

Supporting Information

Resolving Non-Specific and Specific Adhesive Interactions of Catechols at Solid/Liquid Interfaces at the Molecular Scale

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Supporting Information

1) Experimental section

Chemicals and Materials. All chemicals used are of highest grade and were used without further purification (Supplier: Sigma Aldrich). Milli-Q water is used to prepare electrolyte solutions (Merck Millipore purification system) with a resistance of 18.2 M Ω cm and a TOC content of 2 ppb. The thiols 11-Mercapto-1-undecanol (OH-SAM), 11-Amino-1-undecanethiol hydrochloride (NH₂-SAM), 16-Mercaptohexadecanoic acid (COOH-SAM) and 1-Undecanethiol (alkyl-SAM) of highest available purity are obtained from Sigma Aldrich. Titanium pellets for physical vapor deposition are obtained from Goodfellow.

Surface preparation and characterization. Molecularly smooth gold surfaces are prepared by template stripping from Mica.[1] Surface modification is carried out following a recently established protocol.[2] First the freshly stripped surfaces are immersed into an ethanolic solution of a 1/500 mixture of COOH- and OH-thiol. After at least 12 hours of exposure the surfaces are taken out and washed with ethanol, hexane, again ethanol and dried in an N₂ stream. Further modification is carried by covalently binding ethylenediamine to the SAM's free COOH groups. Therefore, the surfaces are immersed into PBS buffer solution containing ethylenediamine, N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and N-Hydroxysuccinimide (NHS) for at least two hours. This reaction step is then repeated with a PBS solution containing O,O'-Bis(2-carboxyethyl)dodecaethylene glycol (HOOC-PEG-COOH), EDC and NHS and a PBS solution containing Dopamine hydrochloride (Dopa), EDC and NHS. After each step the surfaces are washed intensively with PBS solution, water and ethanol and dried in an N₂ stream. The modification protocol results in a polymeric chain with a contour length of 6.7 nm (**Figure 1**). XPS and AFM characterization of the first three reaction steps (SAM, ethylenediamine and HOOC-PEG-COOH) are available elsewhere.[2] XPS characterization of the final reaction step (Dopa) is available below (**Figure S1**). After surface modification and washing the surfaces are immediately mounted into a home-built AFM fluid cell and force spectroscopy is performed. Control experiments to exclude interactions of the polymer backbone with the AFM tip are performed without the final reaction step and no characteristic single-molecular event is visible.

AFM tip preparation and characterization. For all experiments rectangular gold-coated cantilevers are used (CONTGB-G, BudgetSensors). Each tip is cleaned with 95 – 98% concentrated sulfuric acid, two batches of water and ethanol for 60 seconds respectively and dried in an N₂ stream. In case no further surface modification is carried out the tips are mounted immediately into the AFM setup and the experiment is performed. Tip modification with thiols (OH-SAM, NH₂-SAM, COOH-SAM or alkyl-SAM) is carried out by immersing the tip for at least 12 hours into a freshly prepared 1 mM ethanolic solution of the corresponding thiol. After thiol exposure all tips are cleaned with ethanol, hexane, again ethanol, dried in an N₂-stream and immediately mounted into the AFM. For AFM tips coated

with amine-terminated thiols the tip is additionally cleaned in 5mM NaCl at pH 9, followed by rinsing with pure water and ethanol. Coating of the AFM tips with Titania is carried out using physical vapor deposition (PVD). After cleaning the tips are mounted into a PVD and coated with a Ti-layer of 9 nm nominal thickness. To ensure Titania formation the tips were annealed at 100 °C for 60 minutes in pure oxygen atmosphere. Before performing experiments each tip is cleaned again intensively using water and ethanol and dried in an N₂ stream. Presence of Titania on the AFM tip is confirmed using XPS (See **Figure S2**).

AFM Force spectroscopy and data analysis. All experiments are performed under ambient electrolyte conditions using a Nano-wizard (JPK Instruments, Germany). As electrolyte 5 mM NaCl solution with an adjusted pH of 4.2 or 9.0 is used, respectively. The AFM cantilever's sensitivity is extracted from the linear regime of at least seven approach curves. The cantilevers spring constant is estimated using the thermal noise method.[3] Typical spring constants vary between 250 and 500 pN/nm with a sensitivity from 65 to 100 nm/V. Sensitivity and spring constant values are used to convert the raw cantilever deflection versus tip-sample separation into force-distance profiles. The closest approach was set to $D = 0$. Force runs are recorded at constant speed in a square grid pattern with 10 x 10 points separated by 10 nm. At each point 10 force curves are recorded. The maximum force applied during approach is set to 1 nN to ensure tip/surface contact and pick up single molecules. Experiments for all surface/tip combinations used are carried out at various pulling speeds ranging from 0.06 - 2 $\mu\text{m/s}$. All data are recorded and processed using JPK data processing software. All measured force profiles showing single-molecular pulling (2-5%) are collected and aligned to the WLC-model (Inset of **Figure 2A**).

