

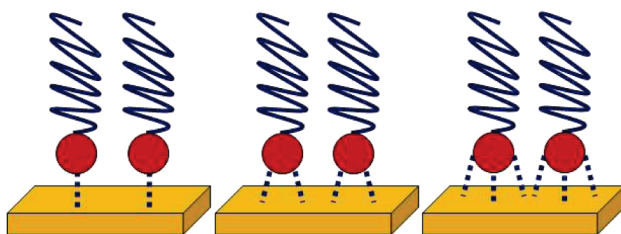
# Multidentate Adsorbates for Self-Assembled Monolayer Films

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## CONSPECTUS



The spontaneous adsorption of organic molecules on a variety of planar and nonplanar substrates, that is, self assembly, can generate films just one molecule thick. These nanoscale, self-assembled monolayer (SAM) films have been extensively used to engineer surfaces with well-defined properties. Their utility has been demonstrated in a wide range of applications, including wetting, adhesion, lubrication, patterning, and molecular recognition. Many SAM systems have been investigated, but alkanethiols adsorbed on gold are the most successful combination. This pairing offers a variety of advantages, including the ability to tune precisely the interfacial properties of a surface through the well-established organic synthetic methodologies that have been developed for preparing custom  $\omega$ -terminated alkanethiols.

Alkanethiolate monolayers are moderately stable at room temperature; however, these films degrade over time and readily desorb upon moderate heating. This shortcoming limits the use of SAMs in applications involving elevated temperatures or harsh environments. Accordingly, new adsorbates with multiple bonding moieties have been created to enhance the stability and versatility of SAMs.

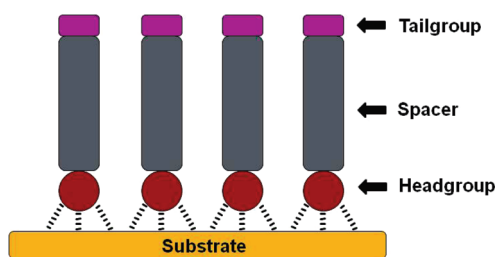
In this Account, we examine a variety of multidentate adsorbate structures that have been used to generate SAMs on planar substrates and on nanoparticles. Each of these chelating adsorbates (bidentates and tridentates) has been designed to generate well-defined organic monolayer films with multiple attachment points to the underlying substrate. This bonding arrangement allows the formation of SAMs with enhanced stability through the entropy-driven “chelate effect”. The research examined here demonstrates that multidentate adsorbates provide robust films: they enable the use of SAMs under conditions that are incompatible with SAMs derived from normal alkanethiols.

Another advantage offered by multidentate adsorbates is the capacity for new paradigms in thin-film composition. In particular, appropriately designed chelating adsorbates can be engineered to have two or more chemically distinct terminal groups that are covalently linked to the same underlying headgroup, without adding steric bulk that might prove detrimental to the resultant assembly. This strategy allows the generation of homogeneously mixed multicomponent surfaces, overcoming the problem of phase separation or “islanding” that is pervasive when two or more chemically distinct adsorbates are used to form mixed SAMs. Such homogeneously mixed films offer the opportunity to fine-tune the interfacial properties of a substrate and to create unique heterogeneous interfaces that are well defined by the chemical composition of the tailgroups exposed at the surface. The insight derived from these studies opens the door to new uses for SAMs, both in surface engineering applications (such as corrosion resistance and soft lithographic patterning) and in the stabilization and manipulation of nanoparticles.

## 1. Introduction

Inorganic chemists recognized long ago that multidentate ligands can be used to generate new classes of metal

complexes in which the multiple bonds between the ligand and the metal give rise to unique geometries, distinct reactivity, and enhanced stability via the well-known



**FIGURE 1.** Illustration of the components of SAMs where multiple bonding interactions between adsorbate and substrate are shown.

“chelate effect”.<sup>1,2</sup> The latter phenomenon arises because the entropy change upon binding a multidentate ligand is more favorable than that of binding the corresponding monodentate ligands.<sup>1,2</sup> From the point of view of surface science, the chelating strategy can be used to generate stable monolayer films, where the interfacial properties of metallic or semiconducting surfaces can be tailored via the use of custom-designed molecular adsorbates.

