Surface Molecular Tailoring Using pH-Switchable Supramolecular Dendron-Ligand Assemblies

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Supporting Information

ABSTRACT: The rational design of materials with tailored properties is of paramount importance for a wide variety of biological, medical, electronic and optical applications. Here we report molecular level control over the spatial distribution of functional groups on surfaces utilizing self-assembled monolayers (SAMs) of pH-switchable surface-appended pseudorotaxanes. The supramolecular systems were constructed from a poly(aryl ether) dendron-containing a dibenzo[24]crown-8 (DB24C8) macrocycle and a thiol ligand-containing a dibenzylammonium recognition site and a fluorine end group. The dendron establishes the space (dendritic effect) that each pseudorotaxane occupies on the SAM. Following SAM formation, the dendron is released from the surface by switching off the noncovalent interactions upon pH stimulation, generating surface materials with tailored physical and chemical properties.

KEYWORDS: self-assembly, binary self-assembled monolayers, functional surfaces, supramolecular systems, pseudorotaxanes

INTRODUCTION

The development of self-assembly processes capable of generating functional surfaces with well-defined and tunable properties promises to have far-reaching consequences for biological and medical applications.1−3 Furthermore, these self-assembly processes can lead to the preparation and tailoring of intricate surfaces with unique properties for electronic and optical applications.4 The ability of molecular compounds to self-assemble on surfaces, giving rise to self-assembled monolayers (SAMs),5 has been exploited extensively over the past decade to modify and tailor the properties of a wide range of metal, metal oxides and semiconductor surfaces. Recently, mixed SAMs have been the subject of much interest because of their precisely controllable size, molecular weight, and hydrophobic and inert chemical composition.19 The development of self-assembly processes capable of generating functional surfaces with well-defined and tunable properties promises to have far-reaching consequences for biological and medical applications.4−7 Furthermore, these self-assembly processes can lead to the preparation and tailoring of intricate surfaces with unique properties for electronic and optical applications.4 The ability of molecular compounds to self-assemble on surfaces, giving rise to self-assembled monolayers (SAMs),5 has been exploited extensively over the past decade to modify and tailor the properties of a wide range of metal, metal oxides and semiconductor surfaces. Recently, mixed SAMs have been the subject of much interest because of their precisely controllable size, molecular weight, and hydrophobic and inert chemical composition.19

Mixed SAMs rely on preparing SAMs from a solution of two or more molecular compounds, which usually have different end group functionalities. This process has several limitations such as the fact that the ratio of the two compounds in the monolayer is rarely identical to their ratio in the solution, because of the preferential adsorption of one of the components. This preferential adsorption means control over not only the density but also the homogeneity of functional groups in mixed monolayers is not straightforward.15 Thus, the formation of two-component monolayers has been reported by several authors16−18 to lead to phase-segregated heterogeneous mixed SAMs with surface ratios different from solution ratios of the components. If we can assemble molecular components in which functional groups are deterministically arranged with special distributions on the molecular scale, we will open access to a new class of surface materials with designed and tailored physical and chemical properties. Starting from this premise, we have devised pH-switchable supramolecular systems that are able to self-assemble on surfaces and contain a molecular component that can vary in steric bulkiness (Figure 1). Poly(aryl ether) dendrons with generations varying from 0 to n ([G0]−[Gn]) serve as ideal steric molecular components because of their precisely controllable size, molecular weight, and hydrophobic and inert chemical composition.19 The dendrons act as space-filling molecular moieties that establish the space that each pseudorotaxane occupies on the surface. Furthermore, the dendrons are bound to the surface by noncovalent interactions and can be released after SAM formation.

ABSTRACT: The rational design of materials with tailored properties is of paramount importance for a wide variety of biological, medical, electronic and optical applications. Here we report molecular level control over the spatial distribution of functional groups on surfaces utilizing self-assembled monolayers (SAMs) of pH-switchable surface-appended pseudorotaxanes. The supramolecular systems were constructed from a poly(aryl ether) dendron-containing a dibenzo[24]crown-8 (DB24C8) macrocycle and a thiol ligand-containing a dibenzylammonium recognition site and a fluorine end group. The dendron establishes the space (dendritic effect) that each pseudorotaxane occupies on the SAM. Following SAM formation, the dendron is released from the surface by switching off the noncovalent interactions upon pH stimulation, generating surface materials with tailored physical and chemical properties.

KEYWORDS: self-assembly, binary self-assembled monolayers, functional surfaces, supramolecular systems, pseudorotaxanes
formation simply by switching off the noncovalent interactions upon raising the pH. Removal of the noncovalently bound dendron spacing groups will expose functional groups on the surface. Thus, by carefully selecting the dendron component, it should be possible to tailor at the molecular level the density and spatial distribution of functional groups on material surfaces.

