained Raman spectra (red) and calculated spectra (blue) for dithienylethenes (a) **1**, (b) **2**, and (c) **3**. The top graphs show the open form spectra, and the bottom graphs show the closed form spectra. Experimental closed form spectra were obtained by a scaled subtraction of the open form spectra from the PSS spectra.

Interestingly, for the analogue of **2** which did not bear the thioacetate substituent, the difference between Φ_c and Φ_o was earlier found to be smaller (Φ_c = 0.37 (366 nm) and Φ_o = 0.23 (440 nm)),[32] which suggests that the photochemistry is influenced significantly by the thioacetate substituent.

UV/vis absorption and ^{1}H NMR spectroscopy of **3** showed changes similar to those of **2** upon irradiation. The UV/vis absorption spectrum of $\mathbf{3_o}$ showed the appearance of a broad absorption at 459 nm upon irradiation at 365 nm and a change reversed upon irradiation with visible light (Figure 1b). ^{1}H NMR spectroscopy showed that the signals mentioned above shift from 7.09 and 7.02 ppm to 6.47 and 6.10 ppm (thiophene moieties) and from 2.06 and 1.81 ppm to 1.72 and 1.67 ppm (central methyl groups), respectively (Figure 2b). The ratio of open/closed for **3** at $PSS_{365\ nm}$ was, however, determined to be only 62:38, which is lower than that of **2**. Irradiation at 312 nm caused the ratio at PSS to shift to 44:56.[46] The quantum yields Φ_c and Φ_o were found to be 0.16 and 0.43, respectively, which is in good agreement with the open/closed ratio obtained at PSS.

Finally, the presence of a thermal barrier for the ring opening of dithienylethenes **2** and **3** in solution was investigated. A $\sim 10^5$ M solution of the dithienylethene in isopentane (irradiated to PSS at 365 nm) was cooled to 120 K and irradiated using a Xe arc lamp (Newport) equipped with a 480 nm long-pass filter. UV/vis absorption spectroscopy was used to follow the ring-opening process. It was found that the solutions of **2** and **3** underwent ring opening fully within 4 s of irradiation, and hence these systems show essentially no thermal barrier to ring opening. In contrast, the UV/vis absorption spectrum of a sample of dithientylethene $\mathbf{1_{PSS365}}$, under these conditions, did not show any noticeable changes even after 60 s of irradiation. This indicates that the thermal barrier for the ring opening of **2** and **3** is significantly lower than that for the ring opening of **1**.

Raman Spectroscopy of Samples in the Solid State. For the three dithienylethenes investigated, Raman spectra were recorded (Figure 3, red spectra) for neat solid samples of both the open form and the mixture at $PSS_{365\ nm}$ (generated in solution). Spectra of the closed form isomers were then obtained by a scaled subtraction of the open form spectra from the spectra obtained at the PSS. The differences between the closed form spectra and PSS spectra were found to be minor, even for dithienylethene **3** which, at the PSS, contains a large

fraction of the open form isomer. This is due to the Raman scattering cross section of the closed form isomer being much greater than that of the open form isomer,[47] and hence the spectral features of the open form isomer are difficult to discern. Furthermore, it was found that under continuous exposure to a focused laser (at 785 nm) of the samples containing the closed forms, ring opening occurred.[48,49] Comparing the Raman spectra of the open and closed forms, several important spectral changes are noted. Raman spectra of the open form isomers of the three dithienylethenes studied were characterized by several strong signals in the region 1400−1600 cm^{-1}, though with a narrow region devoid of strong signals around 1500 cm^{-1} (Figure 3). Spectra of the closed form isomers, on the other hand, show characteristics opposite to this only one or two strong signals around 1500 cm^{-1}. The region 1400−1000 cm^{-1} also shows many differences between the open and closed form isomers, such as a strong signal around 1000 cm^{-1} which was more pronounced in spectra of the open form than in spectra of the closed form. These characteristics were also observed by us and others in the Raman scattering of neat samples of various dithienylethenes.[48,49]

Simulation of Raman Spectra with DFT. In order to confirm that the obtained Raman and SERS spectra originate from the open and closed ring isomers, as well as to assign the observed spectral features to specific vibrational modes, Raman spectra of the three dithienylethenes were calculated using density functional theory (DFT). It was found that spectra calculated with the B3LYP functional (using VWN formula 1 RPA correlation) and the cc-pVTZ basis set resembled the experimentally obtained spectra well (Figure 3, blue spectra). In order to correct for the general overestimation of the calculated wavenumbers,[50] a scaling factor of 0.975 was used, which was found to give a better match between the calculated and experimental spectra than with the factor of 0.965 that is suggested by the Computational Chemistry Comparison and Benchmark Database.[51] It was found that augmentation of the basis set with diffuse functions (which are often important for the accurate calculation of polarizabilities[52,53]) did not result in significant changes in the calculated spectra.