Organic thin films generated by the spontaneous chemisorption of surfactant molecules on solid surfaces are known as self-assembled monolayers (SAMs). These nanoscale films can be easily prepared and used to engineer surfaces with well-defined properties,<sup>3,4</sup> leading to a variety of applications such as controlled adhesion,<sup>5</sup> tunable wettability,<sup>6</sup> corrosion prevention,<sup>7</sup> lubrication,<sup>8</sup> biosensing,<sup>9</sup> and electrode modification.<sup>10</sup> The structures and properties of SAMs have been thoroughly studied, and detailed descriptions can be found in several excellent reviews.<sup>3,11,12</sup> Although various types of organic materials and solid substrates have been used to form SAMs, sulfur-based adsorbates such as dialkyl sulfides (RSR), dialkyl disulfides (RSSR), and particularly alkanethiols (RSH) on gold substrates have become model systems for SAM research. While SAMs formed from sulfides suffer from severe stability issues and conformational defects<sup>13,14</sup> and SAMs formed from disulfides are subject to multilayer contamination due to the low solubility of the adsorbate precursors,<sup>15</sup> both systems still find use as alternatives to the more widely used alkanethiol adsorbates.

Despite their widespread use, SAMs derived from organosulfur-based adsorbates have found limited applicability where film stability is a concern, since the singly bound headgroups can readily desorb or be displaced from the surface by other ligands in solution. For example, normal alkanethiolate SAMs readily decompose when heated in hexadecane to 80 °C<sup>16</sup> and completely desorb from the gold surfaces upon annealing in air at 130 °C.<sup>17</sup> To enhance the film stability, several research groups (including ours) have explored a variety of adsorbate designs where multiple

bonding interactions between the surfactants and the substrates are possible (e.g., Figure 1). Generally, films and materials derived from these adsorbates are more robust than those derived from analogous monodentate adsorbates. To this end, this Account provides an overview of SAMs derived from multidentate adsorbates, with an overall goal of illustrating their utility in emerging nanoscale materials and technologies.

## 2. Multidentate Adsorbates

An attractive strategy to create stable and well-defined organic monolayers centers on the use of surfactants with multiple contacting points, that is, “multidentate” adsorbates. The structures are designed to possess, for example, two (bidentate) or three (tridentate) active headgroups that can interact with the substrate surface, forming either physical or chemical bonds. Accordingly, these structures can “chelate” to the substrate in a manner similar to metal–ligand complexes, providing added stability to both the individual adsorbate and the SAM as a whole. In an early study,<sup>18</sup> Schlenoff et al. argued that, for a molecule possessing a higher number of binding groups, the probability of having all binding groups desorb from the surface simultaneously would be low.

Another advantage of multidentate systems is that they can provide controlled complexity for SAM interfaces, yielding enhanced flexibility in film composition, interfacial properties, and structure. Two or more functional groups can be incorporated into the surfactant to be exposed at the ambient interface to provide monolayers with tunable properties. Such systems, when comprised of independent monothiol adsorbates, are known as “mixed” SAMs. The co-adsorption of different alkanethiols (RSH + R'SH)<sup>19</sup> or the adsorption of unsymmetrical disulfides (RSSR')<sup>20</sup> or sulfides (RSR')<sup>21</sup> are typical methods that have been used to generate mixed SAMs. Unfortunately, the use of a mixture of two separate thiol adsorbates typically leads to domain formation (i.e., “islanding”) on the substrate due to preferred intermolecular interactions.<sup>22</sup> A similar problem occurs with unsymmetrical disulfides, where the S–S bonds dissociate during the adsorption process to generate two phase-separated domains on the surface.<sup>20</sup> As for sulfides, the single surface bond is weakened by the presence of more than one chain; consequently, these films are particularly unstable.<sup>13</sup> Multidentate adsorbates have been developed to generate films that overcome these limitations. Two or more chemically distinct terminal components can be incorporated into the same

