# **Polymerization of Semi-Fluorinated Alkane Thiol Self-Assembled Monolayers Containing Diacetylene Units**

E. M. Cheadle,<sup>†</sup> D. N. Batchelder,<sup>†</sup> S. D. Evans,<sup>\*,†</sup> H. L. Zhang,<sup>†</sup> H. Fukushima,<sup>‡</sup> S. Miyashita,<sup>‡</sup> M. Graupe,<sup>§</sup> A. Puck,<sup>§</sup> O. E. Shmakova,<sup>§</sup> R. Colorado, Jr.,<sup>§</sup> and T. R. Lee<sup>§</sup>

Department of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, U.K., Base Technology Research Centre, Seiko Epson Corporation, Nagano-ken, Japan, and Department of Chemistry, University of Houston, Houston, Texas 77204-5003

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We report the formation and subsequent topochemical polymerization of semi-fluorinated self-assembled monolayers (SAMs) containing diacetylene groups. The SAMs used were formed via the adsorption of the following derivatives:  $CF_3(CF_2)_n(CH_2)_{16}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C \equiv C(CH_2)_{10}SH$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}C \equiv C-C$  $C(CH_2)_{10}SH$  (n = 9, 12) onto the surface of gold. The polymerization of the monolayers was initiated by UV irradiation and was monitored using resonance Raman spectroscopy. SAMs with short semi-fluorinated portions were found to polymerize more effectively than those with longer portions, indicating that steric factors become important with increasing perfluorinated chain length.

### Introduction

Control over the wetting properties of surfaces is of considerable importance from both a fundamental and a commercial perspective. To this end, there has been extensive research on the applications of  $\omega$ -functionalized self-assembled monolayers (SAMs) of alkane thiols on gold to create surfaces with well-defined wettability and adhesion properties.<sup>1,2</sup> The poor durability of these systems, however, has limited their use in such applications. For example, these systems are susceptible to degradation upon exposure to artificial light and sunlight (associated with UV-induced photooxidation)<sup>3</sup> or if heated to elevated temperatures (~100 °C).<sup>4</sup> Thus, mechanisms that enhance their durability either through hydrogen bonding or through the incorporation of polymerizable moieties are of considerable interest.<sup>5-14</sup>

One such approach has been based on the incorporation of diacetylene units. The polymerization of diacetylenes

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is regulated by strict intermolecular spatial requirements between conjugated triple bonds in the monomer species.<sup>15</sup> In SAMs, the equilibrium binding sites of the sulfur headgroups on Au(111) and the packing of the methylene chains fortuitously position the diacetylene groups within the spatial constraints necessary for polymerization. This was first demonstrated by Batchelder et al. in the preparation of methyl-terminated diacetylene SAMs.<sup>7</sup>

Menzel et al. have since extended this research by investigating the effect of the vertical positioning of the diacetylene unit within monolayers of methyl-terminated diacetylene thiols on gold.<sup>8-10</sup> Študies by Kim et al. have investigated hydroxyl- and carboxyl-terminated diacetylene SAMs.  $^{11-\check{1}3}$  In this paper, we report for the first time the formation and subsequent topochemical polymerization of SAMs derived from the adsorption of semifluorinated diacetylene thiols onto the surface of gold. The research presented here evaluates the affect of the sterically bulky fluorocarbon moieties upon the extent of topochemical polymerization.

Using atomic force microscopy (AFM), Alves and Porter found that semi-fluorinated molecules of  $CF_3(CF_2)_7(CH_2)_2$ -SH self-assembled on Au(111), forming a close-packed hexagonal lattice, with a nearest neighbor (NN) spacing of  $5.8 \pm 0.2$  Å and a next nearest neighbor spacing of 10.1 Å.<sup>16</sup> Subsequent AFM and grazing incidence X-ray diffraction experiments by other workers have found similar lattice spacings, although the degree of commensurability between the overlayer and the underlying substrate remains unclear.<sup>16–19</sup> Evidently, the lattice spacing associated with perfluorocarbons is greater than the 4.97 Å usually observed for *n*-alkane thiols. These studies suggest that the optimal packing of the perfluoroalkyl segments requires a deviation of the sulfur binding sites from the usual  $(\sqrt{3} \times \sqrt{3})$ R30° geometry in *n*-alkane thiol SAMs.

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<sup>\*</sup> To whom correspondence should be addressed.

<sup>&</sup>lt;sup>†</sup> University of Leeds.

<sup>&</sup>lt;sup>‡</sup> Seiko Epson Corporation.

<sup>§</sup> University of Houston.

