Simple estimation of van der Waals (vdW) forces experienced by tricosanol molecules near the substrates, in acetone. A lattice of 0.3 nm mesh size and 150 X 150 cells was created. The first 5 lower rows correspond to the 1.5 nm of native silicon oxide; the next few rows were attributed to the silanes of the background and of the nano-features. The rest of the lattice is filled by background acetone molecules. The vdW interaction energy experienced by a segment of a tricosanol molecule at a specific location of the lattice (i,j) was computed as:

\[ E_{vdW}(i,j) = \sum_{k,l} \frac{C_{k,l}}{r_{ij/kl}^6} \]  

[Eq. (1)]

where the summation is performed over the whole lattice, \( r_{ij/kl} \) is the distance between cells (i,j) and (k,l), and \( C_{k,l} \) is a constant depending on the nature of the material in cell (k,l) and on the cell size. The \( C_{k,l} \)'s were computed according to the simplified Lifshitz theory of van der Waals forces in a medium,\(^1\)\(^2\) using as parameters the constants of Table 1. We found \( C_{k,l} = 3.21 \times 10^{-78} \text{ J.m}^6 \) for the interaction between two cells containing alkyl groups in acetone, \(-1.59 \times 10^{-78} \text{ J.m}^6 \) between a cell containing perfluoroalkyl groups and a cell containing alkyl groups in acetone, and \(4.58 \times 10^{-78} \text{ J.m}^6 \) between a cell containing \( \text{SiO}_2 \) and a cell containing alkyl groups in acetone. \( C \) was set to zero for cells containing acetone, and the tricosanol molecule was approximated as a pure alkane chain, a reasonable approximation given the purpose of the simulations.

The influence of the Si substrate was obtained by adding to \( E_{vdW}(i,j) \) the following term:\(^1\)\(^2\)

\[ E_{\text{Si/acetone/alkane}} = - \frac{C_{\text{Si/acetone/alkane}}}{r^3} \]  

[Eq. (2)]
where $C_{\text{Si/acetone/alkane}} (1.04\times10^{-50} \text{ J.m}^3)$ is the constant describing the attractive interaction through acetone between a cell containing alkyl groups and the semi-infinite Si substrate, and $r$ is the distance from the cell to the substrate. This constant was obtained from the published values of the Hamaker constant of Silicon in a vacuum ($\sim2.4\times10^{-19} \text{ J}$),$^{[3,4]}$ and from the values of Hamaker constants of acetone and alkanes computed as outlined above, using standard combination rules.$^{[3]}$ Finally, the van der Waals forces were obtained as the opposite of the gradient of the so-computed vdW energy.$^{[5,6]}$

Table 1. Dielectric permittivity ($\varepsilon$), refractive index (n), and main absorption frequency in the UV ($\nu_e$), used to compute the van der Waals forces experienced between different groups through acetone. The last column provides references to the literature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon$</th>
<th>n</th>
<th>$\nu_e (10^{15} \text{ Hz})$</th>
<th>references</th>
</tr>
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<tbody>
<tr>
<td>alkane</td>
<td>2</td>
<td>1.41</td>
<td>2.9</td>
<td>[1]</td>
</tr>
<tr>
<td>perfluoroalkane</td>
<td>2.1</td>
<td>1.26-1.3</td>
<td>2.9-4.1$^{(a)}$</td>
<td>[1]</td>
</tr>
<tr>
<td>acetone</td>
<td>21</td>
<td>1.36</td>
<td>2.9</td>
<td>[1,2]</td>
</tr>
<tr>
<td>amorphous SiO$_2$</td>
<td>3.82</td>
<td>1.45</td>
<td>3.2</td>
<td>[5,6]</td>
</tr>
</tbody>
</table>

(a) Value reported for poly(tetra-fluoro-ethylene).


