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# Adsorption of Diisocyanides on Gold

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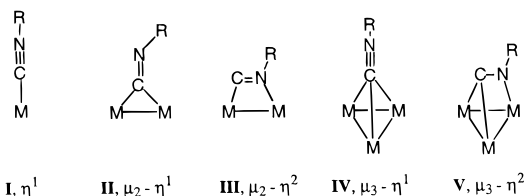
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Four known diisocyanides, 1,6-diisocyanohexane (**1**), 1,12-diisocyanododecane (**2**), 1,4-phenylenediisocyanide (**3**), 4,4'-biphenyldiisocyanide (**4**), and two new diisocyanides, 4,4'-*p*-terphenyldiisocyanide (**5**) and 1,4-di(4-isocyanophenylacetelynyl)-2-ethylbenzene (**6**), were used to prepare self-assembled monolayers (SAMs) on gold. The SAMs were characterized by ellipsometry, by measurement of the advancing water droplet contact angle, and by reflection absorption infrared (RAIR) spectroscopy. SAMs prepared from the diisocyanides **1** and **2**, which have a flexible alkyl chain between the two isocyanide end groups, were found to form monolayer films in which both isocyanide groups are bound to the surface. SAMs prepared from the diisocyanides **3–6**, which have rigid aryl or phenylethynyl structures between the two isocyanide end groups, were found to bind to gold through one CN group. Analyses of the RAIR spectra of these SAMs are consistent with surface selection rules for adsorbates that are oriented with their long molecular axis normal to the surface. Measurements of advancing water droplet contact angles and ellipsometric film thicknesses of SAMs prepared from **3–6** further support a surface structure in which the diisocyanide molecules are oriented vertically with one CN group bound to the surface and the other remote from the surface.

## Introduction

Over the past several years, self-assembled monolayer (SAM) films of thiols on gold have been an area of intense interest.<sup>1–10</sup> Organosulfur compounds also have been shown to form SAMs on copper,<sup>3,5,7–9,11,12</sup> silver,<sup>7</sup> InP,<sup>13</sup> GaAs,<sup>14–18</sup> YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7–δ</sub>, TlBaCaCuO,<sup>19</sup> and silicon.<sup>20</sup> Compared to that of thiols,<sup>21</sup> the adsorption of isocyanides onto metal surfaces is relatively uncharted territory.<sup>22–33</sup>

In general, isocyanides could bind to surfaces by adopting any of the five limiting structures **I–V**. Angelici et al.



reported diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies of isocyanides (CNPh, 1,4-(CN)C<sub>6</sub>H<sub>4</sub>, CNBu<sup>†</sup>) adsorbed from methanol solutions on Au powders.<sup>32,33</sup> These studies showed that isocyanides only bind in an  $\eta^1$  mode (**I** or **IV**). The DRIFTS studies also showed that the gold surfaces were saturated by isocyanides over time. However, the issue of whether saturation coverage corresponds to a 1:1 (type **I**) or a 1:3 (type **IV**) ratio between isocyanide molecules and surface gold atoms has not yet been determined. Steiner et al.<sup>34</sup>

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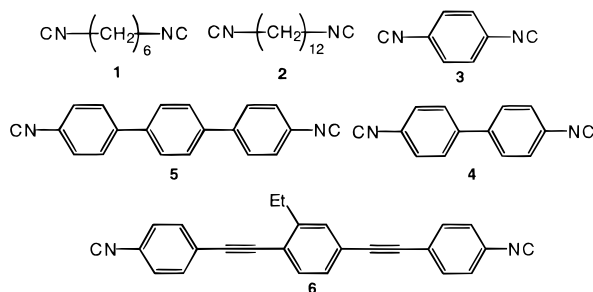
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and others<sup>35</sup> have found that alkylnitriles and alkyldinitriles bind to copper or gold in both  $\eta^1$  and  $\mu_2$ - $\eta^2$  (similar to type **III**) structures. At higher coverages  $\eta^1$  binding is favored. McCauley has reported studies of thin films of 1,6-diisocyanohexane (DICH) on Au and Pt.<sup>27</sup> The flexible diisocyanide DICH can bind to a surface through either one or both of its NC groups, depending on concentration and dosing time. The vertically oriented, singly NC surface attached diisocyanides were found to be polymerizable in the presence of  $\text{Ni}^{2+}$  to form multilayers of controlled thicknesses.<sup>27</sup>