The supramolecular system is based on host–guest inclusion complex formation between a poly(aryl ether) dendron-containing dibenzo[24]crown-8 (DB24C8) and a dibenzylammonium (DBA) thread with a fluorine end functional group and a thiol surface-active headgroup for strong anchoring onto the gold surface upon SAM formation (Figure 1). The assembly and disassembly processes of the supramolecular system based on DB24C8/DBA pseudorotaxane can be controlled simply by acid–base reactions.²⁰ The DB24C8·DBA pseudorotaxane complex is self-assembled and stabilized by [N′−H···O] and [N=C–H−O] hydrogen bonds, which are easily destabilized by deprotonation and raising the pH, and re-established by acidifying. Moreover, additional [C−H···O] and π–π stacking interactions, as well as electrostatic forces, also contribute to the stability of the pseudorotaxane’s formation. In this study, three supramolecular systems were constructed by the self-assembly of (i) DB24C8 with the DBA thiol derivative (DBA-SH), (ii) [G1]-poly(aryl ether) dendron-containing DB24C8 ([G1]-DB24C8) with DBA-SH and (iii) [G2]-DB24C8 with DBA-SH. SAMs of these systems were prepared on gold surfaces, followed by decomplexation and simultaneous backfilling with 3-chloropropanethiol (ClPrSH) to form mixed monolayers (Figure 1). This strategy was investigated for its applicability and effectiveness on providing molecular level control over density and spatial distribution of functional groups in a monolayer.

RESULTS AND DISCUSSION

Synthesis. The DBA-SH, DB24C8, [G1]-DB24C8, and [G2]-DB24C8 were synthesized via multistep synthetic routes. The synthesis of DBA-SH was initiated with the alkylation of 4-hydroxybenzaldehyde by 11-bromoundecene in the presence of K₂CO₃ and NaI to obtain aldehyde 1 (Scheme 1). Fluorobenzylamine was reacted with aldehyde 1 at an elevated temperature to afford the imine, which was subsequently reduced to the secondary amine 2 with NaBH₄. Amine-Boc protection was performed via reaction of 2 with Boc₂O in the presence of NEt₃ and catalytic amount of 4-DMAP to obtain 3. Thioacetylation of 3 was performed via the addition of thiocetate 4 under acidic conditions (TFA) to yield the secondary amine 5. The thioacetylated 5 was acid hydrolyzed (0.1 M HCl) to give the thiol 6, followed by protonation of the secondary amine with HPF₆ to afford the desired DBA-SH as the hexafluorophosphate salt.

[G1]- and [G2]-dendritic alcohols and macrocycle 7 were synthesized according to literature procedures¹¹,¹² (for further details, see the Supporting Information). Macrocycle 7 was base hydrolyzed (NaOH) to afford the desired carboxylic acid functionalized crown ether 8. [G1]- and [G2]-dendritic

Scheme 1. Synthesis of DBA-SH: (i) 11-bromoundecene, K₂CO₃, Acetone, Reflux, 16 h, 81%, (ii) 4-fluorobenzylamine, PhMe, Reflux, N₂(g), 20 h, (iii) NaBH₄, MeOH, Reflux, N₂(g), 20 h, 85%, (iv) Boc₂O, NEt₃, 4-DMAP (cat), THF, rt, N₂(g), 16 h, 71%, (v) HSAc, AIBN (cat), PhMe, Reflux, 2 h, 84%, (vi) TFA, DCM, rt, N₂(g), 6 h, 80%, (vii) 0.1 M HCl, MeOH, N₂(g), 4 h, 71% %, (viii) HPF₆, DCM, rt, N₂(g), 10 min, 91%
alcohols were DCC coupled to carboxylic acid functionalized crown ether 8 with catalytic amount of DMAP to afford the desired esters [G1]-DB24C8 and [G2]-DB24C8 (Scheme 2).

Scheme 2. Synthesis of Poly(aryl ether) Dendron-Containing DB24C8 (i) NaOH(aq) EtOH, reflux, 16 h, 80%, (ii) DCC, 4-DMAP, DCM, rt, N2(g), 16 h, 24% ([G1]-DB24C8), 24% ([G1]-DB24C8), 24% ([G2]-DB24C8), 24% ([G2]-DB24C8), 24% ([G2]-DB24C8), 24% ([G2]-DB24C8), 24% ([G2]-DB24C8), 24% ([G2]-DB24C8), 24% ([G2]-DB24C8), 24% ([G2]-DB24C8), 24% ([G2]-DB24C8), 24% ([G2]-DB24C8), 24% ([G2]-DB24C8), 24% ([G2]-DB24C8).

