

# Quadruply Hydrogen Bonding Modules as Highly Selective Nanoscale Adhesive Agents

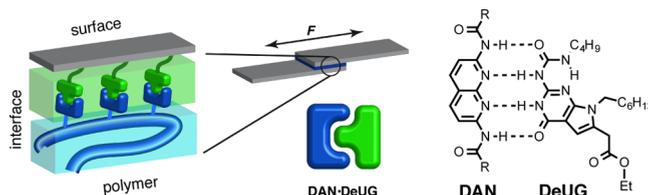
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## ABSTRACT



Covalently linking DNA base analogues DAN, DeUG, or UPy to glass slides led to functional surfaces that could be glued together using a functionalized polystyrene displaying the complementary recognition unit. Nonspecific adhesion was minimized with fluorinated alkane (Teflon-like or Scotchgard-like) surfaces.

Adhesive interactions play a critical role in bringing surfaces together in both a wide range of biological systems and manufactured articles.<sup>1</sup> We recently described<sup>2</sup> the use of an artificial DNA base-pair, DAN·DeUG (**1·2**)<sup>3</sup> as a

quadruple hydrogen-bonded (QHB) nanoscale adhesive agent to bond glass substrates.<sup>4,5</sup> Although the DAN⊕DeUG pair significantly improved adhesion, surfaces lacking the DeUG unit still showed considerable adhesion, which was attributed to hydrogen-bonding interactions with the urea group in the surface-linking group (see **3** in Figure 1). These nonspecific interactions are undesirable when creating orthogonally patterned surface assemblies<sup>6</sup> or switchable adhesive surfaces (e.g., with a redox active eDAN unit<sup>7</sup>). Thus, we sought to maximize the role of the DAN⊕DeUG pair. Herein we describe efforts to minimize the participation of the surface linker unit in the adhesive interaction. In particular, we report the use of fluorinated alkyl linkers to create a Teflon-like surface and also compare mono- and trialkoxysilane groups for the surface covalent connection (see **4** and **5** in Figure 1).

The DeUG unit was previously tethered to surfaces through its urea substituent.<sup>2</sup> In this work, it was more convenient to link DeUG and the surface through the ester group of **2**.<sup>8</sup> To accomplish this goal, DeUG-functionalized surface **4** or **5** was prepared by treating glass slides with

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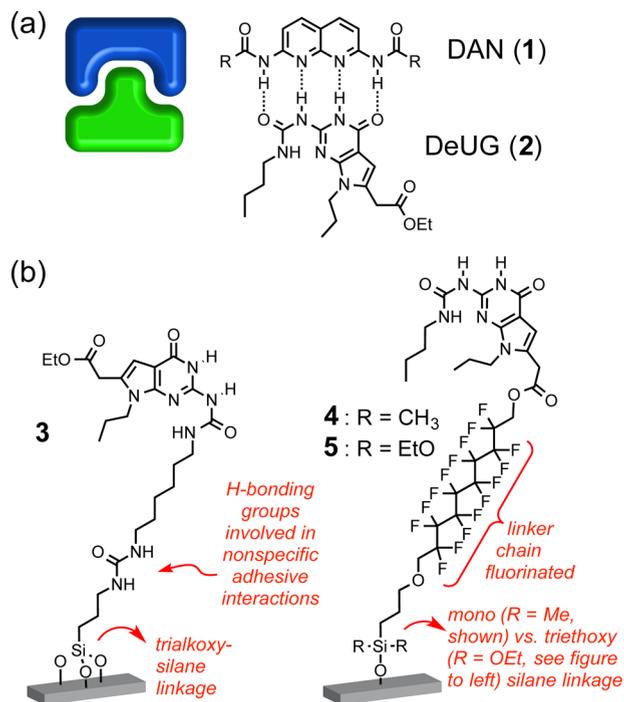
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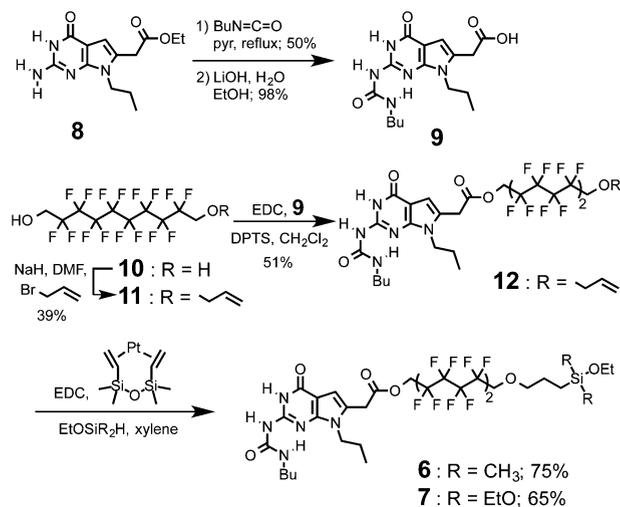
**Figure 1.** (a) DNA base-pair analogues, DAN (1) and DeUG (2) and (b) two different ways to link the DeUG unit to surfaces.

