Unusual two-dimensional multicomponent self-assembly probed by scanning tunneling microscopy

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A. Synthesis

Oligomer 1, decorated with two urea functionalities to promote intermolecular hydrogen bonding, was synthesized as depicted in Scheme 1. First, urea derivative 2 was isolated in quantitative yield by reaction of dodecyl isocyanate and 2-(4-bromophenyl)ethylamine (CH$_2$Cl$_2$, 99% yield). Subsequently, 5,5′-bisstannylated bis-EDOT (3) was prepared by a standard distannylation procedure from bis-EDOT (n-BuLi, Me$_3$SnCl, THF, 74% yield). Finally, a Pd-catalyzed double Stille coupling between compounds 2 and 3 gave the desired oligomer 1 in moderate yield (Pd(PPh$_3$)$_2$Cl$_2$, DMF, 42% yield) as was evidenced by NMR and mass spectroscopy.

Scheme 1: Synthesis of 1.
B. A three-component co-adsorbed mixture...

This point illustrates the significance of hydrogen bonding in the monolayer formation of urea derivatives. The part of the monolayer shown in Figure Suppl1 consists of two \( \text{2}\) lamellae in the lower left corner, of which the carbonyl groups point to the upper right direction, four \( \text{2}\) lamellae (upper part) of which the carbonyl groups point to the lower right direction (notice the change in contrast of the urea groups), and an \( \text{1}\) lamella. In addition, towards the lower right corner, a defect area is indicated. When lamella-type \( \text{1}\) codeposits are formed, defect areas can be formed such as indicated in Figure Suppl1 due to the difference between the \( \text{1}\) lamella width and the \( \text{2}\) lamella width. The formation of this defect area is to a great extent caused by the continued hydrogen bonding in \( \text{2}\) lamellae adjacent to the \( \text{1}\) lamella. Due to geometrical constraints of this particular defect formed, a double layer of solvent molecules (1-octanol) is also co-adsorbed. Note that under the experimental conditions used, 1-octanol by itself does normally not form stable two-dimensional adlayers. However, the defect in the monolayer provides a corral of the right size to immobilise the 1-octanol molecules.
Figure Suppl: STM image of a \( \frac{1}{2} \) mixed monolayer adsorbed at the 1-octanol/graphite interface. Image size: 18 x 18 nm\(^2\). \( I_i = 0.8 \) nA. \( V_i = -0.31 \) V. A monolayer defect is indicated (dashed lines), containing a double row of 1-octanol molecules.