Complexation. The DB24C8⊃DBA-SH, [G1]-DB24C8⊃DBA-SH, and [G2]-DB24C8⊃DBA-SH pseudorotaxanes were formed by complexation of DBA-SH with 2 equiv. of either DB24C8, [G1]-DB24C8 or [G2]-DB24C8 in HPLC MeCN and confirmed by 1H NMR spectroscopy (MeCN-d6, 300 MHz, 25 °C). By way of an example, Figure 2 shows the partial 1H NMR spectra of DB24C8, DBA-SH and DBA-SH supramolecular assemblies were formed by immersing freshly plasma cleaned Au substrates in 10 mM MeCN solutions of the supramolecular complexes for 24 h. In order to create the mixed SAMs, the freshly prepared SAMs of pH-switchable supramolecular dendron-thiol ligand systems were immersed in a mixed MeCN solution of 2 mM NEt3 and 1 mM ClPrSH for 30 min. It is important to note that the backfilling conditions with ClPrSH have been previously demonstrated by us12 not to affect the spatial distribution of a previously immobilized thiol. Pure DBA-SH and ClPrSH SAMs, which were used as controls, were prepared in MeCN solutions of 10 mM DBA-SH and 1 mM ClPrSH, respectively, for 24 h.

SAM formation was evaluated by ellipsometry, contact angle (Table 1) and XPS (Figure 3 and Table 2). The advancing contact angle (θadv) observed for pure monolayer of DBA-SH is 101 ± 1°, which is in good agreement with the literature for chlorine-terminated monolayers (Table 1).25 Note that the hysteresis (θadv – θrec) value of 33° suggests the presence of a sparsely packed monolayer, which is likely due to the electrostatic repulsions of the protonated amino group in the DBA-SH. The θadv of 83 ± 1° for ClPrSH SAM is consistent with previous reports on chlorine-terminated SAMs,26 where the hysteresis of 34° indicates once more the presence of a loosely packed SAM. The lack of order in this monolayer is most likely a result of the weak interactions between the short alkyl chains of the ClPrSH SAM.27

The wettability properties of the monolayers formed from the DB24C8⊃DBA-SH, [G1]-DB24C8⊃DBA-SH, and [G2]-DB24C8⊃DBA-SH supramolecular assemblies were lower than for pure DBA-SH monolayer, with observed θadv of 93 ± 3, 91 ± 2, and 87 ± 2°, respectively. It is assumed that this decrease in wettability is due to the concealment of the very hydrophobic chlorine end group by the longer DBA-SH.

Table 1. Advancing (θa) and Receding (θr) Water Contact Angles and Ellipsometric Thickness for the SAMs Formed

<table>
<thead>
<tr>
<th>SAM</th>
<th>contact angle (deg)</th>
<th>thickness (nm)</th>
<th>ellipsometric</th>
<th>theoretical*</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBA-SH</td>
<td>101 ± 1</td>
<td>68 ± 1</td>
<td>2.00 ± 0.08</td>
<td>2.40</td>
</tr>
<tr>
<td>ClPrSH</td>
<td>83 ± 1</td>
<td>49 ± 3</td>
<td>0.42 ± 0.01</td>
<td>0.51</td>
</tr>
<tr>
<td>DB24C8⊃DBA-SH</td>
<td>95 ± 3</td>
<td>44 ± 4</td>
<td>1.85 ± 0.10</td>
<td>2.27</td>
</tr>
<tr>
<td>[G1]-DB24C8⊃DBA-SH</td>
<td>92 ± 1</td>
<td>57 ± 2</td>
<td>1.78 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>[G2]-DB24C8⊃DBA-SH</td>
<td>91 ± 4</td>
<td>42 ± 3</td>
<td>1.70 ± 0.07</td>
<td>2.11</td>
</tr>
<tr>
<td>[G1]-DB24C8⊃DBA-SH</td>
<td>89 ± 1</td>
<td>56 ± 3</td>
<td>1.65 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>[G2]-DB24C8⊃DBA-SH</td>
<td>89 ± 3</td>
<td>43 ± 2</td>
<td>1.60 ± 0.05</td>
<td>1.69</td>
</tr>
<tr>
<td>[G2]-DB24C8⊃DBA-SH</td>
<td>87 ± 2</td>
<td>55 ± 2</td>
<td>1.45 ± 0.05</td>
<td></td>
</tr>
</tbody>
</table>

*DBA-SH:ClPrSH mixed SAM that was prepared by the initial formation of a supramolecular complex monolayer, followed by simultaneous decomplexation and immersion in a ClPrSH solution. Calculated via MD simulations.
molecule and the terminal end groups belonging to the crown ether or dendrons. The bulkiness of the supramolecular assemblies, which are expected to induce steric effects and complex intermolecular interactions during the self-assembly process, is most likely responsible for the higher contact angle hysteresis observed when compared with the pure DBA-SH SAM.