Comparison of the calculated spectra (Figure 3, blue spectra) with the acquired Raman spectra (Figure 3, red spectra) shows that the bands in the region 1400−1600 cm^{-1} in the spectrum

of dithienylethenes 1_o, 2_o, and 3_o originate from aromatic C=C stretching vibrations confined to only one-half of the molecule as well as from a C=C stretching vibration of the central cyclopentene moiety (Figure 4b−d). For the closed
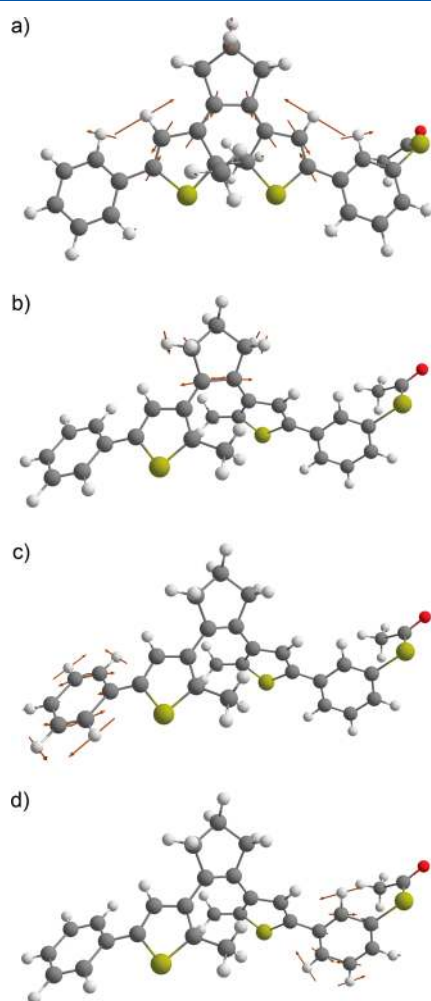

Figure 4. (a) Strongly Raman-active mode (1504 cm^{-1}) in the calculated Raman spectrum of 1_c. (b−d) Three examples of strongly Raman-active modes in the region 1400−1600 cm^{-1} in the calculated Raman spectrum of 1_o. Vectors (orange) indicate the displacement of atoms participating in a vibration.

form isomers, the strong signal observed around 1500 cm^{-1} originates from an aromatic C=C stretching vibration of the molecule's conjugated polyene system (Figure 4a). This observation is in agreement with data reported earlier for related systems.[48] The calculations support the observation that the closed form isomers show increased Raman scattering cross sections compared to the open form isomers.

SERS Spectroscopy in Solution. SERS spectra of each thioacetate-substituted dithienylethene switch were obtained by mixing a solution of the switch in CH$_3$CN with an aqueous suspension of colloidal gold, followed by aggregation by adding aqueous NaCl and measuring the resulting sample by Raman spectroscopy at 785 nm (Figure 5a−c). It was found that the SERS spectra obtained matched the nonresonant Raman spectra of the solid samples to a large extent—in fact, most spectral features were of the same relative intensity. Features in the SERS spectra were, however, broadened compared to those present in the nonresonant Raman spectra, which suggests a greater variation in the chemical environment in which the dithienylethene molecules reside.