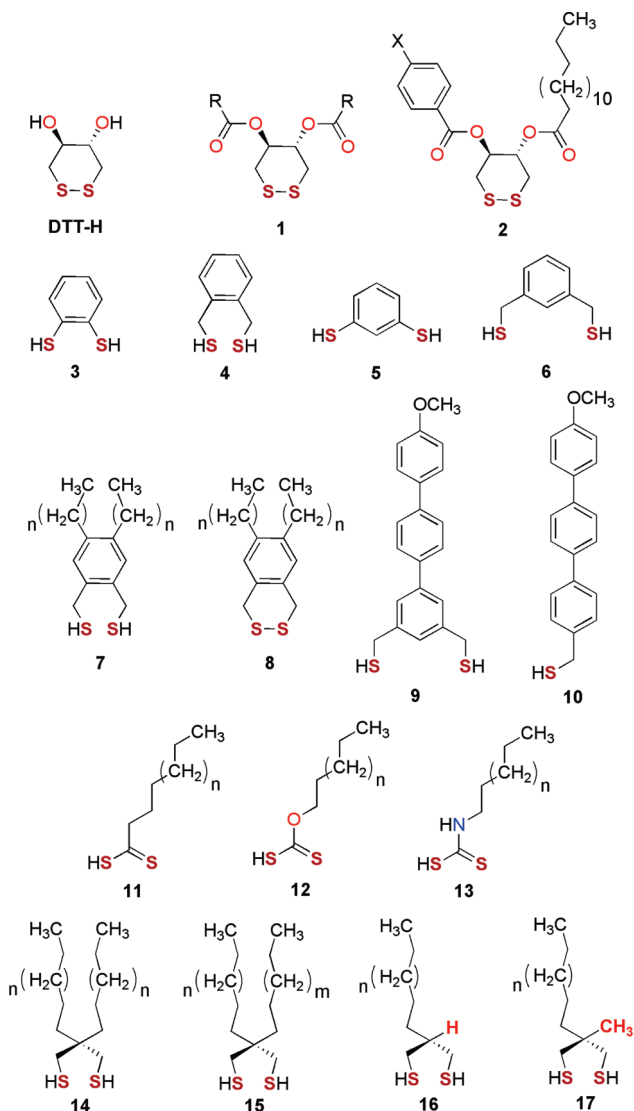


FIGURE 2. Structures of bidentate adsorbates.

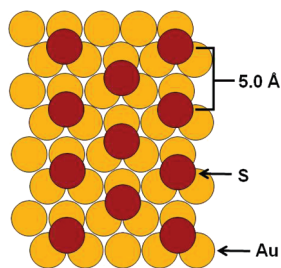
adsorbate, which allows the generation of homogeneously mixed multicomponent surfaces, stabilized by the presence of more than one surface bond. Examples of the utilization of chelating adsorbates to generate such homogeneously mixed SAMs are discussed in the following sections.

**2.1. Bidentate Adsorbates.** Recent interest in SAM research was spurred by the work of Nuzzo and Allara in 1983, where a series of disulfides, **1** (Figure 2), derived from 4, 5-dihydroxy-1,2-dithiane (DTT-H) ( $R = CF_3(CF_2)_6, CH_3(CH_2)_{14}, p-O_2NC_6H_4, CH_3,$  and  $CF_3$ ) were used to form monolayers from solution.<sup>23</sup> An extended study of this disulfide series led the authors to conclude that well-organized organic monolayers can be formed from their spontaneous adsorption onto gold substrates.<sup>24</sup> Given that these studies focused on the spontaneous adsorption of organic disulfides on gold, the advantages of the chelating character were not

considered. In 1997, Cahen and co-workers used a similar DTT-H-based structure to create multifunctional molecular assemblies on gold and  $CuInSe_2$  substrates.<sup>25</sup> The authors generated homogeneously mixed monolayers by grafting two different functional groups on a single adsorbate **2**. Since the two substituents were both covalently bound to the six-membered ring, no phase separation could occur during SAM formation as the S–S bond cleaved to form two thiolate bonds on the surface. Ridley and co-workers extended the use of unsymmetrically substituted 1,2-dithianes to form SAMs on gold for tethered bilayer membrane (t-BLM) biosensors.<sup>26</sup> The authors noted that one of the advantages of using DTT-H as a scaffold for t-BLM components is its potential to enhance the stability of the system, because two sulfur atoms per adsorbate bind to gold.