ethoxysilane **6** or **7**, respectively, whose synthesis began with ester **8**<sup>9</sup> (Scheme 1).<sup>10</sup> Thus, treatment with butylisocyanate in pyridine afforded the corresponding urea in 50% yield, and the ester group was subsequently hydrolyzed with aqueous base to give acid **9** in 98% yield. The fluorinated linker chain synthesis began with the monoallylation of diol **10** to give **11** in 39% yield. Subsequent esterification of **9** with **11** using EDC and DPTS afforded ester **12** isolated in 51% yield.<sup>11</sup> Mono- and triethoxysilanes **6** and **7** were obtained, in 75% and 65% yield, respectively, by hydrosilylation using Karstedt's catalyst and the appropriate hydrosilane.

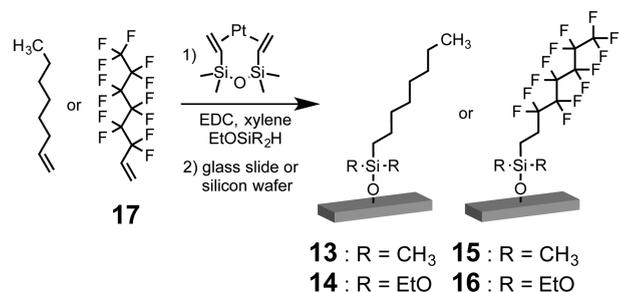
Glass microscope slides and silicon wafers were thoroughly cleaned with piranha solution at 100 °C, washed with water and ethanol, and dried prior to modification with the silane. In addition to coatings using **6** and **7**, control surfaces **13–16** were prepared in the same way by using 1-octene and fluorinated octene **17** (Scheme 2). In each case the surface derivatization was performed with 10 mM solutions of the silane in methylene chloride followed by heating and extensive washing to ensure that only covalently linked compound was left on the surface.

One of the reasons for comparing mono- and triethoxy silanes is that the latter typically gives denser, often polymeric coatings<sup>12</sup> that may provide a higher density of the

### Scheme 1. Synthesis of Silylated DeUG Unit



### Scheme 2. Synthesis of Control Surfaces 13–16



QHB unit, whereas the former might provide more accessible recognition units on the surface. All of the films were characterized using a range of techniques that are detailed in the Supporting Information. Static contact angle measurements of a drop of water on the modified surfaces correlate well with the relative polarity of surface functional groups. For example, the piranha-treated glass slides with no coating gave a contact angle of 10°. In contrast, fluorinated octyl surface **16** and fluorinated DeUG surface **5** gave contact angles of 117° and 71°, respectively.

Atomic force microscopy (AFM) measurements indicated relatively uniform surface coverages with root-mean-square roughness values of < 500 pm.<sup>10</sup> Ellipsometry was performed on analogous films prepared on silicon wafers with measured thickness values that ranged from ca. 1 to 3 nm. In each case the thickness agreed well with dimensions calculated from molecular models suggesting formation of monolayers. Overall, the trialkoxysilanes gave surfaces with somewhat larger contact angles and thicker films than the analogous surfaces prepared from monoalkoxysilanes, suggesting slightly greater surface coverage for the former.

Finally, the elemental and molecular composition of the films on glass and silicon wafers was examined using X-ray

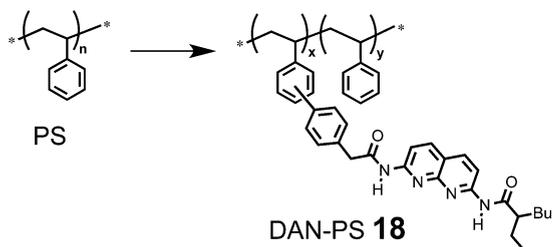
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photoelectron spectroscopy (XPS) and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF-MS).<sup>10</sup> XPS wide-scan survey spectra revealed peaks corresponding to the specific film examined. For example, surface **4** showed C 1s, F 1s, N 1s, O 1s, and Si 2p peaks, whereas surface **3** and those lacking the fluorinated linkers showed no F 1s peak. The MALDI-MS showed molecular fragments corresponding to the organic surface covalently linked. For example, a peak at  $m/z = 334$  observed with a film of **5** on a glass slide corresponds to the DeUG heterocycle with cleavage at the ester bond. Fragments are also observed for the fluorinated linker chain. Full details are available in the Supporting Information.