After decomplexation of DB24C8⊃DBA-SH, [G1]-DB24C8⊃DBA-SH, and [G2]-DB24C8⊃DBA-SH monolayers by means of a base and simultaneous immersion in a ClPrSH solution, the resulting mixed monolayers exhibit θadv of 92 ± 3, 89 ± 2, and 87 ± 2°, respectively. The θadv values obtained are between those of pure DBA-SH (101 ± 1°) and ClPrSH (83 ± 1°) SAMs, and thus consistent with the presence of a DBA-SH:ClPrSH mixed monolayer. Interestingly, the contact angle hysteresis obtained for the mixed monolayers are between 12 and 14° lower than the respective complexed monolayers and comparable to the pure DBA-SH and ClPrSH SAMs. Using the θadv measurements of the pure and DBA-SH:ClPrSH mixed monolayers in conjunction with the application of the Cassie’s equation,28 the ratio of the two surfactants (DBA-SH and ClPrSH) on the mixed monolayers was determined. Cassie’s eq 1 relates the contact angle of a surface of mixed composition to those of pure SAMs

\[
\cos \theta_{adv} = x \cos \theta_{adv1} + y \cos \theta_{adv2}
\]

Where θadv is the water advancing contact angle on the mixed SAM, θadv1 and θadv2 are the contact angles related to the pure SAMs, in this case, formed from DBA-SH and ClPrSH, respectively. x and y are the corresponding surface molar ratios of DBA-SH and ClPrSH, with \(x + y = 1\). By employing this relationship between surface wettability and the surface composition of the mixed SAMs, molar ratios (DBA-SH:ClPrSH) in the mixed SAMs of 1:1, 1:2, and 1:3 were obtained depending on if they were initially formed from either DB24C8⊃DBA-SH, [G1]-DB24C8⊃DBA-SH, or [G2]-DB24C8⊃DBA-SH monolayers, respectively. A trend is shown that indicates that the molar ratio between DBA-SH and ClPrSH decreases as the steric bulk of the initial supramolecular complex increases.

The ellipsometric thickness observed for the different monolayers is shown in Table 1. The monolayer thicknesses obtained for pure DBA-SH and ClPrSH are 2.00 ± 0.08 nm and 0.42 ± 0.01 nm, respectively. These values are in good agreement with the theoretical thicknesses of 2.40 and 0.51 nm, which were calculated through molecular dynamics (MD) simulations for DBA-SH and ClPrSH SAMs on gold surface, respectively (see the Supporting Information for simulation details).

The SAMs of the supramolecular complexes and subsequent mixed monolayers exhibit lower thickness values when compared to pure DBA-SH SAM. Once more, a trend is observed showing that with increasing the bulk of the supramolecular assembly, the thickness values of the SAM of the supramolecular complex monolayer diminish. The thicknesses obtained from the MD simulations show the same trend (Table 1), with the snapshots illustrating that the bulky dendrons drag the DBA-SH down to the surface and occupy a larger surface area in the monolayer (Figure S2). Thus, the ellipsometric thickness decrease can be rationalized by considering that the increased size of the supramolecular assembly leads to the occupation of a larger surface area per molecule, which in turn induces a decrease in the SAM density. Consequently, the reduced monolayer densification is reflected in lower ellipsometric thickness values. Another trend that can be observed is that the thickness of the DBA-SH:ClPrSH mixed monolayer decreases with the steric bulkiness of the initial supramolecular complex. These results can be regarded as a

![Figure 3. XPS spectra of (a) F (1s), (b) N (1s), (c) S (2p), and (d) Cl (2p) for pure DBA-SH and mixed monolayers formed from DB24C8⊃DBA-SH, [G1]-DB24C8⊃DBA-SH, and [G2]-DB24C8⊃DBA-SH.](image-url)
demonstration of an increased amount of the shortest chain, i.e., ClPrSH, in the DBA-SH:ClPrSH mixed SAM by using supramolecular complexes with increasing bulk.

To investigate whether the presence of excess DB24C8, [G1]-DB24C8, or [G2]-DB24C8 influenced the experimental obtained monolayer thicknesses, freshly plasma-cleaned Au substrates were immersed for 24 h in 20 mM HPLC MeCN solutions of the three molecules. The ellipsometric thicknesses of the DB24C8, [G1]-DB24C8, or [G2]-DB24C8 immersed substrates were determined to be 0.20 ± 0.03 nm, 0.18 ± 0.05 nm, and 0.19 ± 0.04 nm. These thicknesses are similar to those found in freshly cleaned Au substrate (0.25 ± 0.06 nm), suggesting that the DB24C8, [G1]-DB24C8, or [G2]-DB24C8 interact weakly with the gold surface and are readily removed through rinsing with copious amounts of HPLC MeCN.

