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Song, W., Martsinovich, N., Heckl, W.M. et al. (1 more author) (2014) Thermodynamics of 4,4 '-stilbenedicarboxylic acid monolayer self-assembly at the nonanoic acid-graphite interface. Physical Chemistry Chemical Physics, 16 (26). 13239 - 13247. ISSN 1463-9076

https://doi.org/10.1039/c4cp01147c

Supporting Information:

Thermodynamics of 4,4’-stilbenedicarboxylic acid monolayer self-assembly at the nonanoic acid-graphite interface

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1. STM Split image.

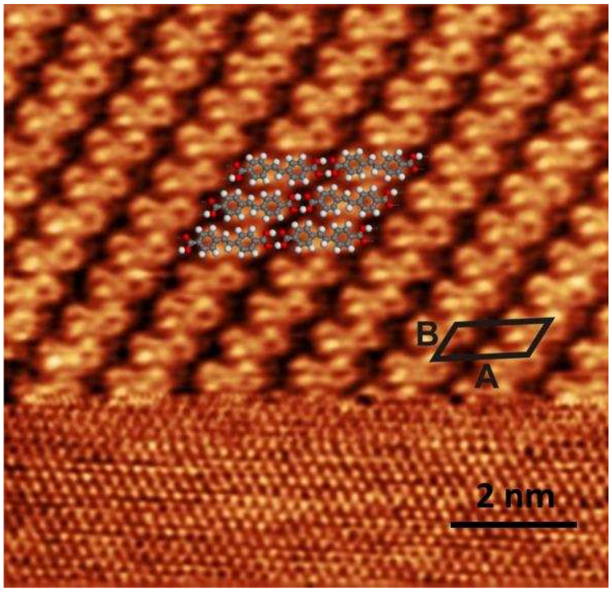

Figure S1. STM split-image of a SDA monolayer at the nonanoic acid-graphite interface. In the lower part the graphite substrate was imaged with atomic resolution by decreasing the tunneling gap. Calibration with this internal standard yields precise lattice parameters for the SDA monolayer of *A*= (16.1 ± 0.1) Å, *B*= (7.5 ±0.1) Å, γ =52° ± 1°. The overlay indicates the arrangement of SDA molecules and the black lines mark the unit cell. (Image size 16.2×15.6 nm², I=50 pA, V_{sample}= -300.0 mV for SDA; I=200 pA, V_{sample}= -1.53 mV for graphite)

Precise lattice parameters of SDA monolayers were obtained from several so called split-images where within the same frame both the adsorbate structure and the graphite lattice were imaged, an example is depicted in Figure S1. Based on the adsorbate lattice parameters and the orientation of the unit cell with respect to the graphite lattice, the closest commensurate superstructure corresponds to the following matrix (referring to the graphite lattice):

$$\begin{pmatrix} 6 & 1 \\ 0 & 3 \end{pmatrix}$$

The match between experimental lattice parameters from STM images (A = (16.1±0.1) Å, B = (7.5±0.1) Å, γ = 52°±1°) and those of the postulated commensurate lattice (A = 16.13 Å, B= 7.38 Å, γ = 52.4°) is excellent.

2. Entropy estimation

Similar to our previous study on terephthalic acid (TPA),[1] the entropy change of self-assembly is estimated by using an approach proposed by Whitesides et al.,[2] where ΔS is partitioned into translational, rotational, vibrational, and conformational entropy. SDA can in principle adopt both trans and cis conformations. Since the cis conformation is rather high in energy, this conformational freedom is neglected in the entropy estimation. Vibrational entropy does not change significantly upon self-assembly and is also disregarded.

Rotational and translational entropy are both assumed to be 0 for molecules in the self-assembled monolayer. Accordingly, the change of rotational entropy is given by $\Delta S_{rot} = S_{rot(adsorbed)} - S_{rot(free)} = 0 - S_{rot(free)} = - S_{rot(free)}$, where $S_{rot(free)}$ corresponds to the rotational entropy of the molecule or complex in solution. Similarly, the change of translational entropy is given by $\Delta S_{trans} = S_{trans(adsorbed)} - S_{trans(free)} = 0 - S_{trans(free)} = - S_{trans(free)}$, where $S_{trans(free)}$ corresponds to the translational entropy of the molecule or complex in solution.

The total entropy change upon adsorption is then given by the sum of rotational and translational entropy of the molecule or complex in solution: $-(S_{rot(free)} + S_{trans(free)})$.

Translational entropies were estimated using the Sackur-Tetrode equation:

$$S_{trans(free)} = -R\ln\left[\frac{1}{c}\left(\frac{2\pi m k_B T e^{5/3}}{h^2}\right)^{3/2}\right] \qquad (1)$$

Here R is the gas constant, c the solute concentration, T the temperature, k_B the Boltzmann constant, h Planck's constant, e Euler's number, and m the mass of the molecule or complex. Since it is well known that in solutions actual concentrations overestimate $S_{trans(free)}$, free volume corrections were used. The free volume of 9A was estimated with the hard cube approximation, assuming that the solution consists of 9A dimers. Accordingly, a mass density of 9A of 0.906 g cm^{-3} and a van der Waals Volume of 346.9 $Å^3$ for 9A dimers yield a free volume of 31.3 mL per liter 9A. For the evaluation of translational entropies, all concentrations were referred to this free volume, leading to an apparent concentration enhancement by a factor of ~32. Translational entropies of SDA and 9A-SDA-9A complexes were evaluated using the experimentally determined critical concentration of 4.1 µmol L^{-1}. For 9A-9A dimers a concentration of 2.86 mol L^{-1} was used, i.e. half of the concentration of 9A in 9A.

Rotational entropies were estimated using the rigid rotor model:

$$S_{rot(free)} = -R\ln\left[\frac{\pi^{1/2}}{\gamma}\left(\frac{8\pi^2 k_B T e}{h^2}\right)^{3/2}(I_1 I_2 I_3)^{1/2}\right] \qquad (2)$$

I_1, I_2, and I_3 are the principal moments of inertia. γ is determined by the symmetry and was assumed 2 for all molecules and complexes considered, i.e. implying two-fold rotational symmetry. However, since rotational symmetry just reduces rotational entropy by $-Rln(\gamma)$, assuming asymmetric complexes (γ=1) would not notably affect the rotational entropy change. For evaluation of the principal moments of inertia molecular mechanics optimized geometries of the corresponding molecules and complexes were used.

As already stated in the manuscript, SDA molecules are solvated in solution and most likely form hydrogen bonded 9A-SDA-9A complexes. Thus adsorption of SDA is associated with dissociation of 9A-SD-9A complexes and recombination of the two released 9A solvent molecules into 9A-9A dimers.

$$\text{9A-SDA-9A}_{sol} \rightarrow \text{SDA}_{ads} + \text{9A-9A}_{sol} \qquad (3)$$

Consequently, the total entropy change of SDA monolayer self-assembly □S_{tot} is comprised of the loss of both translational and rotational entropy of the 9A-SDA-9A complex, the regain of both translational and rotational entropy of the newly formed

9A-9A dimer, and the dewetting entropy associated with the release of solvent molecules from the previously adsorbed solvent monolayer:

$$\Delta S_{tot} = \Delta S_{trans}(9A\text{-}SDA\text{-}9A) + \Delta S_{rot}(9A\text{-}SDA\text{-}9A) - \Delta S_{trans}(9A\text{-}9A) - \Delta S_{rot}(9A\text{-}9A) + \Delta S_{dewet} \qquad (4)$$

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