SERS Spectroscopy on Roughened Gold Beads. The photochemical switching of monolayers of dithienylethenes **1**, **2**, and **3** on gold was studied by their deposition on roughened gold beads, followed by monitoring by SERS spectroscopy (Figure 6a−c, respectively). It was found that SERS spectra of the open isomer matched the SERS spectra obtained using colloidal gold. The SERS spectra of the dithienylethenes at the PSS$_{365 nm}$ with gold beads, however, did not match the SERS spectra obtained in solution but, instead, resembled the spectra of the open form isomers. This was found to be due to the Raman excitation laser (785 nm) inducing rapid ring opening of the closed form. By reducing the laser power as well as decreasing the acquisition time, the spectra of the ring closed isomer could be obtained, though these spectra still showed a large contribution from the ring open isomer. Laser-induced ring opening was also observed during acquisition of Raman spectra of neat samples of the dithienylethenes. One rationale for this observation is that the broadness of the lowest absorption band of the closed form, combined with the high power densities used during the experiments (which were determined to be 2.9 × 10^3 W cm^{-2} and higher), would result in significantly absorption in the NIR region. Furthermore, it has been shown that the lowest absorption band of the closed form of dithienylethenes shifted bathochromically[35] when

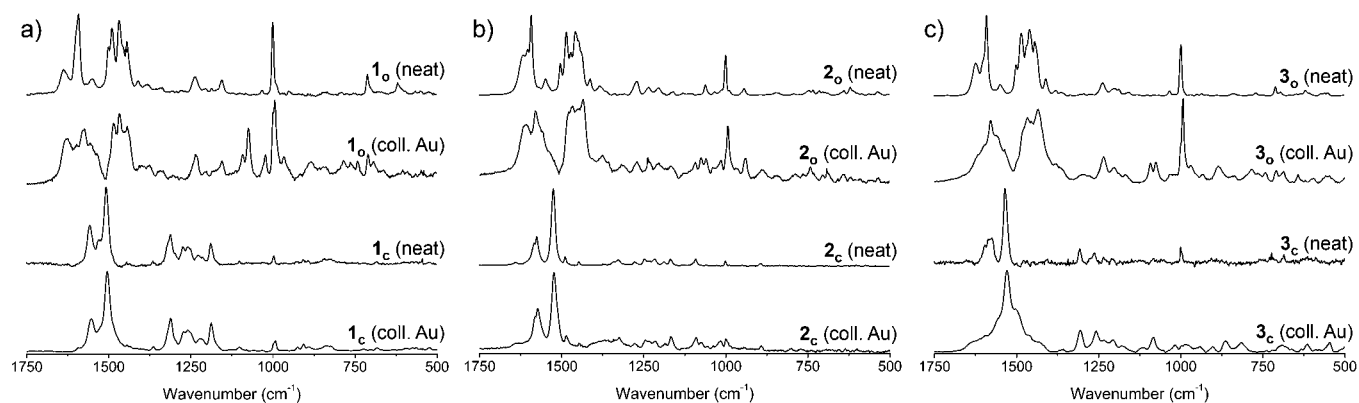**Figure 5.** Raman and SERS spectra of (a) dithienylethene **1**, (b) dithienylethene **2**, and (c) dithienylethene **3**. From top to bottom: Raman spectrum of the open form, SERS spectrum of the open form (colloidal gold), Raman spectrum of the closed form, SERS spectrum of the closed form (colloidal gold). Closed form spectra were obtained by a scaled subtraction of the open form spectra from the PSS spectra.
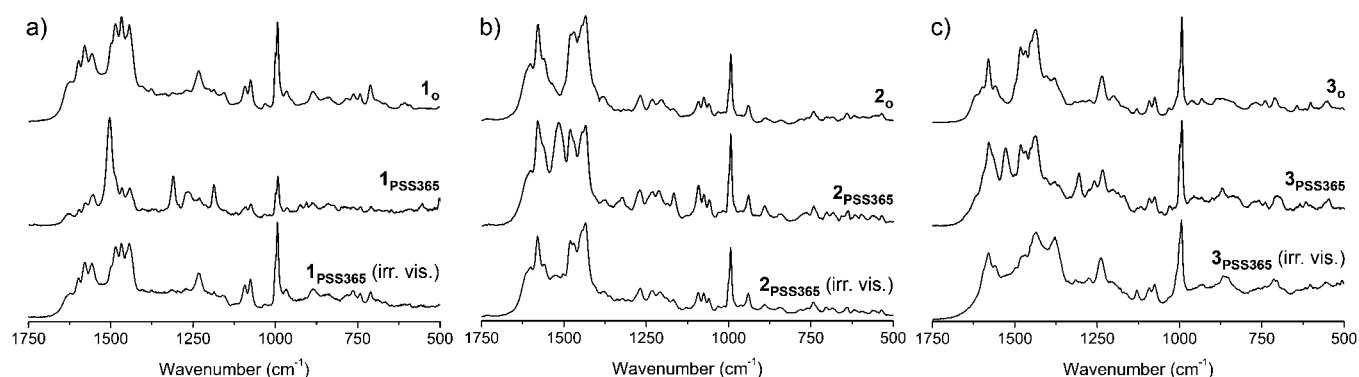
Figure 6. Experimentally obtained SERS spectra of dithienylethenes on roughened gold beads. (a) 1_o (top), 1_o after irradiation at 365 nm (middle), and 1_o after irradiation at 365 nm, then with visible light (bottom). (b) 2_o (top), 2_{PSS365} (middle), 2_{PSS365} after irradiation with visible light. (c) 3_o (top), 3_{PSS365} (middle), 3_{PSS365} after irradiation with visible light.