XPS further confirms the formation of the pure DBA-SH, pure ClPrSH, and complexed and mixed monolayers, showing signals from F (1s), N (1s), and S (2p) on all surfaces (Figure 3). The spectra display N (1s) peaks at 401.4 eV and F (1s), N (1s), and S (2p) peaks at 163.4 eV to the SAM surface. Thus, the F (1s) peaks observed correspond to the thiolate-type sulfur bound to the gold surface.38

The presence of the ClPrSH molecule in the mixed monolayers was demonstrated by the appearance of an additional doublet peak between 202 and 199 eV, which corresponds to Cl (2p) (Figure 3d).39 The Cl (2p1/2) and Cl (2p3/2) doublet peaks is observed at 163.4 eV (S (2p1/2)) and 162.2 eV (S (2p3/2)), which are assignable to the thiolate-type sulfur bound to the gold surface.39

Table 2. Elemental Ratios in the SAMs Formed from Complexed Molecules (complexed) and after Immersion in Mixed Solution of NEt3 and ClPrSH (mixed) Obtained via the XPS Data

<table>
<thead>
<tr>
<th>XPS ratio</th>
<th>DB24C8:DBA-SH</th>
<th>[G1]:DB24C8:DBA-SH</th>
<th>[G2]:DB24C8:DBA-SH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/N</td>
<td>complexed</td>
<td>mixed</td>
<td>complexed</td>
</tr>
<tr>
<td>S/F</td>
<td>0.95 ± 0.05</td>
<td>2.00 ± 0.10</td>
<td>1.10 ± 0.10</td>
</tr>
<tr>
<td>S/N</td>
<td>1.07 ± 0.07</td>
<td>2.03 ± 0.11</td>
<td>1.04 ± 0.11</td>
</tr>
<tr>
<td>S/Cl</td>
<td>2.03 ± 0.13</td>
<td>1.52 ± 0.12</td>
<td>1.25 ± 0.20</td>
</tr>
<tr>
<td>Cl/F</td>
<td>0.98 ± 0.08</td>
<td>2.03 ± 0.19</td>
<td>3.04 ± 0.21</td>
</tr>
<tr>
<td>Cl/N</td>
<td>0.99 ± 0.09</td>
<td>2.01 ± 0.12</td>
<td>3.30 ± 0.18</td>
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</table>

Table 3. Volumes Calculated from vdW Surfaces

<table>
<thead>
<tr>
<th></th>
<th>DB24C8</th>
<th>[G1]:DB24C8</th>
<th>[G2]:DB24C8</th>
</tr>
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<tbody>
<tr>
<td>V (nm3)</td>
<td>0.44</td>
<td>0.88</td>
<td>1.41</td>
</tr>
<tr>
<td>V/V_{vdW}</td>
<td>1</td>
<td>2.0</td>
<td>3.2</td>
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<td>2.0</td>
<td>3.2</td>
</tr>
</tbody>
</table>

and Figure 4). It can be seen that the ratio of the volumes (1:2.0:3.2) correlates well with the corresponding ratio of the DBA-SH and ClPrSH in the mixed monolayer. Our results imply that the surface ratio of two components in mixed SAMs can be well-controlled via careful design of the initial supramolecular complex.

To demonstrate the absence of lateral diffusion of the DBA-SH molecules upon backfilling with ClPrSH on the gold surface and consequent formation of nanoscale phase separated domains, we studied the nanometer-scale mixing characteristics of the formed binary monolayers by voltammetry as previously reported47 using the reductive desorption of the adsorbed thiol molecules. Linear sweep voltammetry was performed with gold on mica as working electrodes that had SAMs formed on them.
The di-ClPrSH SAMs and pure DBA-SH SAMs is ascribed to the desorption of the adsorbed ClPrSH and DBA-SH, respectively. The difference in the Gibbs energy of adsorption of the thiols is 1.085 V (±0.004 V) and −1.146 ± 0.011 V, respectively. Because, following backfilling, the desorption of the DBA-SH:ClPrSH mixed monolayers still displayed a single peak, the results are consistent with the formation of a homogeneous mixed SAM. The formation of the DBA-SH:ClPrSH mixed monolayers from [G1]-DB24C8 and [G2]-DB24C8 (Figure 5d) also did not induce phase separation domains, as revealed by the presence of single cathodic peaks for both mixed SAMs. We observed single cathodic peaks at −1.12 ± 0.034 V and −1.11 ± 0.014 V for SAMs formed of [G1]-DB24C8:DBA-SH and those backfilled with ClPrSH, respectively, whereas the SAMs formed of [G2]-DB24C8:DBA-SH and those backfilled with ClPrSH exhibited single cathodic peaks at −1.128 ± 0.005 V and −1.150 ± 0.041 V, respectively. When a comparison is made between the voltammograms of the different complexed and mixed SAMs and those of pure ClPrSH and DBA-SH, the charge under the desorption peak for the pure SAMs is significantly lower than that of the complexed and mixed SAMs. The desorption charge consists of charge contributions from both faradic processes and capacitance, in which the latter increases for lower packing density in the SAM. The lower charge being passed for pure SAMs can thus be explained by the fact that one-component SAMs (i.e., pure ClPrSH and pure DBA-SH SAMs) allow better packing of the SAM, leading to a smaller contribution of the charging current to the total desorption charge. In summary, the fact that we see one single peak for all the mixed SAMs, with no reductive peak observed at the lower potentials associated with pure ClPrSH, confirms that we have a well-mixed binary monolayer without domains and phase separation.