Aromatic moieties have also been used as a support framework for an alternative form of a chelating adsorbate. This class of bidentate adsorbate was introduced by Kim and co-workers who reported the self-assembly of 1,2-benzenedithiol (**3**) on gold and silver surfaces.<sup>27</sup> Kinetic studies showed that the dithiol **3** on gold had an adsorption rate constant  $\sim 10$  times smaller than that of *n*-octadecanethiol (ODT). On the other hand, the desorption rate of the film derived from **3** was  $\sim 200$  times slower than that of the ODT film, suggesting that the monolayer formed from the dithiol is more stable than the normal alkanethiol film. In a subsequent paper, *o*-xylene- $\alpha,\alpha'$ -dithiol (**4**) was used to form a close-packed, highly ordered monolayer on gold.<sup>28</sup> The intervening methylene units at the sulfur headgroups provided added flexibility to the structure and possibly put the two sulfurs in ideal positions to coordinate to the gold substrate. A molecular model of the targeted dithiols shows that the two sulfur atoms can span 5.0 Å with no steric or torsional strain,<sup>29,30</sup> which makes possible their binding to the Au(111) surface in a fashion similar to that of normal alkanethiols.<sup>31</sup> Interestingly, the exact location of sulfur on the gold lattice is still controversial, with several experimental and theoretical data suggesting that hollow sites, top sites, and bridge sites are all tenable.<sup>32–36</sup> Moreover, recent models suggest the involvement of gold adatoms, where one (Au-adatom–monothiolate)<sup>32</sup> or two sulfur atoms (Au-adatom–dithiolate)<sup>33,35</sup> are bound to a gold adatom that has been lifted from the gold surface. For simplicity, Figure 3 illustrates only one possible structure of well-packed alkanethiol SAMs on Au(111).

A kinetic study showed that the formation of thin films with **4** was  $\sim 10$  times faster than that of the ODT film, which is a reversal from the results obtained with **3**. However,



**FIGURE 3.** One of many proposed models of alkanethiol SAMs on Au(111), where the sulfur atoms occupy the 3-fold hollows in a hexagonal arrangement with S–S nearest neighbor spacing of  $\sim 5.0$  Å.<sup>31–36</sup>

Tao et al. noted in a study involving aromatic monothiols that the insertion of one methylene unit between the aryl and the thiol group improved intermolecular interactions; a bond angle preference for the sulfur atom of benzyl mercaptan ( $sp^3$ ) as compared to that of thiophenol ( $sp$ ) was also observed.<sup>37</sup> Thus, the different behavior between **3** and **4** can be attributed to the extra methylene unit, which diminishes steric interference of the headgroups and offers flexibility in binding to gold surfaces. Additionally, thermodynamic studies<sup>28,38</sup> found the adsorption free energies ( $\Delta G_{\text{ads}}^\circ$ ) of **4** and ODT on gold surfaces to be  $-28.9$  and  $-23.0$  kJ/mol, respectively.

Lim et al. also explored 1,3-benzenedithiol (**5**) and 1,3-benzenedimethanethiol (**6**) on gold and silver nanoparticle surfaces; however, the coordination of one or two sulfurs depends on the adsorbate structure and concentration.<sup>39,40</sup> In the case of **5**, both sulfur atoms adsorb to the metal substrate to provide a chelating structure; in contrast, **6** adopts this conformation only at adsorbate concentrations below monolayer coverage, while possessing an upright geometry (i.e., one S–metal linkage) as the concentration increases. Apparently, addition of the methylene group makes the head unit more flexible, and the assembly occurs quickly at high concentration, allowing only one sulfur to anchor on the surface (kinetic product). In contrast, the adsorption of both sulfur atoms is thermodynamically favored at low concentrations.

Two alkyl chains were incorporated into the structure of **4** to provide 1,2,4,5-tetrasubstituted benzenes (**7**).<sup>30</sup> The SAMs derived from these dithiols were densely packed and highly ordered. Thermal desorption studies of these SAMs in solution showed that the monolayers were more robust than analogous normal alkanethiolate and aromatic monothiolate SAMs.<sup>30,41</sup> The authors also investigated SAMs derived from the corresponding aromatic disulfides (**8**)<sup>42</sup> and found that incomplete or disordered monolayers were formed. The authors suggested that the conformational constraints introduced by the cyclic nature of the disulfide

along with the conjoined rigid aromatic ring hindered the chemisorption of the disulfide, leading to a poorly organized monolayer. Bruno et al. recently broadened the use of *meta* aromatic **6** by examining the packing ability of 4-methoxyterphenyl-3'',5''-dimethanethiol (**9**) compared with 4-methoxyterphenyl-4''-methanethiol (**10**) on gold films and nanoparticles.<sup>43</sup> Studies showed that the dithiol **9** needed higher temperatures for the carbon species to be completely removed from the substrate regardless of its lower packing density compared with the monothiol **10** film. These studies further confirm that chelation enhances the stability of monolayers.