We describe the self-assembly of diisocyanide monolayers, prepared from diisocyanides **1–6** (CN–R–NC),



where the spacer group, R, includes both flexible alkyl chains and rigid phenyl and phenyl ethynyl groups. SAMs of these diisocyanides were characterized by advancing water contact angle, reflectance absorption infrared (RAIR) spectroscopy, and ellipsometry. These data indicate that the diisocyanides bind to gold surfaces exclusively in an  $\eta^1$  mode (type **I** or **IV**). The diisocyanides that have rigid phenyl or phenyl ethynyl moieties between the two isocyanide end groups formed SAMs with only one of the isocyanides bound to the surface. The diisocyanides that have flexible alkyl chains between the isocyanide groups formed SAMs with both isocyanides bound to the surface, when introduced from 1 mM  $\text{CH}_2\text{Cl}_2$  solutions.

## Experimental Section

**General Procedures.** All solvents were spectrophotometric or HPLC grade. Solvents were dried over the appropriate drying agents and distilled prior to use. Absolute ethanol (McCormick) was used without further purification. 1,4-Phenylene diisocyanide (**3**), 1,6-hexane diisocyanide (**1**), benzyltriethylammonium chloride, and 2-ethylaniline were purchased from Aldrich and used without further purification. The amines 1,12-diaminododecane (Aldrich), 4,4'-diaminobiphenyl (Fluka), and 4,4'-diamino-*p*-terphenyl (Lancaster) were used as received. 4-Ethylaniline was prepared according to a published procedure.<sup>36</sup>  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a General Electric QE-300 spectrometer and referenced to tetramethylsilane. IR spectra were taken on a Perkin-Elmer 1710 or a Mattson Research Series RS1 FTIR. Melting and boiling points are uncorrected. EI and CI mass spectra were measured on a Finnigan 4000 mass spectrometer, whereas the high-resolution mass spectra were recorded using a Kratos MS-50 mass spectrometer. Elemental analyses were performed in house by Dr. H. D. Lee.

**Preparation of Optically Flat Au Substrates.** Gold surfaces were prepared on silicon (100) wafers purchased from International Wafers that were precoated with a 100 Å Cr layer followed by a 2000 Å Au layer. The gold substrates were cut into 20 mm  $\times$  30 mm wafers. Prior to surface modification, the wafers were cleaned in an air plasma, employing a OPHTOS microwave power generator. Surfaces prepared in this way showed no contamination in RAIR spectra and were totally wetted by water.

The gold substrates described here were used for RAIR spectroscopy, ellipsometry, and contact-angle studies.

**Reflection–Absorption Infrared (RAIR) Spectroscopy.** The RAIR spectroscopic measurements were performed on a Mattson Research Series (RS1) infrared spectrometer with a narrow band liquid nitrogen cooled MCT detector using a custom-built evacuated stage with  $f/20$  optics. The p-polarized light was incident at  $86^\circ$ . After triangular apodization the spectral resolution was  $4\text{ cm}^{-1}$ . For each sample and reference, a total of 1024 scans was collected.

**Optical Ellipsometry.** All measurements were carried out on a rotating analyzer ellipsometer equipped with a tungsten source, operated at 6330 Å. The angle of incidence was  $70^\circ$ . Several areas on the sample were measured. The refractive indices for **1–6** were taken as 1.5.

**Contact-Angle Measurement.** Advancing water contact angles were obtained with a home-built goniometer. The experiments were performed at room temperature. The sample chamber atmosphere was saturated with water vapor by filling the well of the chamber with water. The advancing contact angle was determined by lowering the needle to the surface and injecting 1  $\mu\text{L}$  of deionized water onto the surface. The drop advanced over the surface. After the needle was raised, both sides of the drop were measured and several areas of the sample were examined and averaged.