It is important to highlight that the absence of diffusion, and thus formation of domains, has been ensured by carrying out the backfilling only for 30 min at room temperature while the dendron has been removed. The simultaneous removal of the dendron and backfilling inhibits any desorption or reorganization of the DBA-SH molecule. The results are supported by XPS data, which showed no desorption of the DBA-SH molecule and thus, no exchange takes place with ClPrSH. Furthermore, as previously reported by several groups, surface diffusion of thiols at room temperature is extremely slow, with only a raise in temperature increasing such diffusion. The estimated diffusion coefficients are generally reported around 1 × 10^{-17} to 1 × 10^{-18} cm^2 s^{-1} at elevated temperatures (e.g., 90–100 °C). Furthermore, studies carried out by Lahann and co-workers also support our results because they have shown that low-density SAMs are structurally stable for 4 weeks under a variety of storage conditions: air at room temperature, argon at room temperature and 4 °C, and ethanol at room temperature. Thus, the linear sweep voltammetry studies and previous literature provide supporting evidence for the absence of lateral diffusion and nanometer-scale phase separation on the gold surfaces.
CONCLUSION

In summary, a powerful and effective methodology for tailoring the spacing of chemical functional groups on material surfaces has been demonstrated through utilizing SAMs of pH-switchable pseudorotaxanes, such as DB24C8⊃DBA-SH, [G1]-DB24C8⊃DBA-SH, or [G2]-DB24C8⊃DBA-SH. Following SAM formation with the supramolecular complexes, the DB24C8-based bulky group is released from the surface by switching off the noncovalent interactions upon pH stimulation, exposing a low-density DBA-SH monolayer on which the vacant space is backfilled with a second functional SAM, i.e., ClPrSH. An incremental increase in the size of the bulky group from DB24C8 to [G1]-DB24C8 and then to [G2]-DB24C8 has led to an incremental decrease in the ratio of the DBA-SH:ClPrSH mixed SAM from 1:1 to 1:2 and then to 1:3, as demonstrated by contact angle and XPS analysis. Molecular dynamics simulations also suggest that the volume of the bulky group increases accordingly. This strategy was elegantly designed, and is sufficiently flexible, to be applied to a broad range of nanoparticles and other nanomaterials. Now that the validity of exploiting supramolecular interactions for the design of surfaces with well-defined density and spatial distribution of functional groups has been established, we anticipate that this strategy will play a significant role in the future of functionalized surface materials for wide variety of biological, medical, electronic, and optical applications.

EXPERIMENTAL SECTION

Materials. Commercially available chemicals were purchased from Sigma-Aldrich and solvents from Fisher Scientific or VWR and used as received. Thin-layer chromatography (TLC) was carried out on aluminum plates coated with silica gel 60 F254 (Merck 5554). For the aryl-based compounds the TLC plates were air-dried and analyzed under a short wave UV lamp (254 nm), whereas for the aliphatic compounds the TLC plates were air-dried and developed in a KMnO4 dip. Column chromatographic separations were performed on silica gel 120 (I24C8 Chrom 32–63, 60 Å).

Synthesis of DBA-SH. Compound 1. A slurry of 4-hydroxybenzaldehyde (2.09 g, 17.13 mmol), 11-bromoundecene (4.83 g, 20.72 mmol) and K2CO3 (4.76 g, 34.49 mmol) in acetone (50 mL) was heated under reflux for 16 h. The resultant reaction mixture was allowed to cool to room temperature and K2CO3 was filtered off and the solvent removed in vacuo. The resultant crude solid was dissolved in a minimum amount of DCM and adsorbed onto silica followed by purification by flash column chromatography (gradient elution; 0 to 20% EtOAc in hexane, increase in increments of 10% after each 100 mL of eluent) to yield a white solid (3.83 g, 81%).

1H NMR (300 MHz, CDCl3, Me4Si, 25°C) δ H ppm: 9.86 (s, 1H), 7.81 (d, 2H, J=8.75 Hz), 6.97 (t, 2H, J=8.75 Hz), 5.86−5.72 (m, 1H), 5.01−4.89 (m, 2H), 4.01 (t, 2H, J=6.55 Hz), 2.05−1.98 (m, 2H), 1.84−1.74 (m, 2H), 1.31−1.26 (m, 12H), 297 ([M + Na]+, 100%), m/z (ESMS): found, 297.1828; calcd mass for C18H26O2Na, 297.1831.