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Table 1. Materials Studied					
sample name	molecular formula				
ODT F3 F4 F10 F13 F10H2	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>17</sub> SH CF <sub>3</sub> (CF <sub>2</sub> ) <sub>2</sub> (CH <sub>2</sub> ) <sub>16</sub> C=C-C=C(CH <sub>2</sub> ) <sub>10</sub> SH CF <sub>3</sub> (CF <sub>2</sub> ) <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> C=C-C=C(CH <sub>2</sub> ) <sub>10</sub> SH CF <sub>3</sub> (CF <sub>2</sub> ) <sub>9</sub> (CH <sub>2</sub> ) <sub>11</sub> C=C-C=C(CH <sub>2</sub> ) <sub>10</sub> SH CF <sub>3</sub> (CF <sub>2</sub> ) <sub>12</sub> (CH <sub>2</sub> ) <sub>11</sub> C=C-C=C(CH <sub>2</sub> ) <sub>10</sub> SH CF <sub>3</sub> (CF <sub>2</sub> ) <sub>12</sub> (CH <sub>2</sub> ) <sub>21</sub> C=SH				

Table 1 Materials Studied

Scheme 1. Synthesis of Semi-Fluorinated Diacetylene Thiols

CF3(CF2)n(CH2)ml + Me3Si-C=C-C=C-SiMe3

CF<sub>3</sub>(CF<sub>2</sub>)<sub>n</sub>(CH<sub>2</sub>)<sub>m</sub>-C≡C-C≡CH

1.	n-BuLi / Hexane
2.	Br(CH <sub>2</sub> ) <sub>10</sub> Br

CF3(CF2)n(CH2)m-C=C-C=C-(CH2)10Br

 $CF_3(CF_2)_n(CH_2)_m-C \cong C-C \equiv C-(CH_2)_{10}SH$ 

n = 2,3 and m = 16n = 9,12 and m = 11

The specific adsorbates used to prepare the SAMs described in this paper,  $CF_3(CF_2)_n(CH_2)_{16}C \equiv C - C \equiv$  $C(CH_2)_{10}SH$  with n=2 (F3) and n=3 (F4) and  $CF_3(CF_2)_{n}$  $(CH_2)_{11}C \equiv C - C \equiv C(CH_2)_{10}SH$  with n = 9 (F10) and n = 12(F13), are shown in Table 1. Polymerization of these SAMs was monitored using resonance Raman spectroscopy with excitation wavelengths of 514 and 633 nm. In an attempt to understand the observed polymerization properties, in particular the dependence of the effective conjugation length on the length of the perfluoroalkyl segment, the SAMs were characterized prior to any UV irradiation using contact angle goniometry, AFM, and grazing angle (reflection-absorption) Fourier transform infrared (FTIR) spectroscopic measurements. Results from studies of the degradation of these monolayers upon prolonged UV exposure and thermal treatment will be published elsewhere.

## **Experimental Section**

**Synthesis.** All thiol adsorbates used for SAM formation were prepared using the general synthetic strategy shown in Scheme 1. Unless noted otherwise, all reagents and starting materials were purchased from commercial suppliers and used without purification. The semi-fluorinated alkyl iodides,  $CF_3(CF_2)_{n^-}(CH_2)_{16}I$  (n = 2, 3) and  $CF_3(CF_2)_n(CH_2)_{11}I$  (n = 9, 12), were synthesized using previously reported methods;<sup>20</sup> analytical data for each iodide are provided below. A stepwise description of the synthesis of F10, which is representative of that used to prepare all thiol adsorbates, is detailed below. Analytical data for all major intermediates and product thiols are also provided. Nuclear magnetic resonance (NMR) spectra were collected in CDCl<sub>3</sub> with a General Electric QE-300 NMR spectrometer operating at 300 mHz. High-resolution mass spectra were obtained at Rice

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 $CF_3(CF_2)_9(CH_2)_{11}C \equiv C - C \equiv CH$ . The starting material, bistrimethylsilylbutadiyne (1.76 g, 9.05 mmol), was dissolved in 20 mL of dry tetrahydrofuran (THF) and cooled to −78 °C under argon. An aliquot (6.03 mL) of a solution containing methyllithium–lithium bromide complex (1.50 M in diethyl ether) was added dropwise. The mixture was allowed to warm to room temperature and was then stirred for 3.5 h. The mixture was again cooled to −78 °C, and a solution of  $CF_3(CF_2)_9(CH_2)_{11}I$  (7.22 g, 9.05 mmol) in THF (20 mL) was added, followed by the addition of 20 mL of hexamethylphosphoramide (HMPA). Stirring was continued at room temperature for 1 h. A saturated aqueous solution of NH<sub>4</sub>Cl (100 mL) was added, and the mixture was extracted with hexane (100 mL, 5×).