**4,4'-Biphenyldiisocyanide (4).** All isocyanides were prepared by slight modification of a literature procedure.<sup>37</sup> As an example, **4** was synthesized as follows: To a round-bottom flask was added 0.10 g (0.5 mmol) of 4,4'-diaminobiphenyl which was dissolved in  $\text{CH}_2\text{Cl}_2$ . Then 25 mL of 50/50 w/w KOH was added, followed by 0.25 mol % benzyltriethylammonium chloride. To the  $\text{CH}_2\text{Cl}_2$ /KOH solution was added 0.13 g (2.3 equiv, 1.1 mmol) of  $\text{CHCl}_3$ . The reaction mixture was gently refluxed for 4–6 h, after which time 100 mL of  $\text{H}_2\text{O}$  was added. The organic layer was extracted twice with 100 mL of  $\text{H}_2\text{O}$  and then once with 100 mL of saturated aqueous NaCl. The organic layer was dried over  $\text{MgSO}_4$  and the solvent evaporated, yielding **5**, 0.074 g (67% crude product yield). The product was further purified by crystallization from  $\text{CH}_2\text{Cl}_2$ /pentane. IR:  $\nu(\text{CN})$ ,  $2127\text{ cm}^{-1}$ , no  $\text{NH}_2$  bands were observed.  $^1\text{H}$ NMR:  $\delta$  7.48 (d), 7.73 (d) ppm. MS:  $m/z$  204. HRMS Calc for  $\text{C}_{14}\text{H}_8\text{N}_2$ : 204.0687 amu. Found: 204.0676 amu.

**4,4'-*p*-Terphenyldiisocyanide (5).** The diisocyanide **5** was prepared by a procedure similar to that described for **4**, with a 52% yield. IR:  $\nu(\text{CN})$ ,  $2125\text{ cm}^{-1}$ , no  $\text{NH}_2$  bands were observed.  $^1\text{H}$ NMR:  $\delta$  7.48 (d), 7.67 (d), 7.72 (s, middle ring protons) ppm. MS:  $m/z$  280. HRMS Calc for  $\text{C}_{14}\text{H}_8\text{N}_2$ : 280.1000 amu. Found: 280.0994 amu.

**1,12-Diisocyanododecane (2).** Diisocyanide **2** was prepared using the same method as described for **4**; however, **2** was purified by fractional distillation (bp  $130^\circ\text{C}$  at 0.04 mmHg). After distillation, **2** was obtained in 32% yield. IR:  $\nu(\text{CN})$ ,  $2148\text{ cm}^{-1}$ , no  $\text{NH}_2$  bands were observed.  $^1\text{H}$ NMR:  $\delta$  3.38 (m), 1.65 (m) ppm.  $^{13}\text{C}$  NMR:  $\delta$  26.4, 28.8, 29.3, 29.7, 29.8, 41.8 (1:1:1 triplet), 158.7 (1:1:1 triplet, isocyanide carbon) ppm. MS:  $m/z$  220. HRMS (M + H) Calc for  $\text{C}_{14}\text{H}_{25}\text{N}_2$ : 221.2018 amu. Found: 221.2007 amu. Anal. Calc for  $\text{C}_{14}\text{H}_{24}\text{N}_2$ : C, 76.31; H, 10.98; N, 12.42. Found: C, 76.01; H, 11.03; N, 12.42.

**1,4-Di(4-isocyanophenylethynyl)-2-ethylbenzene (6).** 2-Ethylaniline (5 g, 41 mmol) was weighed in air into a beaker equipped with a stirring bar and a spatula to prevent vortex formation.  $\text{H}_2\text{O}$  (250 mL) with  $\text{NaHCO}_3$  (5.2 g, 62 mmol) was then added. Under vigorous stirring,  $\text{I}_2$  (11.5 g, 45 mmol) was added in approximately 0.5–1.0 g portions every 2–3 min over a 0.5 h period at room temperature. The solution was allowed to stir for 4 h. The deep red/purple organic layer was separated in a separatory funnel, before solidification of the 4-iodo-2-ethylaniline. A near quantitative yield for 4-iodo-2-ethylaniline was obtained. The product was found to be a purple/red crystalline solid at room temperature, different from the oil described previously.<sup>38</sup> Mp:  $36.2^\circ\text{C}$ .  $^1\text{H}$ NMR:  $\delta$  1.48 (t,  $\text{CH}_2$ ), 2.75 (q,  $\text{CH}_3$ ), 3.81 (s, br,  $\text{NH}_2$ ), 6.43 (d, ring proton ortho to amine), 7.22 (m,