Compound 2. 4-Fluorobenzylamine (1.23 g, 9.84 mmol) was added to a solution of 1 (2.70 g, 17.13 mmol) in PhMe (15 mL) and stirred under reflux for 16 h. The resultant reaction mixture was allowed to cool to room temperature and the solvent was removed in vacuo. Thin-layer chromatography (TLC) was carried out on aluminum plates coated with silica gel 60 F254 (Merck 5554). For the aryl-based compounds the TLC plates were air-dried and analyzed under a short wave UV lamp (254 nm), whereas for the aliphatic compounds the TLC plates were air-dried and developed in a KMnO4 dip. Column chromatographic separations were performed on silica gel 120 (I24C8 Chrom 32–63, 60 Å).
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vacuo to a white precipitate. A suspension of NaBH₄ (0.72 g, 19.74 mmol) in MeOH (15 mL) was added dropwise to the white precipitate and the resultant solution was heated under reflux in a N₂(g) atmosphere for 16 h. The reaction mixture was partitioned in 2 M HCl (20 mL) and DCM (20 mL). The aqueous layer was extracted with DCM (2 x 25 mL), dried (MgSO₄), filtered and solvent removed in vacuo. The resultant crude oil was purified by flash column chromatography (elucent: hexane) to yield a colorless oil (3.27 g, 84%). ¹H NMR (300 MHz, CDCl₃, Me₂Si, 25 °C) δ ppm: 7.14 (bs, 4H), 7.02 (t, 2H, J = 7.82 Hz), 6.85 (d, 2H, J = 8.72 Hz), 4.35–4.28 (bm, 4H), 3.96 (t, 2H, J = 6.44 Hz), 2.88 (t, 2H, J = 7.26 Hz), 2.34 (s, 3H), 1.82–1.77 (m, 2H), 1.65–1.50 (m, 2H), 1.15–1.45 (m, 14H). ¹³C NMR (75 MHz, CDCl₃, Me₂Si, 25 °C) δ ppm: 196.0, 163.0, 158.4, 155.9, 133.9, 129.7, 115.4, 115.2, 114.5, 81.0, 67.8, 60.4, 48.4, 30.6, 29.5, 29.4, 29.3, 28.8, 28.5, 26.1. m/z (ESMS): 582 ([M⁺]+, 100%). m/z (HRMS): found, 582.3042; calcld mass for C₂₅H₂₆NO₂SF, 582.2939.

Compound 4. A solution of TFA (8 mL) in DCM (20 mL) was added dropwise at 0 °C under a N₂(g) atmosphere to a solution of compound 2 (1.90 g, 4.95 mmol), NEt₃ (1.00 g, 9.90 mmol), and 4-DMAP (catalytic amount) in THF (15 mL) and further stirred for 16 h at room temperature under a N₂(g) atmosphere. The reaction mixture was quenched with H₂O (20 mL) and the aqueous solution was filtered and concentrated in vacuo. The resultant crude solid was dissolved in THF (25 mL). The combined organic layers were washed with 0.1 M HCl, whereupon a white precipitate was formed that was collected by suction filtration (1.07 g, 80%). ¹H NMR (300 MHz, CDCl₃, Me₂Si, 25 °C) δ ppm: 7.72 (dd, 2H, J = 1.98 Hz, 7.57), 6.12–6.10 (m, 8H), 3.87–3.79 (m, 14H), 3.50–3.44 (m, 2H), 2.60–2.56 (m, 2H). m/z (ESMS): 491 ([M⁺]+, 100%). m/z (HRMS): found, 491.1913; calcld mass for C₂₃H₂₄NO₃S, 491.1917.

DBA-Sh. To a solution of compound 6 (0.59 g, 1.30 mmol) in DCM (20 mL) was added hexafluorphosphoric acid (60% in water, 0.20 mL, 1.45 mmol) dropwise at 0 °C under a N₂ atmosphere. The resultant reaction mixture was stirred for a further 10 min at room temperature. After 10 min, H₂O (20 mL) was added and the aqueous layer was extracted with DCM (2 x 20 mL). The combined organic layers were dried (MgSO₄), filtered and the solvent removed in vacuo. The resultant crude solid was purified by flash column chromatography (gradient elution; from 0 to 10% EtoAc in hexane, increase in increments of 5% per 100 mL of eluent) and the solvent was removed to yield a white solid (0.68 g, 91%). ¹H NMR (300 MHz, CDCl₃, Me₂Si, 25 °C) δ ppm: 2.77 (dd, 2H, J = 1.98 Hz, 7.57), 6.52–6.48 (m, 8H), 3.87–3.79 (m, 14H), 3.50–3.44 (m, 2H), 2.60–2.56 (m, 2H). m/z (ESMS): 491 ([M⁺]+, 100%). m/z (HRMS): found, 491.2589; calcld mass for C₂₃H₂₄NO₃S, 491.2580.

Synthesis of [G1]DB24C8 and [G2]DB24C8. Compound 8. A solution of NaOH (0.22 g, 5.50 mmol) in H₂O (1 mL) was added to a solution of compound 7 (1.44 g, 2.77 mmol) in EtOH (10 mL) and the resultant reaction mixture was heated under reflux for 16 h. The reaction mixture was allowed to cool to room temperature and concentrated in vacuo and acidified with 0.1 M HCl, whereupon a white precipitate was formed that was collected by suction filtration (1.07 g, 80%). ¹H NMR (300 MHz, CDCl₃, Me₂Si, 25 °C) δ ppm: 7.72 (dd, 2H, J = 1.98 Hz, 7.57), 6.52–6.48 (m, 8H), 3.87–3.79 (m, 14H), 3.50–3.44 (m, 2H), 2.60–2.56 (m, 2H). m/z (ESMS): 491 ([M⁺]+, 100%). m/z (HRMS): found, 491.1913; calcld mass for C₂₃H₂₄NO₃S, 491.1917.