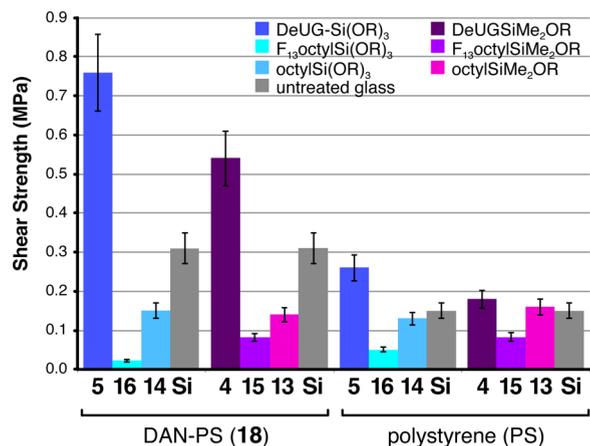
**Scheme 3.** Synthesis of DAN-Functionalized PS **18**



With the functionalized glass plates in hand, attention was turned to the adhesives that would bond two plates together. Thus, commercially available polystyrene (PS) underwent C–H borylation and Suzuki–Miyaura cross coupling to give PS-DAN **18** (Scheme 3).<sup>2,10</sup> The functionalized polymer used in all studies contained 4.5 mol % DAN units, and GPC showed it to have  $M_n = 73$  kDa with a polydispersity index, PDI, of 1.8. As a control, unfunctionalized PS with  $M_n = 69$  kDa and PDI = 2.0 was utilized.

The procedure for bonding the glass plates together with adhesive is the same as used previously.<sup>2</sup> Thus, a pair of glass slides was set using 10  $\mu\text{L}$  of 10 mg/mL of each polymer solution in  $\text{CH}_2\text{Cl}_2$  with a contact area of ca. 1.5 cm  $\times$  2.5 cm. The sample was clamped with binder clips and cured at room temperature for 24 h. The adhesive properties of PS and DAN-PS **18** were measured using lap-shear tests. These tests were accomplished by placing the resultant samples in a load-frame equipped with a 500 N load-cell and shearing each at 1 mm  $\text{min}^{-1}$  until failure. A mixture of adhesive and cohesive failure was observed in each case. The mean shear strength calculated from 10 runs of each sample is shown in Figure 2.

The highest shear strength (0.76 MPa) was observed with glass plates coated with film **5** and using the DAN-PS adhesive **18**, whereas the weakest bond (0.02 MPa) was with the DAN-PS **18** between slides coated with fluorinated octane film **16** (two left-most bars in Figure 2). The octyl triethoxysilane coated surface **14** gave a significantly higher level of adhesion (0.15 MPa) than did the fluorinated surface, but both **16** and **15** gave less nonspecific adhesion than a butylurea control surface examined in our previous work.<sup>2</sup> Thus, the design principle of using a



**Figure 2.** Mean shear strengths for six prepared surfaces (**4**, **5**, and **13–16**) and uncoated glass bonded by unfunctionalized PS and DAN-functionalized PS **18**. Error bars represent 1 SD for  $n = 5$ . In comparing shear strength for DAN-PS **18** on DeUG-Si(OR)<sub>3</sub> **5** to **18** on surfaces **16**, **14**, or untreated glass, the calculated  $p$ -values were all  $< 0.00003$ . The comparison of **18** on **5** to **18** on **4** gave a  $p$ -value of 0.00008.

fluorinated alkyl surface to maximize the DeUG–DAN interactions and to minimize nonspecific adhesion was successful.

It is generally accepted that the extent of adhesion in a particular system will be proportional to the surface free energy. For example, fluorocarbon surfaces have low surface energies and are known<sup>13</sup> to be antifouling and to be highly resistant to water, even being called superhydrophobic,<sup>14</sup> although the origin of this effect may be in their larger exposed surface area.<sup>15</sup> However, adhesion to fluorinated surfaces is not always weaker. In the case of simple transparent tape peel tests on polydimethylsiloxane (PDMS), hydrocarbon (HC), and fluorocarbon (FC) monolayers, it was found that the strength of adhesion followed the opposite order FC > HC > PDMS.<sup>16</sup> This was attributed to a model where the viscoelastic adhesive undergoes slippage along a more or less rigid solid, where PDMS is the most flexible and the FC surface the most rigid. The choice of polystyrene for the adhesive was in part driven by its glassy nature at ambient temperature, removing the possibility of viscoelastic flow in the lap shear measurements.

In looking at the remaining data in Figure 2, several other trends are apparent. The use of commercial PS, as in our previous study, gave weaker adhesion with shear strength values for uncoated glass and surfaces **4**, **5**, and **13–16** that ranged from 0.05 to 0.25 MPa. The DAN-PS

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did show some increased interaction with uncoated glass, presumably by hydrogen bonding between the heterocycle and the SiOH group. Finally, the films prepared using monoalkoxysilane **6** (i.e., surface **4**) exhibited weaker adhesion than its trialkoxysilane counterpart, suggesting that the lower level of coverage is not offset by the recognition unit being more accessible.

The results reported here show that QHB recognition units can be covalently attached to surfaces through siloxane groups and that highly fluorinated linking groups have the advantage that they do not interfere with polymer adhesion and they minimize nonspecific adhesion. The results represent a step toward the development of orthogonal surface recognition systems and smart surfaces where adhesive interactions can be turned on and off reversibly.

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**Supporting Information Available.** Synthetic and compound characterization details, contact angle measurements, XPS data, MALDI-TOF-MS data on surfaces, ellipsometry data, and lap-shear results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The authors declare no competing financial interest.