The combined hexane layers were washed with brine (500 mL), dried with MgSO<sub>4</sub>, and concentrated by rotary evaporation. The crude product was suspended in 40 mL of dimethylformamide, and 2 g of potassium fluoride dihydrate was added. The reaction mixture was stirred vigorously at room temperature for 1 h. The mixture was treated with 50 mL of 3 N aqueous HCl and was extracted with hexane (100 mL, 5×). The combined organic layers were washed with saturated aqueous NaHCO<sub>3</sub> (500 mL) and brine (500 mL), dried with MgSO<sub>4</sub>, and concentrated by rotary evaporation. The residue was purified by chromatography on silica gel using hexane as the eluent. Yield: 3.15 g (48%). <sup>1</sup>H NMR: 2.25 (t, J = 7 Hz, 2H), 1.97–2.15 (m, 2H), 1.91 (s, 1H), 1.50–1.65 (m, 2H), 1.25–1.44 (m, 16H).

*CF*<sub>3</sub>(*CF*<sub>2</sub>)<sub>9</sub>(*CH*<sub>2</sub>)<sub>11</sub>*C*≡*C*−*C*≡*C*(*CH*<sub>2</sub>)<sub>10</sub>*Br*. An aliquot of CF<sub>3</sub>-(CF<sub>2</sub>)<sub>9</sub>(CH<sub>2</sub>)<sub>11</sub>CCCCH (3.15 g, 4.36 mmol) was dissolved in 30 mL of dry THF and cooled to 0 °C in an ice bath. A slight excess of *n*-BuLi (1.92 mL of a 2.50 M solution in hexane) was added, and the reaction mixture was stirred at 0 °C for 1 h. Solid 1,-10-dibromodecane (6.54 g, 21.8 mmol) was added, followed by 20 mL of HMPA. Stirring was continued for 1 h. Saturated aqueous NH<sub>4</sub>Cl (100 mL) was added, and the mixture was extracted with hexane (100 mL, 5×). The combined extracts were washed with brine (500 mL), dried with MgSO<sub>4</sub>, and concentrated by rotary evaporation. The crude product was purified by chromatography on silica gel using hexane as the eluent. Yield: 0.67 g (16%). <sup>1</sup>H NMR: 3.39 (t, *J* = 7 Hz, 2H), 2.23 (t, *J* = 7 Hz, 4H), 1.94−2.12 (m, 2H), 1.84 (quint, *J* = 7 Hz, 2H), 1.20−1.58 (m, 32H).

*CF*<sub>3</sub>(*CF*<sub>2</sub>)<sub>9</sub>(*CH*<sub>2</sub>)<sub>11</sub>*C*≡*C*−*C*≡*C*(*CH*<sub>2</sub>)<sub>10</sub>*SH*. Measured aliquots of NaSH (0.24 g, 4.3 mmol) and CF<sub>3</sub>(CF<sub>2</sub>)<sub>9</sub>(CH<sub>2</sub>)<sub>11</sub>CCCC(CH<sub>2</sub>)<sub>10</sub>Br (0.67 g, 0.71 mmol) were dissolved in 20 mL of absolute ethanol and sonicated under argon at 50 °C for 6 h. The mixture was poured into 50 mL of 1 N aqueous HCl and extracted with hexane (100 mL, 5×).

The combined extracts were washed with saturated aqueous NaHCO<sub>3</sub> (100 mL) and brine (100 mL), dried with MgSO<sub>4</sub>, and concentrated by rotary evaporation. The product thiol was purified by chromatography on silica gel using hexane as the eluent. Yield: 0.25 g (35%). <sup>1</sup>H NMR: 2.50 (q, J = 7 Hz, 2H), 2.23 (t, J = 7 Hz, 4H), 1.94–2.12 (m, 2H), 1.20–1.63 (m, 35H). HRMS: [M]<sup>+</sup> calcd for C<sub>35</sub>H<sub>43</sub>F<sub>21</sub>S, 894.2750; found, 894.2754.

Note: We have observed polymerization and/or decomposition of all neat thiol products upon storage under ambient conditions. Long-term storage is, however, possible by keeping the thiols dissolved in solution under air-free and light-free conditions.

 $CF_3(CF_2)_2(CH_2)_{16}I$ . <sup>1</sup>H NMR: 3.14 (t, J = 7 Hz, 2H), 1.90–2.07 (m, 2H), 1.80 (quint, J = 7 Hz, 2H), 1.50–1.62 (m, 2H), 1.10–1.39 (m, 24H).

 $CF_{3}(CF_{2})_{3}(CH_{2})_{16}$ I. <sup>1</sup>H NMR: 3.17 (t, J = 7 Hz, 2H), 1.96–2.14 (m, 2H), 1.80 (quint, J = 7 Hz, 2H), 1.54–1.62 (m, 2H), 1.20–1.40 (m, 24H).