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ring proton para to ethylene), 7.36 (d, ring proton ortho to ethylene) ppm.  $^{13}\text{C}$  NMR:  $\delta$  12.89, 24.00, 79.68, 117.5, 130.9, 135.6, 136.9, 144.4. MS:  $m/z$  247 ( $\text{M}^+$ ). Anal. Calc for  $\text{C}_8\text{H}_{10}\text{IN}$ : C, 38.39; H, 4.08; N, 5.67. Found: C, 38.50; H, 3.96; N, 5.44.

4-Iodo-2-ethylaniline was converted to the diethyltriazene according to a general literature preparation of triazenes.<sup>39</sup> Pure 4-iodo-2-ethyl-*N,N*-diethyltriazobenzene was obtained by fractional distillation. The fraction boiling at  $170^\circ$  at 0.15 mmHg gave 88% yield.  $^1\text{H}$  NMR:  $\delta$  1.25 (m, methylene of phenyl substituted and amino substituted), 2.81 (q, methyl of phenyl substituted), 3.61 (q, methyl of amino substituted) ppm, and ring protons in a similar region to that for 4-iodo-2-ethylaniline.  $^{13}\text{C}$  NMR:  $\delta$  15.48 (methyl of phenyl and amino substituted), 24.88 (methylene of phenyl and amino substituted), 89.47, 115.7, 135.47, 138.1, 141.4, 148.7 ppm. MS:  $m/z$  331 ( $\text{M}^+$ ). Anal. Calc for  $\text{C}_{12}\text{H}_{20}\text{IN}_3$ : C, 43.52; H, 5.48; N, 12.69. Found: C, 43.18; H, 5.51; N, 12.30.

To a benzene solution of 4-iodo-2-ethyl-*N,N*-diethyltriazobenzene was added 5 equiv of MeI.<sup>40</sup> The reaction mixture was refluxed for 72 h followed by  $\text{H}_2\text{O}$  washes and distillation, yielding 1,4-diiodo-2-ethylbenzene (82% isolated yield). Bp:  $132^\circ\text{C}$  at 0.15 mmHg.  $^1\text{H}$  NMR:  $\delta$  1.20 (t), 2.65 (q), 7.195 (doublet of doublets for proton para to the ethyl group), 7.509 ppm (d, proton meta to ethyl group), 7.569 ppm (d, proton ortho to ethyl group).  $^{13}\text{C}$  NMR:  $\delta$  14.58, 34.20, 94.60, 100.16, 136.78, 137.56, 141.03, 149.04 ppm. MS:  $m/z$  331 ( $\text{M}^+$ ). Anal. Calc for  $\text{C}_{12}\text{H}_{20}\text{IN}_3$ : C, 43.52; H, 5.48; N, 12.69. Found: C, 43.18; H, 5.51; N, 12.30.

Bis(triphenylphosphine)palladium chloride catalyzed the cross coupling of 4-ethynylaniline<sup>36</sup> (0.69 g, 5.9 mmol) with 1,4-diiodo-2-ethylbenzene (1.0 g, 2.8 mmol), affording 0.67 g (71% crude product yield) of 1,4-(4-aminophenylethynyl)-2-ethylbenzene. IR spectrum (KBr):  $\nu(\text{C}\equiv\text{C})$  2201  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  1.28 (t), 2.86 (q), 3.93 (s, br,  $\text{NH}_2$ ), 6.65 (d, outer ring protons), 7.26 (dd, proton para to ethyl on center ring), 7.33 (d, outer ring protons), 7.38 (d, proton meta to ethyl group on center ring), 7.41 (s, proton ortho to ethyl group on center ring) ppm. MS: 336 ( $\text{M}^+$ ); 337 ( $\text{M} + \text{H}$ ). HRMS Calc for  $\text{C}_{24}\text{H}_{20}\text{N}_2$ : 336.1626 amu. Found: 336.1629 amu.