immobilized on gold through a thiol linker. An additional consideration with regard to ring-opening is two-photon excitation, which was observed for SAMs of spiropyrans under the same conditions, recently.[54] Thermally induced ring opening can however be excluded both due to the thermal stability of the dithienyl ethenes[24] and the absence of thermal reversion in spiropyrans under the same conditions.[54]

In agreement with data for the symmetric dithienylethene **1** (as observed by UV/vis absorption spectroscopy for **1** on gold nanoparticles,[35] by cyclic voltammetry for **1** on gold bead electrodes,[36] and by STM for **1** on Au(111)[37,38]), it was found that the photochemically induced switching of **1** on gold was possible in both directions. 1_o deposited on gold beads could be ring closed by irradiation at 365 nm, and the resulting ring closed species was observed by SERS. Subsequent ring opening was achieved by irradiation with visible light or by prolonged exposure to the 785 nm laser used to acquire the Raman spectra. However, for the two asymmetric dithienylethenes, **2** and **3**, it was found that photochemical cyclization was inhibited as irradiation at 365, 312, or 254 nm did not result in the desired ring closing. Ring opening, on the other hand, was not inhibited—when 2_o or 3_o was first irradiated (365 nm) and then deposited on gold, irradiation of the beads with visible light resulted in ring opening. The origin of the inhibition of ring closing is not fully understood. One rationalization is that the photochemistry of the open form isomers is quenched by interaction with the gold surface, a phenomenon that has been observed for a related dithienylethene[35] as well as for other types of photochromic switches attached to gold.[55] We speculate, however, that the inhibited ring closing is not related to the packing of the SAM, as ring closing was also not observed when **2** was embedded in a dodecanethiol–dithienylethene mixed monolayer on gold.[37,38]

SERS Spectroelectrochemistry with 1 on Roughened Gold Beads. For several systems, including dithienylethene **1**, it has been shown that ring closing and opening can be induced electrochemically in solution[27,28] as well as when adsorbed on smooth gold beads.[36] This electrochemical switching takes place via a dicationic intermediate.[56] Electrochemistry combined with SERS spectroscopy was used to obtain more information about the cationic species involved, the results of which are summarized in Figure 7. Figure 7a shows the cyclic voltammogram of a ring-closed SAM of **1** on a roughened gold bead, with the two reversible redox waves at 0.38 and 0.68 V.[36] Oxidation of the bead at 0.95 V gave rise to two major signals at 1527 and 1206 cm^{-1} as well as several less intense signals
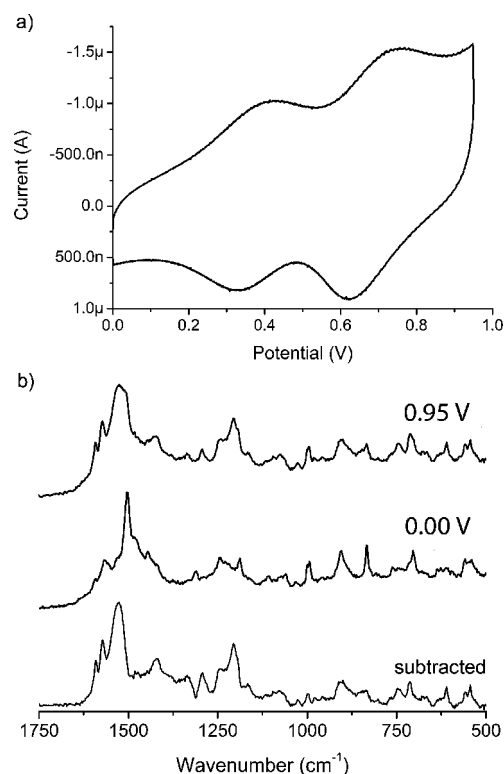

Figure 7. SERS spectroelectrochemistry of dithienylethene **1c**. (a) Cyclic voltammogram (0.00–0.95 V) of **1c** on a roughened gold bead. (b) SERS spectra of **1** at an applied potential of 0.95 V (top), **1** at an applied potential of 0.00 V (middle), and a scaled subtraction of the two spectra (bottom).