 $CF_3(CF_2)_9(CH_2)_{11}I$ . <sup>1</sup>H NMR: 3.17 (t, J=7 Hz, 2H), 1.90–2.15 (m, 2H), 1.80 (quint, J=7 Hz, 2H), 1.52–1.63 (m, 2H), 1.10–1.42 (m, 14H).

 $CF_{3}(CF_{2})_{12}(CH_{2})_{11}I$ . <sup>1</sup>H NMR: 3.18 (t, J = 7 Hz, 2H), 1.95–2.13 (m, 2H), 1.81 (quint, J = 7 Hz, 2H), 1.50–1.64 (m, 2H), 1.15–1.42 (m, 14H).

 $CF_3(CF_2)_2(CH_2)_{16}C \equiv C - C \equiv CH.$  <sup>1</sup>H NMR: 2.24 (t, J = 7 Hz, 2H), 1.90–2.10 (m, 2H), 1.92 (s, 1H), 1.42–1.62 (m, 2H), 1.15–1.41 (m, 26H).

 $CF_3(CF_2)_3(CH_2)_{16}C \equiv C - C \equiv CH.$  <sup>1</sup>H NMR: 2.25 (t, J = 7 Hz,

2H), 1.89–2.11 (m, 2H), 1.94 (s, 1H), 1.43–1.62 (m, 2H), 1.11–1.38 (m, 26H).

 $CF_3(CF_2)_{12}(CH_2)_{11}C \equiv C - C \equiv CH.$  <sup>1</sup>H NMR: 2.26 (t, J = 7 Hz, 2H), 1.98–2.15 (m, 2H), 1.97 (s, 1H), 1.50–1.65 (m, 2H), 1.22–1.44 (m, 16H).

 $CF_{3}(CF_{2})_{2}(CH_{2})_{16}C \equiv C - C \equiv C(CH_{2})_{10}Br.$ <sup>1</sup>H NMR: 3.39 (t, J = 7 Hz, 2H), 2.22 (t, J = 7 Hz, 4H), 1.90–2.10 (m, 2H), 1.83 (quint, J = 7 Hz, 2H), 1.10–1.59 (m, 42H).

 $CF_{3}(CF_{2})_{3}(CH_{2})_{16}C \equiv C - C \equiv C(CH_{2})_{10}Br.$ <sup>1</sup>H NMR: 3.39 (t, J = 7 Hz, 2H), 2.22 (t, J = 7 Hz, 4H), 1.94–2.12 (m, 2H), 1.83 (quint, J = 7 Hz, 2H), 1.20–1.60 (m, 42H).

 $CF_3(CF_2)_{12}(CH_2)_{11}C \equiv C - C \equiv C(CH_2)_{10}Br$ . <sup>1</sup>H NMR: 3.39 (t, *J* = 7 Hz, 2H), 2.22 (t, *J* = 7 Hz, 4H), 1.98-2.15 (m, 2H), 1.84 (quint, *J* = 7 Hz, 2H), 1.20-1.60 (m, 32H).

 $CF_{3}(CF_{2})_{2}(CH_{2})_{16}C \equiv C - C \equiv C(CH_{2})_{10}SH.$ <sup>1</sup>H NMR: 2.53 (q, J = 7 Hz, 2H), 2.25 (t, J = 7 Hz, 4H), 1.93-2.13 (m, 2H), 1.20-1.68 (m, 45H). HRMS: [M]<sup>+</sup> calcd for C<sub>33</sub>H<sub>53</sub>F<sub>7</sub>S, 614.3756; found, 614.3750.

 $CF_{3}(CF_{2})_{3}(CH_{2})_{16}C \equiv C - C \equiv C(CH_{2})_{10}SH.$ <sup>1</sup>H NMR: 2.49 (q, J = 7 Hz, 2H), 2.22 (t, J = 7 Hz, 4H), 1.93-2.12 (m, 2H), 1.20-1.61 (m, 45H). HRMS: [M]<sup>+</sup> calcd for C<sub>34</sub>H<sub>33</sub>F<sub>9</sub>S, 664.3730; found, 664.3724.

 $CF_3(CF_2)_{12}(CH_2)_{11}C \equiv C - C \equiv C(CH_2)_{10}SH.$ <sup>1</sup>H NMR: 2.50 (q, J = 7 Hz, 2H), 2.22 (t, J = 7 Hz, 4H), 1.94 - 2.15 (m, 2H), 1.20 - 1.62 (m, 35H). HRMS: [M]<sup>+</sup> calcd for C<sub>38</sub>H<sub>43</sub>F<sub>27</sub>S, 1044.2654.