Another type of chelating SAM generated from aliphatic dithiocarboxylic acids (ADTCAs; **11**) was reported by Lee and co-workers.<sup>44</sup> Stability tests of SAMs derived from **11** under argon, in air, and under oxygen atmospheres showed that they were less stable than the corresponding alkanethiolate SAMs, despite the potential of the chelate effect to enhance the stability of these bidentate ligands.<sup>45</sup> The authors noted the fragile nature of the dithiocarboxylic acid itself, which undergoes facile decomposition upon exposure to mild reagents and conditions.<sup>46</sup> Similar bidentate structures including xanthic acids **12** and dithiocarbamic acids **13** have also been used to form monolayers on gold. Moore compared SAMs derived from **12** with those derived from corresponding versions of **11** and alkanethiols, finding that the former SAM was more disordered and lower in effective packing chain density relative to the latter two films.<sup>47</sup> The SAM derived from **12** also desorbed more easily than those derived from **11** and the alkanethiols. Moore rationalized these results on the basis of the fragile character of the xanthic acid adsorbate.<sup>48</sup>

In 1999, Shon and Lee introduced a unique type of chelating adsorbate that incorporates four substituents at a single branchpoint.<sup>49</sup> The new adsorbates **14** ( $[\text{CH}_3-(\text{CH}_2)_{n-3}]_2\text{C}[\text{CH}_2\text{SH}]_2$ , **CnCn**), described as "spiroalkanedithiols", have two alkyl chains attached to the branchpoint carbon along with the two methylenethiol headgroups. Well-packed and highly oriented SAMs can be generated by using relatively long alkyl-chain adsorbates, which exhibit conformational order only slightly lower than that of analogous alkanethiolate SAMs. The authors also proposed that the chelating dithiol **14** was unable to bind to the 3-fold hollow sites on gold surfaces since the maximum span of the two sulfur atoms, without introducing bond-angle strain, is  $\sim 4.8$  Å.<sup>29,49</sup>

The general structure of **14** also offers the ability to create mixed SAMs from unsymmetrical spiroalkanedithiols (e.g., **15**).

The topographic AFM images presented by Shon et al. of SAMs generated from **C10C17** ( $[(\text{CH}_3(\text{CH}_2)_7][\text{CH}_3(\text{CH}_2)_{14}]\text{C}[\text{CH}_2\text{SH}]_2$ ) showed no phase separation, as had occurred with the coadsorption of two analogous alkanethiols ( $\text{CH}_3(\text{CH}_2)_9\text{SH} + \text{CH}_3(\text{CH}_2)_{16}\text{SH}$ ).<sup>50</sup> Another systematic study of **15** where one alkyl chain was gradually shortened to generate progressively unsymmetrical structures also showed that these unsymmetrical adsorbates could generate films with evenly distributed or homogeneously mixed alkyl chains across the surfaces.<sup>51</sup> Shon et al. also studied the formation of SAMs by using "monoalkanedithiol" **16**, where only one alkyl chain was attached to the branchpoint carbon ( $\text{CH}_3(\text{CH}_2)_{n-3}\text{CH}[\text{CH}_2\text{SH}]_2$ , **CnC2**).<sup>52,53</sup> In comparison with **14** and normal alkanethiols (**n-Cn**), **16** provided well-defined monolayers but exhibited reduced crystallinity due to a lowering in chain density, leading to more conformationally disordered and more tilted chains from the surface normal. These studies showcased the ability to use such monoalkanedithiol-based structures to control surface density.<sup>54</sup> Kinetic studies suggested the following rates of adsorption for the thiols: **CnC2**  $\approx$  **n-Cn**  $>$  **CnCn**.<sup>55</sup> For **n-Cn** and **CnCn**, two kinetic adsorption regimes were observed: a fast initial regime where  $\sim 80\text{--}90\%$  of the monolayer was formed and a slower orientation-ordering regime where the alkyl chains became more densely packed and highly crystalline. In contrast, **CnC2** exhibited a single rapid adsorption regime, in which an initial steady-state physisorption was immediately followed by a chemisorption step, leading ultimately to complete monolayer formation.