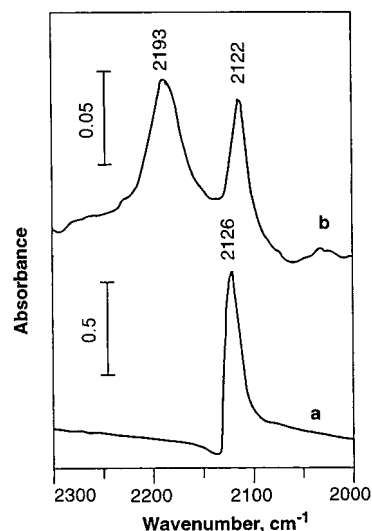
To a round-bottom flask was added 1,4-(4-aminophenylethynyl)-2-ethylbenzene (0.10 g, 0.29 mmol) which was dissolved in 50 mL  $\text{CH}_2\text{Cl}_2$ . Next, 25 mL of 50 wt % aqueous KOH was added, followed by 0.25 mol % benzyltriethylammonium chloride. To the  $\text{CH}_2\text{Cl}_2/\text{KOH}$  solution was added 0.08 g (2.3 equiv., 0.67 mmol) of  $\text{CHCl}_3$ . The reaction mixture was gently refluxed for 4–6 h, followed by the addition of 100 mL of  $\text{H}_2\text{O}$ . The organic layer was extracted with  $2 \times 100$  mL of  $\text{H}_2\text{O}$  followed by  $1 \times 100$  mL of brine and was dried over  $\text{MgSO}_4$ , and the solvent was evaporated, yielding 0.040 g of **6** (38% crude product yield). IR spectrum (KBr):  $\nu(\text{C}\equiv\text{C})$  2198  $\text{cm}^{-1}$ ,  $\nu(\text{C}\equiv\text{N})$  2122  $\text{cm}^{-1}$ , no  $\text{NH}_2$  bands were observed.  $^1\text{H}$  NMR:  $\delta$  1.30 (t), 2.88 (q), 7.39 (d, outer ring), 7.46 (s, proton ortho to ethyl on center ring), 7.49 (d, proton meta to ethyl on center ring), 7.54 (d, proton para to ethyl on center ring), 7.57 (d, outer ring) ppm. MS:  $m/z$  356 ( $\text{M}^+$ ); 357 ( $\text{M} + \text{H}$ ). HRMS: Calc for  $\text{C}_{26}\text{H}_{16}\text{N}_2$ : 356.1313 amu. Found: 356.1309 amu.

**Self-Assembled Monolayers (SAMs).** Self-assembled monolayer SAMs for all molecules were formed in approximately 1.0 mM  $\text{CH}_2\text{Cl}_2$ , THF, ethanol, or methanol solutions. Deposition times varied from 2–4 h for octadecanethiol (ODT)<sup>4</sup> to 12–14 h for **1–6**.

## Results and Discussion

**Synthesis of New Diisocyanides.** The new diisocyanides **5** and **6** were prepared from the corresponding diamines. All of the diisocyanides **1–6** were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{13}\text{C}$  APT NMR, IR, mass spectrometry, high-resolution mass spectrometry, and elemental analysis.

**Diisocyanide SAM Formation.** SAMs of the diisocyanides **1–6** were prepared by immersing a plasma-cleaned gold substrate into a dry  $\text{CH}_2\text{Cl}_2$  or THF solution of the isocyanide (ca. 1.0 mM) for 12 h. The substrates



**Figure 1.** Isocyanide absorptions for 4,4''-*p*-terphenyldiisocyanide **5** in the region 2000–2300  $\text{cm}^{-1}$ : (a) KBr pellet of **5**; (b) RAIR spectrum of **5** on a gold surface.