**Substrate Preparation.** For all experiments other than the molecular resolution lattice imaging using the AFM, the substrates were prepared by evaporating gold onto polished silicon wafers or glass microscope slides, with a chromium underlayer to promote adhesion of the gold. To remove excess grease, the glass slides were initially ultrasonicated in Decon 90 followed by Milli-Q water. After this treatment, the cleaning procedure was the same for both glass and silicon substrates.

The slides were cleaned by ultrasonication in methanol for 30 min and then cleaned by either immersion in "piranha" solution (H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>, 7:3) for 5–10 min or treatment with argon ion plasma for 1 min. The slides were then rinsed thoroughly in methanol (Aldrich HPLC grade), dried in a stream of nitrogen, and placed directly into the evaporator. The evaporator used was an Edwards Auto 306 Turbo. A vacuum of  $<5 \times 10^{-6}$  mbar was used, and 150 Å of chromium was evaporated onto the wafer, followed by 1000–2000 Å of gold (99.99%). The gold slides were cleaned again immediately prior to use in either a piranha solution (1–2 min) or an argon ion plasma before being rinsed in isooctane.

**Monolayer Preparation.** Monolayers were formed by the spontaneous adsorption of the thiols onto the gold surface for  $\sim$ 12 h from 0.03 mM isooctane solutions for a period of 12 h. Substrates removed from the solution were rinsed thoroughly with isooctane and dried under a flow of nitrogen.

**Polymerization of the Monolayers.** Polymerization was effected through exposure to 254-nm UV light from a Hg(Ar) UV pen lamp (UV Products Ltd.) with a nominal power at the sample of 4.75 mW/cm<sup>2</sup>. The polymerization was conducted under an atmosphere of oxygen-free nitrogen.

**Raman Spectroscopy.** Raman spectra were obtained using a Renishaw Raman imaging microscope, using either a 25-mW He–Ne laser (wavelength = 632.8 nm) or a 25-mW Ar<sup>+</sup> laser (wavelength = 514.4 nm). Neutral density filters were used to reduce the power incident on the samples to ~1 mW to avoid any possible laser damage. All spectra were taken using a ×50 Olympus objective (NA = 0.80). Integration times are indicated for each spectra.

**AFM.** AFM experiments were carried out on SAMs adsorbed on gold substrates that had been annealed using a hydrogen flame.<sup>18</sup> A NanoScope III (Digital Instruments, Inc., Santa Barbara, CA) was used for all experiments. The measurements were performed in contact mode (10- $\mu$ m scanner) in air using a silicon nitride cantilever having a nominal spring constant of 0.38 N/m. Contact forces were determined from force–distance curves during approach and retract cycles recorded before and during imaging. The contact force, including the force due to cantilever bending and the adhesive contribution due to capillary and van der Waals forces, was typically 30 nN and never in excess of 70 nN. Maximum contrast was obtained in the lateral force images.<sup>21</sup> All the images shown are raw data that were plane fitted. For quantitative analysis, "up" and "down" scans were averaged in order to compensate for thermal drift. Images were analyzed by applying the autocorrelation filter to a selected area of the resolved lattice. Cross-sectional plots were subsequently collected from the observed hexatic lattice in three directions. The repeat length in these directions was obtained from the frequency plots by taking the distance at the maximum spectral density.<sup>19</sup> Images of a  $CF_3(CF_2)_9(CH_2)_2SH$  (F10H2) monolayer, which is known to exhibit a hexagonal lattice with a NN spacing of 5.8 Å, were used to postcalibrate the images of the semi-fluorinated diacetylene thiols.<sup>16–19</sup>

**Contact Angle Measurements.** The samples were placed on a stage beneath a square-cut needle with a 0.5-mm bore. Using a microsyringe, captive drops of Milli-Q water were advanced and receded across the sample surface. Sessile drops of hexadecane were formed using a glass capillary tube. The drops were illuminated from behind by a sodium lamp and imaged using a Navitar zoom lens coupled to a  $\times 2$  extension tube (total magnification of up to  $\times 22$ ) on a Hamamatsu C3077 CCD camera. The images were viewed on a high-resolution monochrome video monitor and captured and measured using Accuware software. Contact angles quoted in this paper were averaged over at least three drops per sample, with angles being measured at both edges of the drop and also averaged over more than one sample of each type.

**FTIR Measurements.** Grazing angle IR spectra were collected at an incident angle of  $80^{\circ}$  using a Bruker IFS-48 spectrometer. Spectra were taken after being purged in dry air for at least 16 h and were background subtracted from a reference spectrum of freshly cleaned gold under the same conditions. Spectra were collected for 2000 scans at a resolution of 2 cm<sup>-1</sup>.

