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# Surface modification *via* 'lock and key' specific self-assembly of polyhedral oligomeric silsequioxane (POSS) derivatives to modified gold surfaces

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**Diaminopyridine (DAP) functionalized POSS derivatives self-assemble on thymine functionalized monolayers on gold surfaces affording hybrid inorganic/organic surfaces.**

Surface modification through non-covalent interactions provides a powerful tool for the control of both the chemical and physical properties of surfaces. A number of techniques have been employed to modify these properties, including Langmuir-Blodgett deposition,[1] electrostatic interactions,[2] ionic coordination[3] and interfacial hydrogen bonding.[4]

The use of designed recognition elements provides a means for enhancing the specificity, and hence the versatility of surface modification procedures. While interfacial binding using engineered recognition elements has been used in sensor systems,[5] this approach has not been widely applied to surface modification strategies.[6] To provide a system for exploring recognition-mediated surface modification, we have synthesized polyhedral oligomeric silsequioxanes (POSSs) functionalized with specific recognition elements. POSS derivatives feature a variety of attributes that make them attractive as surface modification agents.[7] These three-dimensional, inorganic/organic hybrids are ~1.5 nm in diameter, presenting a large cross-section for efficient surface coverage. POSS derivatives are stable to a variety of conditions, making them useful modifiers for polymeric[8] and ceramic[9] systems, as well as applications including nonablatives, atomic-oxygen resistance, and thermal protection. In this communication, we report the recognition-mediated modification of thymine terminated self-assembled monolayers (SAMs) on gold surfaces using complementary diaminopyridine-functionalized POSS derivatives† (**POSS-DAP**)[10] (Fig. 1).

Thymine-functionalized SAM **1** was prepared by immersing gold films in a 10 mM ethanolic solution of a 1:3 ratio of thymine thiol[11]/octanethiol for 16 h at room temperature. Films were then washed with a hexane/chloroform (1:1) solution to remove any free thiol. Interaction of surface **1** with **POSS-DAP** was explored by immersing the surfaces in a 5 mM solution of diaminopyridine **POSS-DAP** in hexane/chloroform (1:1) for 10 minutes, and drying *in vacuo*. To confirm that the **POSS-DAP** interacts with the monolayer through specific hydrogen bonding, control surface **2** featuring the n-methylthymine functionality, and octanethiol surface **3** were prepared and studied in similar fashion.

Specific **POSS-DAP** deposition on surface **1** was confirmed by X-ray photoelectron spectroscopy (XPS). The characteristic peak corresponding to Si was present after deposition of the **POSS-DAP** on the Au surface (Fig. 2b). In contrast, XPS of the control surfaces **2** and **3** showed no measurable Si present after dipping in **POSS-DAP** solution. Further confirmation of effective surface modification was provided by the dramatic decrease of the Au peak after **POSS-DAP** deposition onto surface **1**, with very little or no change observed in the Au peaks of control surfaces **2** and **3** (Fig. 2a). Ellipsometric measurements at multiple positions of **POSS-DAP**-modified surface **1** provided a thickness for the POSS layer of 18 ± 3Å, indicating that **POSS-DAP** was deposited as a monolayer rather than as

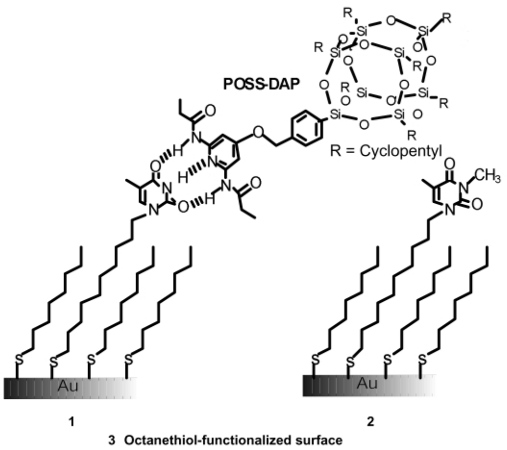

**Fig. 1** Schematic illustration of the binding of **POSS-DAP** to thymine-functionalized SAM **1**, n-methylthymine-functionalized SAM **2** and octanethiol SAM **3**.