**Table 1.** Reflection Absorption Infrared Spectroscopy  $\nu(\text{CN})$  Data and Bulk IR Data for Diisocyanides **1–6** on Au

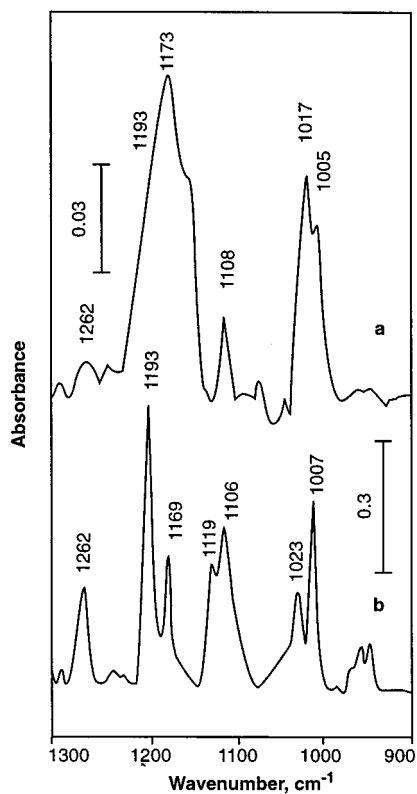
compound	$\nu(\text{CN})$ ( $\text{cm}^{-1}$ )		
	surface bound	unbound	bulk (KBr) reference
1	2223		2146
2	2235		2148
3	2181	2120	2125
4	2191	2121	2126
5	2194	2121	2129
6	2191	2120	2124

were then thoroughly rinsed with generous amounts of solvent and dried under nitrogen. The substrates were immediately placed into the analysis chamber of the RAIR spectrophotometer for surface IR measurements.

**Reflection Absorption Infrared Spectroscopy.** While bulk (KBr) IR spectra of **3–6** show only one  $\nu(\text{CN})$  band, the RAIR spectra of **3–6** show two well-resolved bands. Angelici and co-workers reported two isocyanide bands observed by DRIFTS spectroscopy for isocyanide **3** adsorbed on gold powder.<sup>32,33</sup> One of the bands is consistent with an unbound CN group when compared to the IR spectrum of a bulk sample of **3** as a KBr pellet. The other band is higher in frequency and is consistent with a CN group bound in an  $\eta^1$  (type **I** or **IV**) coordination mode to gold. Gold is an s-band metal and  $d\pi/p\pi^*$ , back-donation to the isocyanide is not to be expected. Thus, the  $\nu(\text{CN})$  frequency of a coordinated isocyanide group on a gold surface would be expected to be observed at higher frequency than that for an uncoordinated isocyanide group. A comparison of a bulk IR spectrum of **5** as a KBr pellet and a RAIR spectrum of a SAM of **5** on gold is presented in Figure 1. Table 1 summarizes the  $\nu(\text{CN})$  IR spectral data for **1–6** in the bulk (KBr) and compared to the RAIR spectrum of SAMs of **1–6** on gold. We note that **6** also had an additional band in bulk IR and RAIR spectra at 2166  $\text{cm}^{-1}$  which is assigned to the internal carbon–carbon triple bond. In contrast, the diisocyanides with flexible chains showed only one isocyanide stretch at 2223  $\text{cm}^{-1}$  for **1** and 2235  $\text{cm}^{-1}$  for **2**. These high frequencies indicate CN groups bound to gold and suggest that **1** and **2** with their more flexible alkyl chains form SAMs with both isocyanides bound to the surface. The RAIR and bulk IR spectra of **5** contained similar IR absorption band positions in the range from 800 to 3500  $\text{cm}^{-1}$ . A detailed analysis

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**Figure 2.** IR spectra of **4** in the region 900–1300  $\text{cm}^{-1}$ : (a) RAIR spectrum of a SAM of **4** on a Au surface; (b) FTIR spectrum of **4** (KBr pellet).