#### **Results and Discussion**

Monolayers of the monomers were formed by adsorption from isooctane solutions that had been previously filtered using 0.2-µm poly(tetrafluoroethylene) (PTFE) filters to remove any gross polymer product. All monolayers emerged autophobic, i.e., they were unwet by the solutions from which they were formed. Following adsorption, the wetting properties, composition, and structure of the resulting monolayers were characterized through contact angle goniometry, AFM, and grazing angle (reflection– absorption) FTIR measurements. Resonance Raman spectra were taken of samples that were irradiated by UV for 1 min under an atmosphere of nitrogen.

**Polymerization upon UV Irradiation.** The highly conjugated polydiacetylene (PDA) backbone exhibits strong excitionic optical absorption in the visible region of the spectrum.<sup>15</sup> PDA thin films and LB mulitlayers appear either red or blue, depending upon the effective conjugation length of the PDA backbone. Thin films of PDAs in the so-called "red phase" are thought to possess shorter effective conjugation lengths as compared to those in the "blue phase".<sup>15,22</sup> Traditionally, UV/vis absorption spectroscopy has been used to characterize PDA thin films.<sup>22</sup> However, for PDA monolayers on gold films, interference from plasmon absorption precludes the use of this technique.<sup>8</sup>

Raman spectra of the PDA backbone exhibit intense resonant enhancement when the wavelength of the exciting laser lies within the optical absorption band; thus, tuning the excitation wavelength allows selective enhancement of the polymer phase of interest.<sup>22–24</sup> Figure 1 shows typical examples of resonance Raman spectra of all monolayers obtained using an excitation of wavelength

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**Figure 1.** Resonance Raman spectra, at 633-nm excitation, of all monolayers upon exposure to UV for 60 s. The integration time for monolayers of F3 and F4 was 30 s; for monolayers of F10 and F13, the integration time was 120 s.



**Figure 2.** Resonance Raman spectra, at 514-nm excitation, of all monolayers upon exposure to UV for 60 s. Integration time was 30 s.

633 nm (He–Ne laser) after 60 s of UV irradiation. At this wavelength, the excitation is in resonance exclusively with the polymer in the blue phase.<sup>22–24</sup> The vibrational modes at ~1450 and 2070 cm<sup>-1</sup> correspond to the stretching vibrations of the double and triple bonds of the PDA backbone, respectively.

The other bands observed in the Raman spectra of PDAs are due to vibrational modes involving the coupling of side group vibrations to those of the backbone. It is clear from the spectra in Figure 1 that monolayers of F3 and F4 both contained the polymer in the blue phase. A close examination of the spectrum for the monolayer of F10 reveals the presence of some blue-phase material, while the spectrum for the monolayer of F13 displays no notable presence of this highly conjugated phase. Neither shorter nor longer periods of irradiation led to the observation of resonance Raman bands for monolayers of F13 at this excitation wavelength. While the amount of blue-phase material cannot be quantified from the spectra in Figure 1, there is a clear qualitative correlation between the amount of blue-phase material present and the length of the fluorocarbon segment. We can thus conclude that increasing the length of the perfluorinated chain must affect the molecular packing in such a manner that inhibits the polymerization reaction and/or reduces the effective conjugation length of the PDA backbone.

As shown in Figure 2, resonance Raman spectra were observed for all samples excited at 514 nm. At this wavelength, the excitation is in resonance with polymer in both the red and the blue phases.<sup>22-24</sup> Detailed analysis suggests that the double-bond stretch for monolayers of F3 and F4 is comprised of two peaks (see Figure 3). The



**Figure 3.** Resonance Raman scattering for the C=C stretch of the PDA backbone showing the blue-phase and red-phase components at  $\sim$ 1460 and  $\sim$ 1500 cm<sup>-1</sup>, respectively.

components can be attributed to polymer phases of differing conjugation length present within the monolayer, as observed previously for LB monolayers and multilayers<sup>22,23</sup> and alkane thiol SAMs.<sup>9</sup> The component at ~1460 cm<sup>-1</sup> is attributed to weak resonance excitation of the longer effective conjugation length blue phase, while the component at ~1500 cm<sup>-1</sup> is attributed to resonance excitation of the shorter effective conjugation length red phase, which is near maximum resonance.

Consistent with the results for excitation at 633 nm, the blue-phase component of the double-bond peak comprises a greater proportion of the total peak area for F3 monolayers than it does for monolayers derived from F4 and F10 and is nonexistent for monolayers derived from F13. Furthermore, it appears that the amount of red-phase material present also decreases as the length of the fluorocarbon chain increases. We note that the contact angles measured for all SAMs did not change appreciably following the 60 s of UV irradiation described in this study.

