Dynamic effects in friction and adhesion through cooperative rupture and formation of supramolecular bonds

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Isothermal titration calorimetry (ITC) of ditopic connector 3

1.00 mL of a 1.23 mM solution of β-CD in water at pH 6.40 was titrated with 25 injections of 10 µL each of a 8.545 mM solution of ditopic connector 3. The observed heat signals shown below were corrected with the corresponding heats of dilution of compound 3 were fitted with the program Launch NanoAnalyze version 3.1.2 for 1 independent binding site (Fig.1). The stoichiometry ratio \( n \approx 0.5 \) is due to the ditopic binding valency of 3.

![Graph showing corrected heat rate and normalized fitted values](image)

Fig.1: Heat changes for calorimetric titrations of 3 to a β-CD solution (top), normalized measured heats of injections and best-fit values (bottom).
Connector concentration dependence of the friction and adhesion force

In order to investigate how the connector molecule concentration influences friction and adhesion, force measurements with varying connector concentration were performed (Fig.2). For low concentrations a monotonous increase up to a concentration of about 3 µM with a subsequent saturation regime are observed. From the Langmuir fit we can determine a binding constant of $K_{\text{friction}} = (1.6 \pm 0.5) \times 10^6$ 1/M for the friction force which is in good agreement with the Langmuir binding constant in adhesion $K_{\text{adhesion}} = (1.0 \pm 0.28) \times 10^6$ 1/M. The binding constants obtained for the β-CD SAMs are about two orders of magnitude higher than the binding constant obtained in solution from ITC measurements. The higher binding constant at surfaces in comparison to the binding in solution has been described before for monotopic guests (Mulder, J. Am. Chem. Soc. 2004, 6627–6636) and can be explained by the higher concentration of guests at the surface and hosts in the confinement. For all AFM experiments in our study, a connector molecule concentration of 10 µM was chosen in order to work in the saturation regime of the Langmuir curve.

![Graphs showing mean adhesion and friction force as a function of connector molecule concentration.](image)

*Fig.2: Mean adhesion (left) and friction (right) force as a function of connector molecule concentration recorded with a pulling velocity of 250 nN/s and a sliding velocity of 100 nm/s, the solid line represents a Langmuir fit to the data.*