of the RAIR spectra, based on surface selection rules, provides additional evidence that the diisocyanides **3–6** form SAMs with the long molecular axis oriented nearly normal to the surface. For example, biphenyldiisocyanide (**4**) has IR absorptions that can be assigned following the system of substituted benzene normal modes, (**1–20a,b**), with symmetry labels appropriate for the local symmetry ( $C_{2v}$ ) (Figure 2).<sup>41</sup> In particular, the bands at 1023, 1119, 1169, and 1262  $\text{cm}^{-1}$  in the bulk spectrum of **4** (Figure 2, curve b) are assigned to (**18a**,  $a_1$ ), (**18b**,  $b_2$ ), (**9a**,  $a_1$ ), and (**3**), respectively. The net dipole moment change associated with the **18a** and **9a** modes is parallel to the long molecular axis. Modes **18b** and **3**, on the other hand, involve atomic displacements with net dipole moment changes perpendicular to the long axis of the molecule. The relative intensities of these modes for **4** adsorbed on Au are enhanced (**18a**, **9a**) and suppressed (**18b**, **3**) (Figure 2, curve a) when compared to those of the bulk (KBr) spectrum. This is consistent with surface selection rules for molecules oriented with their long molecular axis normal to the surface.

**Advancing Contact-Angle Measurements.** Advancing contact-angle measurements were performed on the same substrates as used for surface IR spectra. The rigid (**3–6**) and flexible (**1–2**) diisocyanides had distinctly different contact angles (Table 2). Advancing water droplet contact-angle measurements for **3–6** were 62° to 63°. This is consistent with expectations for a relatively hydrophilic, polar isocyanide-terminated SAM. In contrast, the alkyl chain diisocyanides **1** and **2** showed contact angles from 72° to 78°, which are more characteristic of a hydrophobic surface, but not one as hydrophobic as octadecanethiol SAMs (111° to 114°).<sup>24</sup> In comparison, Bain and co-workers

**Table 2.** Advancing Contact Angles and Ellipsometric Film Thicknesses for Diisocyanides **1–6** on Au

compound	contact angle ( $\theta_a$ )	ellipsometry	
		obs ( $\text{\AA}$ )	calc ( $\text{\AA}$ )
1	72	8	13.5
2	78	14	21.1
3	63	10	10.3
4	63	14	14.6
5	62	21	18.8
6	62	27	24

reported an advancing contact angle for 1,12-dodecanedithiol (the thiol analogue of **2**) to be 77°. They also proposed that the molecules formed “loops” and that both thiol groups were attached to the surface. These data suggest that the diisocyanides **1** and **2** form SAMs with both isocyanides bound to the surface but that the diisocyanides **3–6** form SAMs with only one isocyanide bound to the surface.

**Ellipsometry.** Ellipsometry data for **3–6** agreed with theoretical lengths calculated with the long molecular axis oriented normal to the surface. The alkyl chain diisocyanides **1** and **2** showed film thicknesses significantly less than the calculated film thicknesses based on an all trans configuration, again suggesting that these diisocyanides form SAMs with both isocyanides bound to the surface. Ellipsometry data are summarized in Table 2.

**Surface Reactions.** Previous work with dithiols, such as biphenyl dithiol, has demonstrated that rigid dithiols form SAMs with the long molecular axis nearly normal to the surface.<sup>42–44</sup> For example, we have reported previously that the dithiol SAMs act as “chemically sticky” surfaces for the subsequent attachment of gold nanoclusters.<sup>44</sup> The diisocyanide SAMs were exposed to a beam of nanometer-sized crystalline gold clusters in a vacuum chamber held at  $10^{-6}$  Torr described elsewhere.<sup>45,46</sup> The sample was then placed in a UHV STM chamber for further characterization. Compared to the previously reported dithiol SAMs, which were found to strongly anchor gold nanoclusters so that they could be imaged by STM,<sup>44</sup> gold clusters do not adhere as strongly to diisocyanide SAMs of **3–6**. In the case of the diisocyanide SAMs, the gold clusters could only be imaged reproducibly when they were pushed against a step edge. This difference may be attributed to a stronger S–Au compared to RNC–Au interaction.