Stability tests were conducted, and the results showed the following trend in thermodynamic stability: **CnC2**  $>$  **CnCn**  $\gg$  **n-Cn**.<sup>56</sup> The authors rationalized these observations on the basis of the chelating ability of the headgroups; surprisingly, tailgroup interactions appear to play a markedly lesser role. The desorption of thiolate-based films is believed to occur via disulfide formation,<sup>57</sup> which, in the case of these 1,3-propanedithiolate monolayers, leads to 1,2-dithiolanes (five-membered rings).<sup>58</sup> Dithiolane formation is calculated to be energetically disfavored due to ring strain ( $\sim 3.6$  kcal/mol).<sup>56,58</sup> When we compare the dithiols, SAMs derived from **16** have greater conformational flexibility (due to having only one alkyl tailgroup), which enhances their binding ability and gives rise to a slightly greater stability than SAMs derived from **14**. The stability of **16** was also studied in comparison with the analogous dithiocarboxylic acid **11** and normal alkanethiol on copper surfaces, and the authors found that the dithiol **16** could be used to generate

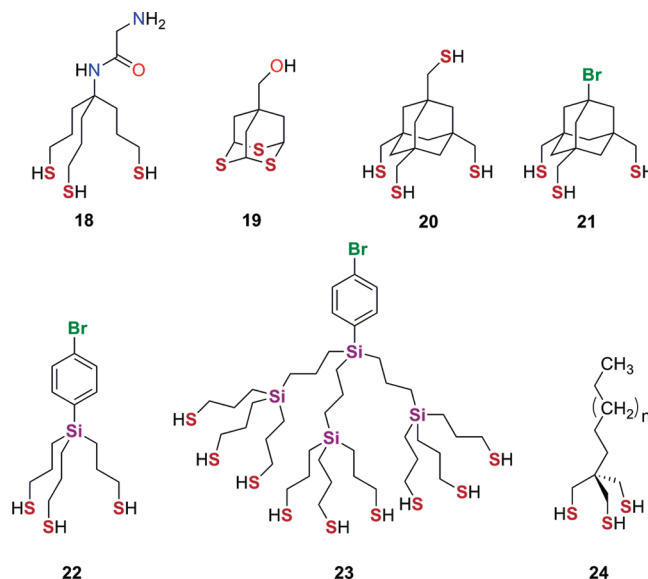


FIGURE 4. Structures of tridentate adsorbates.

the most stable film upon anodic and cathodic desorption tests.<sup>59</sup>

In further efforts to gain insight into the relationship between adsorbate structure and SAM packing density, Park et al. prepared a series of 2-alkyl-2-methylpropane-1,3-dithiols, **17**, where a methyl group was embedded at the branchpoint carbon ( $[(\text{CH}_3(\text{CH}_2)_{n-3}][\text{CH}_3]\text{C}[\text{CH}_2\text{SH}]_2$ , **CnC3**).<sup>60</sup> This new series of adsorbates was used to generate SAMs with even lower chain densities and conformational order compared with the **16** SAMs, which likely arises from the steric bulk of the methyl group at the branchpoint of these adsorbates.