**Monolayer Characterization Prior to Polymerization/UV Irradiation.** From the resonance Raman spectra of the polymerized monolayers, it would appear that the optimal packing of the alkyl segments required for a highly conjugated PDA backbone is compromised by the increasing influence of the more bulky fluorocarbon units. To investigate this hypothesis, the packing and order within the monolayers were examined prior to polymerization using AFM, wetting, and FTIR measurements.

Figure 4 shows typical AFM images obtained from samples F3, F13, and for comparison F10H2. Images of F4 and F10 are given in the Supporting Information. The measured lattice constants are given in Table 2. In contrast to SAMs of the semi-fluorinated thiol F10H2, all of the semi-fluorinated diacetylene SAMs were more difficult to image with molecular resolution and displayed fewer and smaller ordered domains. Hexagonal lattices with NN spacings of ~6.5 Å were imaged for all of the semi-fluorinated diacetylene SAMs, with no measurable difference between them (see Table 2). We note, however, that in the case of the F3 SAM a region of distorted hexatic lattice was also imaged.

If the perfluorinated segments of the monolayer were close-packed and oriented normal to the surface, the lattice spacing would be 5.55 Å, and each molecule would occupy a surface area of  $\sim$ 27 Å<sup>2</sup>.<sup>25</sup> The experimentally determined NN spacing of 6.5 Å corresponds to a surface area of 37

<sup>(25)</sup> *Polymer Handbook*, 3rd ed.; Brandup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; p V/37.



**Figure 4.** Molecular resolution AFM lateral force images of SAMs derived from (a) F10H2, (b) F3, and (c) F13.

 ${
m A}^2$  per molecule, implying that the perfluorinated tail groups are tilted significantly with respect to the surface normal.

On the basis of the assumptions that the fluorinated tail groups are not pinned at either end and that they attain a minimum volume, our measurements suggest that the fluorocarbon segments of the semi-fluorinated diacetylenes tilt by approximately 44° from the surface normal. While this value is somewhat greater than that usually found for alkane thiols on Au(111), it is surpris-

 Table 2. Lattice Constants and Contact Angles for Thiol

 Monolayers on Gold

			$H_2O^b$		
adsorbate	lattice constant (Å)	$\theta_{a}$	$\theta_{\rm r}$	$\Delta \theta$	$\theta$
F3	$6.4\pm0.2^{a}$	118	109	9	68
F4	$6.6\pm0.2$	120	110	10	72
F10	$6.5\pm0.2$	122	115	7	77
F13	$6.5\pm0.2$	122	117	5	77
F10H2	$5.8\pm0.2$	117	108	9	67

<sup>*a*</sup> A distorted hexatic lattice with constants  $a = 5.9 \pm 0.5$  Å,  $b = 5.8 \pm 0.3$  Å, and  $c = 6.4 \pm 0.3$  Å was also observed. <sup>*b*</sup> Contact angle data are averages for samples prepared on different batches of substrate and are reproducible to  $\pm 1-2^{\circ}$ .



**Figure 5.** High-frequency grazing incidence FTIR spectra showing the C–H stretching region.

ingly not that dissimilar to an alkyl chain tilt of 42° found for carboxylic acid-functionalized diacetylene-containing SAMs.  $^{\rm 13}$ 

The wetting properties of the monolayers prior to polymerization were determined by measuring the contact angles of water and *n*-hexadecane (see Table 2). The contact angles observed for the semi-fluorinated monolayers are characteristic of perfluoromethyl-terminated SÅMs.<sup>26,27</sup> The hexadecane and water contact angle values suggest that the adsorbates with the longest semifluorinated chains produce surfaces having the lowest surface free energies. Furthermore, the decrease in the contact angle hysteresis also suggests that the chemical heterogeneity of the SAMs decreases as the length of the perfluorinated segment increases. Because the AFM analysis indicates that the surface density of the fluorinated groups is similar for all of these SAMs, the differences in wettability probably arise from differences either in the dispersion force interactions due to the thickness of the semi-fluorinated region or in the distance of interfacial dipole contributions arising from the fluorocarbon-hydrocarbon junction.<sup>27</sup>

The "high-frequency" (C–H stretching) region of the grazing incidence FTIR spectra for all of the SAMs is shown in Figure 5. A spectrum for a  $CH_3(CH_2)_{17}SH$  (ODT) monolayer on Au(111) is shown for comparison. Because the fluorocarbon-terminated SAMs studied here contain no methyl groups, their high-frequency spectra consist of only the antisymmetric ( $\nu_a$ -CH<sub>2</sub>) and symmetric ( $\nu_s$ -CH<sub>2</sub>) stretching bands of the methylene groups.<sup>28</sup> The diacety-

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<sup>(27)</sup> Fukushima, H.; Seki, S.; Nishikawa, T.; Takiguchi, H.; Tamada, K.; Abe, K.; Colorado, R.; Graupe, M.; Shmakova, O. E.; Lee, T. R. *J. Phys. Chem. B* **2000**, *104*, 7417.