(Figure 7b). Reduction by applying a potential of 0.0 V reverted the spectrum to that of the closed form. These spectral changes observed upon oxidation are similar to those that were observed for a hexaphenylbenzene structure bearing six dithienylethene units.[57] In addition, it was also attempted to obtain spectra of the monocationic species by applying a potential that lies in between the two redox waves. However, reproducible spectra could not be obtained in this way. Similar studies could not be performed with **2** and **3** as we found that their oxidation potentials lie above that of the gold substrate.

Low-Temperature Switching on Roughened Gold Beads. In order to investigate the photochemical ring opening of dithienylethenes **1**, **2**, and **3** at low temperatures, roughened

gold beads carrying SAMs were cooled and characterized by SERS spectroscopy. Ring opening was achieved by repeated spectral acquisition, thus exposing the sample to the excitation laser (785 nm), thereby allowing the ring opening to be followed over time. During these experiments, the laser intensity was set to ≤9 mW, and only short acquisition times (up to 1 s) were used in order to prevent local heating of the bead. Ring opening over time was observed at 300 K for all three dithienylethenes investigated. The experiments were repeated at 100 and 200 K to investigate the temperature dependence of ring opening.

For dithienylethene 1_c, repeated spectral acquisition at 100 K did not show ring opening, which is in agreement with earlier studies[29] that demonstrated that the ring-opening process at this temperature is inhibited. At 200 K, ring opening was observed, albeit at a very slow rate. Finally, at 300 K, ring opening was observed at a rate much faster than was observed for 200 K. These data indicate a thermal barrier in the ring-opening process is present when **1** is tethered to a gold surface, which is in agreement with data obtained for dithienylethene 1_c in solution.[29]

For dithienylethenes 2_c and 3_c, it was expected that the thermal barrier to ring opening would be lower than that of 1_c, based on findings for the unsubstituted analogue of dithienylethene 2_c in solution.[32] However, at 100 and 200 K, neither 2_c nor 3_c showed evidence for ring opening. This suggests that the thermal barrier for these molecules is actually higher than for dithienylethene 1_c. This data contrasts markedly to that obtained in solution studies. There is currently no explanation for these differences between the solution experiments and experiments on gold substrates. At 300 K, ring opening of 2_c and 3_c on gold beads was observed.

CONCLUSION

The photochemical behavior of SAMs of three dithienylethene photochromic switches on gold has been investigated using SERS. SERS spectra obtained with colloidal gold; roughened gold beads were found to be similar to the Raman spectra of the pure compounds, and their spectral features could be correlated to specific vibrational modes through DFT calculations. In addition, the dicationic species of one dithienylethene was successfully detected using SERS spectroelectrochemistry. It was found that, adsorbed onto gold, the symmetric dithienylethene could be switched reversibly while the two asymmetric dithienylethenes could only be switched from the closed to the open form. Low-temperature SERS experiments show that for all three dithienylethenes the ring-opening mechanism has a thermal barrier. In contrast to data obtained in solution, the asymmetric dithienylethenes adsorbed on gold display a barrier to photochemical ring-opening that is higher than that of the symmetric dithienylethene adsorbed on gold. These findings provide insight into the photochemically and electrochemically driven isomerization of dithienylethenes and provide an example of how these molecules can behave differently in the solution phase from when adsorbed onto a metal surface. The results indicate that, in future studies, extrapolation of solution data for a series of analogous switches to their corresponding SAMs is not trivial.

ASSOCIATED CONTENT

ⓈSupporting Information
Experimental procedures for the preparation of **2**, **3**, and their precursors; ¹H NMR, APT, IR absorption, and Raman spectra for **2**, **3**, and their precursors; detailed UV/vis absorption spectra for the photochemical switching of **2** and **3**; ¹H NMR spectral data for 2_o, 2_{PSS365}, 3_o, and 3_{PSS312}; Cartesian coordinates for molecular geometries calculated with DFT. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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