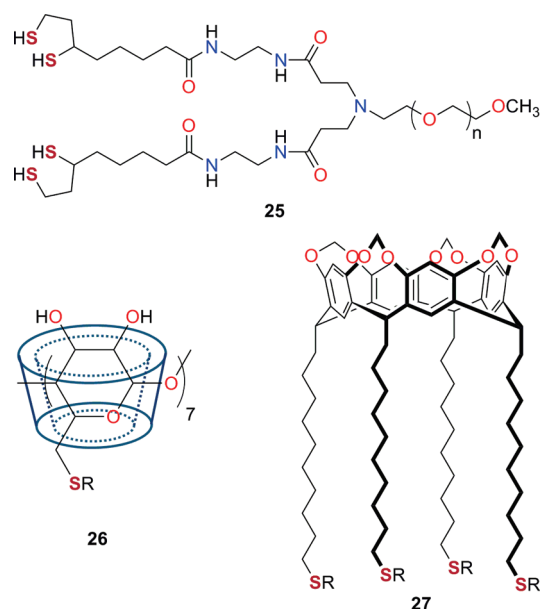
**2.2. Tridentate Adsorbates.** Tridentate structures have been utilized to engineer monolayer assemblies where three active headgroups on a single adsorbate can bind to the solid surface (e.g., Figure 4). An aminotrithiol-based structure **18** was introduced by Whitesell and Chang in 1993.<sup>61</sup> Fox and co-workers used the aminotrithiol **18** as an effective linkage for binding surface probes (i.e., two optically addressable fluorescent chromophores and a redox-active reagent) on gold substrates.<sup>62</sup> XPS analysis revealed that the chelating tripod was not completely bound through all three thiol headgroups, probably due to severe steric interactions as suggested by molecular modeling.<sup>62</sup> Nonetheless, once the film was formed, the authors reported that **18** was not displaced by long chain alkanethiols under conditions where monothiol adsorbates were readily displaced,<sup>63</sup> indicating an enhanced stability for SAMs derived from this trithiol ligand.

Whitesell and co-workers further explored two sulfur-containing adamantane derivatives, **19** and **20**, finding that

both adsorbates bound to gold via all three surface-oriented sulfur atoms.<sup>64</sup> Kitagawa et al. examined the chemisorption of the bromine-terminated **21** adsorbate and similarly found that all three sulfur atoms were bound to the surface of gold.<sup>65</sup> Additionally, SAMs formed from **21** showed an ordered two-dimensional crystal structure with a hexagonal arrangement of the adsorbed molecules on the Au(111) substrate. The distance between two intramolecular sulfur atoms was reported to be  $\sim 5.0$  Å.<sup>31</sup> Therefore, the three legs in these adamantane derivatives bind on gold similarly to alkanethiols, without generating any geometric change that might lead to an increased molecular strain in the structure. An extended study by Katano et al. also confirmed the three-point contacts of **21** on Au(111) surfaces and the highly ordered SAMs that were formed.<sup>66</sup>

Silicon has also been used as a core component for tripod-shaped adsorbates. Yam et al. introduced the silicon trithiolate **22**.<sup>67</sup> Approximately 20% of free thiol moiety remained on the monolayer surface as observed via XPS, which is in agreement with the results obtained from the similar carbon-core aminotrithiol **18**.<sup>62</sup> Nevertheless, these films still exhibited greater stabilities in hot solvents compared with ODT films due to the multiple attachment points between the adsorbate molecules and the gold surface. The bromophenyl density on the surface could be manipulated by increasing the generation of the dendron, creating a structure with nine thiol headgroups (**23**).<sup>67</sup>

Park et al. recently introduced a trithiol structure **24** based on the "spiroalkanedithiol" design.<sup>68</sup> These adsorbates (**t-Cn**) were synthesized and used to form SAMs along with their bidentate analogues, **16 (CnC2)** and **17 (CnC3)**, to provide systematic control in packing density. Although SAMs derived from **24** showed the lowest packing density for the surface alkyl chains, a preliminary evaluation showed that the tridentates generated the most thermodynamically stable films, while the **16** and **17** films were similar to each other in thermal stability, but nevertheless more thermally stable than normal alkanethiol analogs. This trend was confirmed by Srisombat et al. for SAMs on both flat gold and colloidal gold, where the thermal stabilities were found to correspond to the degree of chelation (i.e., **t-C18** > **C18C2**  $\approx$  **C18C3** > **n-C18**; tridentate > bidentate > monodentate).<sup>69</sup> These findings were consistent with studies of the bidentates **16** and **17** and tridentate **24** on large gold nanoparticles ( $\sim 20$ – $50$  nm in diameter)<sup>70</sup> and studies of their electric potential stability on flat gold.<sup>71</sup> The data presented in these papers support an argument that the chelate effect is the



**FIGURE 5.** Structures of multidentate bis(DHLA)–PEG–OCH<sub>3</sub> and cyclodextrin- and resorcinarene-based adsorbates (where R = H or alkyl).

key to enhancing monolayer stability and for stabilizing nanoparticles in solution (i.e., preventing aggregation).