<sup>(28)</sup> We note that the weak peak seen at around  $3020 \text{ cm}^{-1}$ , positive in the spectrum for ODT and negative in the spectra of F13, F3, and F4, is due to water present in the background in different amounts.

lene groups within the monolayers vibrationally decouple the neighboring methylene chains.<sup>8,29</sup> As a result, the methylene bands arise from a superposition of contributions from both the "lower" (between the Au-S and the diacetylene unit) and the "upper" (between the diacetylene unit and the perfluorinated tail) alkyl chains. The packing, orientation, and conformational state of the upper and lower alkyl portions are influenced by their length (which determines the strength of the van der Waals interactions per chain) and the constraints imposed by (i) the binding to the Au surface, (ii) the presence of the rigid diacetylene chromophore, and (iii) the steric hindrance of the rigid perfluorinated units.

From Figure 5, the  $v_a$ -CH<sub>2</sub> and  $v_s$ -CH<sub>2</sub> modes for all of the semi-fluorinated diacetylene monolayers exhibit maxima at 2918 and 2850 cm<sup>-1</sup>, respectively, indicating that portions of the alkyl chains in these monolayers are in a highly ordered crystalline-like environment. In all cases, we found that the  $\nu_a$ -CH<sub>2</sub> bands exhibit asymmetry on the high-frequency side. Such an asymmetry has been observed previously for monolayers incorporating a diacetylene or sulfone group.<sup>2,6,8,29</sup>

It has been postulated that this asymmetry may be associated with a perturbation of the configuration and packing of the methylene units in the adjoining chains, leading to a disordered conformation of the alkyl chains.<sup>29,30</sup> We note further that spectra of simple semi-fluorinated alkane thiols adsorbed on gold and silver also show asymmetry on the high-frequency side of the  $v_a$ -CH<sub>2</sub> band.27

While the  $v_a$ -CH<sub>2</sub> and  $v_s$ -CH<sub>2</sub> peaks recorded for monolayers of F3 and F4 have a similar full width at halfmaximum to those found for ODT, both are significantly broader in the spectra of F10 and F13. This result suggests that the alkyl chains in monolayers derived from F10 and F13 exist in a more "loosely-packed" and disordered state as compared to those derived from F3 and F4. It seems likely that this disorder exists predominantly in the upper alkyl chains of the molecules in order to accommodate any mismatch between the packing of the diacetylene units, the alkyl chains, and the perfluorinated tail groups.

The "mid-frequency" (1400–1100 cm<sup>-1</sup>) grazing angle FTIR spectra (provided as Supporting Information) show the C–F stretching modes.<sup>31-36</sup> The assignment of the intense bands observed in this region for both PTFE, *n*-fluorocarbon oligomers, and monolayers of semifluorinated materials has been an issue of continued

debate and requires systematic treatment.<sup>31–36</sup> Dramatic changes in the spectra occurred as the length of the fluorocarbon segment was decreased from F13 and F10 to F4 and F3. The origin of these changes is unclear, plausibly arising through a combination of changes in conformation, ordering, and orientation of the fluorocarbon segments within the monolayers.

#### Conclusions

AFM, wetting, and grazing angle FTIR studies indicate that all of the semi-fluorinated diacetylene thiols formed close-packed SAMs on gold substrates. Polymerization of the monolayers upon irradiation by UV was monitored using resonance Raman spectroscopy. Overall, the resonance Raman spectra suggest that, as the length of the fluorocarbon tail is increased (and as the length of the alkyl chain separating it from the diacetylene moiety is decreased), topochemical polymerization within the monolayer is severely restricted. Because the length of the lower alkyl chain is fixed, the degree of polymerization is most likely controlled by the amount of disruption induced in the upper alkyl chain by the mismatch between the packing of the diacetylene units, the alkyl chains, and the perfluorinated tail groups. It is also possible that the steric bulk of the large perfluorinated groups induces a perturbation of the polymer backbone, thereby reducing the effective conjugation length in the polymerized films. As a whole, our results suggest that the conjugation length is governed by the interplay between the interactions of alkyl and perfluorinated chains and is dependent upon their relative lengths.

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Supporting Information Available: Molecular resolution images of SAMs derived from F4 and F10 and the midfrequency (1400–1100 cm<sup>-1</sup>) grazing angle FTIR spectra for the series F3–F13. This material is available free of charge via the Internet at http://pubs.acs.org.

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