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MeSi, 25 °C δC ppm: 190.0, 166.1, 160.2, 153.1, 151.1, 148.9, 148.3, 138.5, 133.7, 127.6, 125.6, 124.1, 122.8, 114.5, 114.1, 112.0, 106.9, 101.5, 71.5, 71.4, 71.3, 70.0, 69.8, 69.6, 69.4, 66.4, 31.3. m/z (ESMS): 929 ([M+] 100%); m/z (HRMS): found, 929.4502; calcld mass for C54H66O12, 929.4452.

[G2]/DB24C8. According to the synthetic procedure described for [G1]/DB24C8 compound B (0.25 g, 0.51 mmol), (G2)2 (0.54 g, 0.55 mmol), DCC, (0.05 g, 0.66 mmol), and DMAP (catalytic amount) were reacted in DCM (35 mL) and purified by flash column chromatography (graded elution: 0 to 10% EtOAc in hexane, increments of 5% per 150 mL of eluent used) to afford white crystals (0.33 g, 54% yield). 1H NMR (300 MHz, CDCl3, Me4Si, 25 °C) δH ppm: 7.66 (dd, 1H, J = 1.90, 9.00 Hz), 7.53 (d, 1H, J = 1.90 Hz), 7.38 (d, 8H, J = 8.54 Hz), 7.34 (d, 8H, J = 8.05 Hz), 6.87–6.91 (m, 1H, SH), 6.66 (s, 4H), 6.58 (s, 2H), 5.25 (s, 2H), 4.95 (s, 8H), 3.81 (d, 8H, J = 7.66 Hz), 3.30 (d, 8H, J = 7.60 Hz), 3.13 (s, 16H). 13C NMR (75 MHz, CDCl3, MeSi, 25 °C) δC ppm: 190.0, 166.1, 160.2, 153.1, 151.1, 148.9, 148.3, 138.5, 133.7, 127.6, 124.1, 122.8, 114.5, 114.1, 112.0, 106.9, 101.5, 71.5, 71.4, 71.3, 70.0, 69.8, 69.6, 66.4, 31.3. m/z (ESMS): 1465 ([M + Na]+, 100%); m/z (HRMS): found, 1465.7309; calcld mass for C74H90NaO12, 1465.7379.

Compound Characterization. NMR. 1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVIII300 (300.13 MHz) spectrometer. 13C NMR spectra were recorded on a Bruker AVIII 400 (75.5 MHz) using Pendent pulse sequences. All chemical shifts are quoted in ppm to higher frequency from MeSi using either deuterated chloroform (CDCl3) or methanol (CD3OD) as the lock and the residual solvent as the internal standard. The coupling constants were expressed in hertz (Hz) with multiplicities abbreviated as follows: s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, and m = multiplet.

Mass spectrometry (MS). Electron impact mass spectroscopy (EI-MS) was performed on a VG Prospec. Low- and high-resolution electrospray mass spectrometry was performed on a Micromass time-of-flight (TOF) instrument using methanol as the mobile phase. The electrolyte was a 0.5 M KOH solution prepared fresh each day. Formaldehyde was added at a concentration of 200 mM to the electrolyte.

Contact Angle Measurements. Dynamic contact angles were determined using a home-built contact angle apparatus, equipped with a charged coupled device (CCD) KP-MIE/K camera (Hitachi) that was attached to a personal computer for video capture. QWin Video Analysis software v1.96 (First Ten Angstroms) was used for the analysis of the contact angle of a droplet collected using a micropipette. The contact angle was determined from an Equation 2 formulated in terms of the angle of incidence (θ2) and the dynamic contact angle (θd).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial support of this work by the Leverhulme Trust (F/00094/AW, F/00094/BD and ECF/2013-603), Royal Society (2009/R3), Wellcome Trust (WT091285MA), EPSRC (EP/K027263/1), the European Commission under the FP7-NMP project Hysens (263091), the Research Grants Council of Hong Kong (201412), and the University Grants Committee of Hong Kong SAR (AoE/P-03/08). Also, we acknowledge the University of Leeds EPSRC Nanoscience and Nanotechnology Facility (LENNF) for access to the XPS. This research was in part supported through Birmingham Science City: Innovative Uses for Advanced Nanoscience.
Materials in the Modern World (West Midlands Centre for Advanced Materials Project 2), supported by Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF). This work was also supported by the National Basic Research Program (2011CB808604) and the National Natural Science Foundation of China (21273102). We are grateful to the High Performance Computing Centre of Nanjing University for providing the IBM Blade cluster system.

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