Separately, Srisombat et al. studied the chemical stability of small gold nanoparticles ( $\sim 2$  nm) coated with thiol-based SAMs.<sup>72</sup> The particles were immersed in a solution of potassium cyanide, and the ability of each ligand to resist etching of the gold was measured. These studies showed the following trend in stability: **C18C3**  $\gg$  **C18C2** > **t-C18**  $\gg$  **n-C18**. In this case, the diminished chain packing density of **24** relative to that for **16** and **17** apparently allowed cyanide ions to penetrate and etch the gold particles. Furthermore, the steric hindrance provided by the additional methyl group on **17** at the branchpoint carbon helped block the cyanide ions from reaching the gold nanoparticle surface; thus, **17** provided markedly greater resistance to chemical decomposition than **16**, revealing the complex interplay between adsorbate structure and nanoparticle stability.

**2.3. Beyond Tridentate.** Although a variety of stable highly chelated SAMs have been generated from oligomeric or polymeric adsorbates<sup>73</sup> and by UV or electron-beam irradiation of preformed monodentate SAMs,<sup>74,75</sup> this Account focuses on SAMs generated from discrete multidentate molecules. Recent work by Mattoussi and co-workers examined the stability of gold nanoparticles and semiconductor quantum dots (QDs) functionalized with bidentate (i.e., thioctic acid, TA, and dihydrolipoic acid, DHLA)<sup>76,77</sup> and tetradentate (i.e., bis(TA) and bis(DHLA))<sup>78</sup> poly(ethylene glycol) ligands (e.g., **25** in Figure 5). These ligands enhance

colloidal stability under harsh conditions (e.g., extreme pH, high salt concentrations, thiol-rich environments, and the presence of metal etchants). In studies using even more highly chelated molecular adsorbates, researchers investigated SAMs derived from multidentate cyclodextrin-based (**26**)<sup>79–81</sup> and resorcinarene-based (**27**)<sup>82–84</sup> thiols and sulfides. Although enhanced stability was reported for some of these systems, the films typically contained a number of defects as judged by electrochemical probes; correspondingly, the long alkyl chains used to support the terminal cyclodextrin and resorcinarene moieties were poorly ordered as judged by IR spectroscopy.

### 3. Conclusions

This Account has examined a variety of multidentate adsorbate structures that have been used to generate well-defined organic monolayer films. These unique adsorbates offer the opportunity to tune the interfacial properties of surfaces ranging from those that are ultraflat (atomically smooth) to those that are nonplanar (e.g., nanoparticles). The enhanced stability of SAMs formed from multidentate adsorbates permits the development of nanoscale coatings that are more robust than those derived from monodentate adsorbates, allowing their use in harsh environments (e.g., at elevated temperatures or in the presence of chemical etchants). Future studies will target the development of multidentate adsorbates having chemically distinct tailgroups for the generation of uniquely well-defined chemically heterogeneous interfaces.

#### BIOGRAPHICAL INFORMATION

**Pawilai Chinwangso** was born in 1982 in Tak, Thailand. She earned her B.S. in Chemistry from Chiang Mai University in 2004. She entered the graduate program in Chemistry at the University of Houston in the fall of 2004, where her research has focused on the formation of mixed multicomponent self-assembled monolayers derived from multidentate adsorbates. She obtained her Ph.D. in December 2009 and is now working as a Postdoctoral Fellow in the Department of Electrical and Computer Engineering at the University of Houston.

**Andrew C. Jamison** was born in 1960 in Shreveport, Louisiana. He received his first degree (BBA) from Texas Wesleyan College in 1982. After working in the paint industry, he returned to school to obtain a B.S. in Chemistry from the University of Houston in 2004. He is currently pursuing his Ph.D. degree at the University of Houston, where his research explores the impact of partially fluorinated adsorbates on the formation of well-ordered self-assembled monolayer films.

**T. Randall Lee** was born in 1962 in Daingerfield, TX. He began his career in research under the guidance of Professor Ken Whitmire

at Rice University, where he received his B.A. in 1985. He obtained a Ph.D. from Harvard University in 1991 under the direction of Professor George Whitesides and worked as an NIH Postdoctoral Fellow at the California Institute of Technology with Professor Robert Grubbs from 1991 to 1993. He is now a Professor of Chemistry and Chemical Engineering at the University of Houston and holds the title of Cullen Distinguished University Chair. His research interests include materials chemistry and nanotechnology.

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