**Displacement Formation of Self-Assembled Monolayers.** SAMs of the rigid diisocyanides **3–6** can also be formed by direct displacement of a pre-existing SAM of octadecanethiol (ODT). A series of experiments were performed to demonstrate that displacement occurs on a flat gold surface. First, an ODT SAM was prepared as previously described<sup>24</sup> and a RAIR spectrum recorded (Figure 3a). The freshly prepared ODT SAMs on gold were exposed to an approximately 1.0 mM solution of **5**. After 16 h the samples were removed and rinsed with solvent. If the solvent used was aprotic and anhydrous, then the displacement reaction proceeded smoothly, leading to

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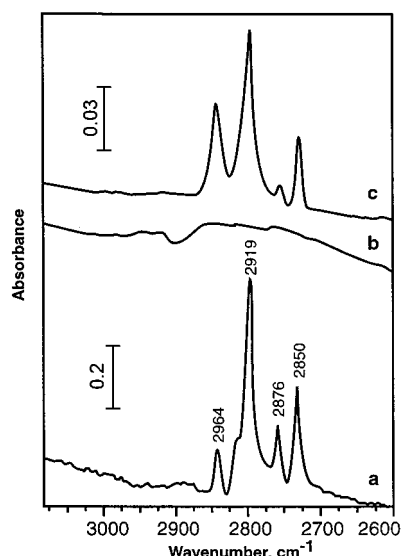
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**Figure 3.** RAIR spectra (a) of a SAM of ODT on Au, (b) following exposure of an ODT sample to a 1 mM solution of **5** in dry  $\text{CH}_2\text{Cl}_2$ , and (c) following exposure of a sample ODT SAM to a 1 mM solution of **5** in EtOH.

RAIR spectra that showed the disappearance of spectral features attributed to ODT and growth of the spectral features characteristic of SAMs of **5** (Figure 3b). However, if the solvent was protic or wet, the ODT SAM was unaffected (Figure 3c). SAMs of **5** were indistinguishable by ellipsometry and contact-angle measurements when compared to those prepared from plasma-cleaned Au and **5**. Since it is known that SAMs of thiols on gold can be prepared from disulfides as well as thiols, the microscopic, reversible process of disulfide "reductive elimination" from the surface induced by an entering isocyanide is not unreasonable. The solvent dependence noted for this process is based on the relative solvation versus interchain packing of the ODT alkyl chains. The less polar solvents such as dry THF or  $\text{CH}_2\text{Cl}_2$  can effectively solvate ODT chains, thus disrupting interchain packing and providing access to the surface to the isocyanide. More polar solvents such as MeOH and EtOH or wet THF cannot effectively

solvate the ODT chains, interchain packing persists, and the ODT monolayer remains impervious to the isocyanides. A similar example of solvent-polarity-dependent partitioning has been reported earlier in the case of mixed monolayers of  $\text{HO}(\text{CH}_2)_{11}\text{SH}$  and  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ .<sup>47</sup>

### Conclusions

Self-assembled monolayers of diisocyanides **1–6** have been prepared and characterized by ellipsometry, by measurement of advancing water droplet contact angle, and by reflection absorption infrared (RAIR) spectroscopy. SAMs prepared from the diisocyanides **1–2**, that have a flexible alkyl chain between the two isocyanide end groups, were found to form monolayer films in which both isocyanide groups are bound to the surface. SAMs prepared from the diisocyanides **3–6**, that have rigid aryl or phenylethynyl structures between the two isocyanide end groups, were found to bind to gold through only one CN group. Analyses of the RAIR spectra of these SAMs are consistent with surface selection rules for adsorbates that are oriented with their long molecular axis normal to the surface. Measurements of advancing water droplet contact angles and ellipsometric film thicknesses of SAMs prepared from **3–6** further support a surface structure in which the diisocyanide molecules are oriented vertically with one CN group bound to the surface and the other remote from the surface. In all cases on gold, isocyanides bind in a terminal (type **I**) fashion to the surface. Initial STM studies suggest that the surface-unattached CN groups of vertically oriented diisocyanides bind gold nanoclusters less strongly than the corresponding dithiols.

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