Self-Assembled Arrays of Peptide Nanotubes by Vapor Deposition Method

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Supplementary information

HPLC based structure elucidation of ADNT array composition

High performance liquid chromatography (HPLC) was used to elucidate the structure of the molecule that forms the order structures. The results indicate that the vapor deposition product consists from one main component, namely Cyclo-Phe-Phe peptide (80%) and the rest is the starting material H-Phe-Phe-OH peptide (20%). Both compounds were identified through comparison of their retention times and UV spectra with those of the known commercial reference standards (9.83 minutes for the starting material H-Phe-Phe-OH peptide and 22.48 minutes for the final material Cyclo-Phe-Phe peptide respectively). Peak purity was confirmed by data from a diode array detector (DAD). The retention times of the starting compound H-Phe-Phe-OH peptide and the resulting Cyclo-Phe-Phe peptide were almost identical to the retention times of the known reference compounds in the cross injections. Furthermore, a comparative study was carried out with the vapor deposited sample and the diastereomers H-(L)Phe-(D)Phe-OH peptide and H-(D)Phe-(L)Phe-OH peptide. No peak corresponding to H-(L)Phe-(D)Phe-OH or H-(D)Phe-(L)Phe-OH was obtained in the chromatogram.

Surface morphology influence on wettability of peptide arrays

The surface morphology can play an important role in the preparation of a superhydrophobic or a highly-hydrophobic surface, as in ADNT surface. The Wenzel model was used to describe the roughness effect in this case. Surfaces which behave according to Wenzel's model exhibit a high contact angle hysteresis, as with the
ADNT array (contact angle hysteresis of ~40º). In the Wenzel model the contact angle is dependent on the roughness in the following manner:

\[
\cos(\theta_A) = r \cos(\theta_Y)
\]

Where \(\theta_A\) is the apparent contact angle, \(r\) is the ratio of the total surface area to the projected surface area and \(\theta_Y\) is the Young's intrinsic contact angle. In order to investigate the roughness affect on our wettability measurements, the surface roughness was calculated by analysis of SEM images, and the intrinsic contact angle was found according to Wenzel’s model.

<table>
<thead>
<tr>
<th>Peptide sequence</th>
<th>(\theta_A)</th>
<th>Roughness Wenzel model</th>
<th>(\theta_Y) Wenzel model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylalanine</td>
<td>104.5º</td>
<td>1.043</td>
<td>105.3º</td>
</tr>
<tr>
<td>Di-phenylalanine</td>
<td>122.5º</td>
<td>1.015</td>
<td>122.2º</td>
</tr>
<tr>
<td>Tetra-phenylalanine</td>
<td>131.3º</td>
<td>1.021</td>
<td>130.2º</td>
</tr>
<tr>
<td>Penta-phenylalanine</td>
<td>139.6º</td>
<td>1.025</td>
<td>137.6º</td>
</tr>
</tbody>
</table>

Table S1

Table S1 shows that the surface morphology of the various peptide nanostructures surfaces are not significantly different. Additionally, the intrinsic contact angles are very similar and are in fact within the error bars in Fig. 3c. Thus, the increase in contact angle is the result of the difference in the physico-chemical structure of the phenylalanine peptides².
**Figure legend**

**Fig S1**: Top view SEM image of the vapor deposited peptide nanotubes indicates their hollow cavities.

**Fig S2**: The ToF-SIMS positive ion spectrum of the vertically aligned peptide nanotubes shows a peak of 295 M/Z corresponds to singularly charged ion MH⁺ of cyclo-Phe-Phe peptide.

**Fig S3**: Scanning electron microscopy image of the ADNT after the vapor deposition of H-(D)Phe-(D)Phe-OH peptide at an angle of 50 degrees. Scale bar=20 µm.

**Fig S4**: (a) XRD and azimuthally averaged grazing incidence WAXD patterns of an ADNT array deposited from the vapor phase on a glass surface. (b) Two-dimensional grazing incidence WAXD pattern. The numbers 1-6 denote the corresponding peaks in the WAXD pattern in (a). The meridional doublet (#4) and the near meridional peaks (#5) clearly demonstrate preferred orientation of constituent crystallites in the nanotubes.

**Fig S5**: Vapor deposition of mono- tri- tetra- and penta-phenylalanine. SEM images of (a) phenylalanine (b) tri-phenylalanine (c) tetraphenylalanine and (d) pentaphenylalanine.

**Table legend**

**Table S1**: Apparent and intrinsic contact angles according to Wenzel model.

*Decimal point is due to statistical averaging
Fig. S2
Fig. S3
Fig. S4
Fig. S5
References