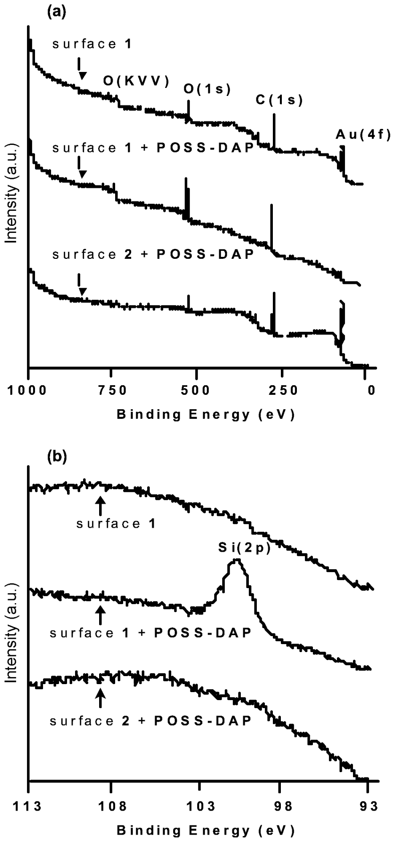

**Fig. 2** (a) XPS survey scans of surface **1**, surface **1** + **POSS-DAP**, and surface **2** + **POSS-DAP** recorded with take-off angles of 15°. (b) XPS spectra for surface **1**, surface **1** + **POSS-DAP**, and surface **2** + **POSS-DAP** showing the Si region.

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island aggregates or multilayers. Finally, grazing angle FT-IR measurements of the **POSS-DAP**-modified surface **1** shows an intense peak at 1100 $\mathrm{cm}^{-1}$ arising from the asymmetric Si–O–Si stretching vibration as well as additional bands in the 1700–1300 $\mathrm{cm}^{-1}$ region after **POSS-DAP** surface modification (Fig. 3).

Functional demonstration of surface modification was provided using dynamic contact angle measurements with water (Table 1). After **POSS-DAP** deposition, the contact angle of surface **1** dramatically increases, indicating the formation of a much more hydrophobic surface. In contrast, control surfaces **2** and **3** show a negligible change in contact angle after exposure to **POSS-DAP**. The small hysteresis changes after **POSS-DAP** deposition indicate that surface **1** is uniformly modified with POSS functionality.[12]

In summary, we have demonstrated highly specific 'lock and key' functionalization of SAM surfaces through controlled host–guest interactions. Using this strategy, we were able to control both the chemical and physical nature of the surface through deposition of POSS-based surface modification agents. This strategy enhances the versatility of current functionalization strategies by exploiting the diversity of currently available host–guest dyads[13] to allow orthogonal deposition of surface modifiers. Research in this direction is currently underway, and will be reported in due course.

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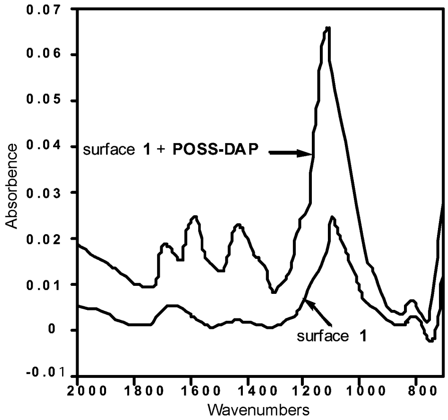

**Fig. 3** Grazing angle (86 degree incident) reflection absorption infrared spectra of surface **1** before (bottom) and after (top) deposition of **POSS-DAP**.

**Table 1** Dynamic water contact angles for surfaces **1**–**3** before and after POSS deposition[a]

| Substrate | Advancing (°) | Receding (°) | Hysteresis (°) |
|---|---|---|---|
| Surface **1** | 74.5 | 64.8 | 9.7 |
| Surface **1** + **POSS-DAP** | 89.8 | 76.7 | 13.1 |
| Surface **2** | 73.0 | 63.2 | 9.7 |
| Surface **2** + **POSS-DAP** | 74.6 | 63.1 | 11.5 |
| Surface **3** | 91.5 | 77.8 | 13.7 |
| Surface **3** + **POSS-DAP** | 91.3 | 75.8 | 15.4 |

[a] Values reported here are an average of at least six measurements, and are ±2°.

## Notes and references

† For **POSS-DAP**: $\delta_H$ ($CDCl_3$, 200 MHz): 7.80–7.55 (m, 4H), 7.50–7.3 (m, 4H),2.00–1.3 (m,46H), 1.18 (t, 6H), 0.94 (brq, 6H). MALDI MS: $(M + H)^+$ 1226. FT-IR(neat): 2949, 2864, 2360, 1697, 1584, 1438, 1111, 668 $\mathrm{cm}^{-1}$. Mp > 350 °C.

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