2) XPS characterization of modified gold surfaces and modified AFM tips

All data were recorded using the high power mode of *Quanterra 2* (Physical Electronics). Here, x-ray damage is reduced by generating the photoelectrons by continuously scanning a $100 \times 1000 \mu\text{m}^2$ sized area (100 W). All data were recorded with a pass energy of 55 eV and a spectral resolution of 0.05 eV. In order to obtain a good signal to noise ratio 3 sweeps for the Au 4f signal and 10-30 sweeps for all other signals were used. The gold peak at 84 eV was used for calibration of all spectra shown in **Figure S1**.

The C 1s spectrum of the fully functionalized surface indicates that more than one carbon species is present (**Figure S1a**). The peak at 284.8 eV is correlated to the aliphatic carbon atoms of the SAM. The peak at 285.7 eV is related to the aliphatic CH₂ groups next to OH groups or ether groups. The peak at 287.0 eV correlates to CH₂ groups in neighborhood to C=O groups and the peak at 288.3 eV is related to the carbonyl carbon atom. The ratio between carbonyl carbon and nitrogen signal at 400 eV (**Figure S1b**) is as expected 1:1.1 (expected ratio: 1:1), because each carbonyl is connected to a nitrogen. The S 2p spectrum (**Figure S1c**) is fitted by two Gaussians in a ratio of 1:2. The signal at 162.2 eV is typical for thiol bond to gold. The absence of other sulfur species is an indication for good SAM quality.

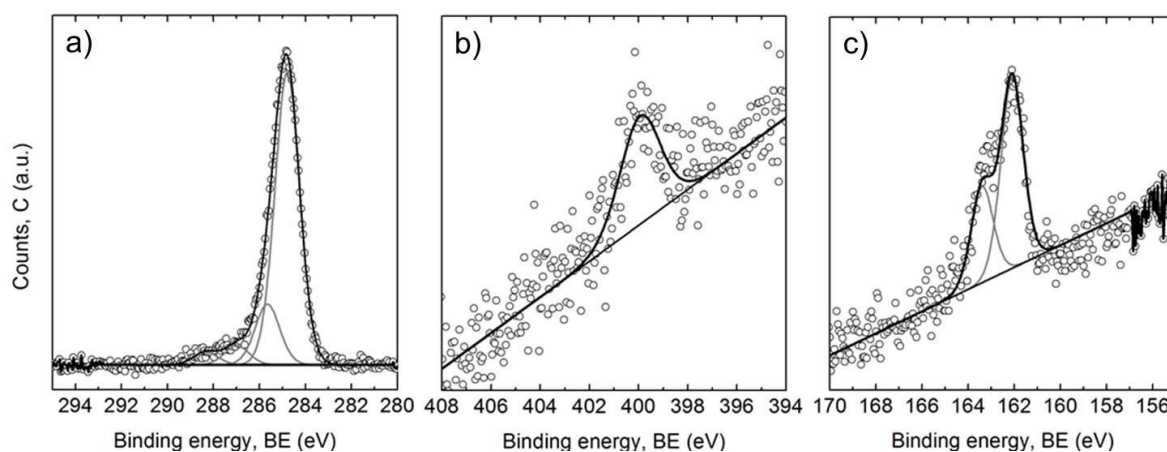


Figure S1: a) C 1s spectrum, b) N 1s spectrum and c) S 2p spectrum of the DOPA functionalized surface.

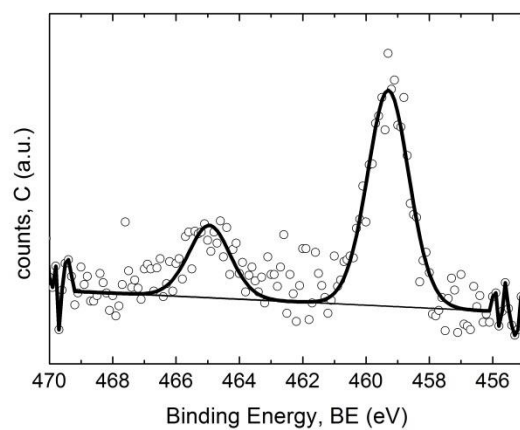


Figure S2: Ti 2p spectrum of a Ti coated AFM cantilever indicating successful Titania modification of AFM tips. The spectrum was acquired on an AFM chip. Acquisition of an XPS-signal arising just from the tip itself is not possible.

3) DLVO fit equation and parameters

AFM approach curves can be fit using the following model, consisting of a superposition of Van-der-Waals and electric double forces (See **Figure 2** in main text):

$$\frac{F(D)}{2\pi R} = \frac{-A_H}{6D^2} + \frac{\varepsilon\varepsilon_0}{\lambda_D} [2\psi_A\psi_B e^{-D/\lambda_D} + (\psi_A^2 + \psi_B^2)e^{-2D/\lambda_D}]$$

With R being the effective tip radius of the AFM-probe, A_H the Hamaker-constant, ε the relative permittivity, ε_0 the vacuum permittivity, ψ_A and ψ_B the surface potential of the AFM tip (NH₂-SAM in the case of Figure2) and functionalized gold surface and λ_D the Debye-length. **Table S1** shows a complete set of suitable parameters to fit AFM approach curves in 5 mM NaCl.

Table S1:

parameter	value
A_H	$4.5 \cdot 10^{-21}$ J
R	$1.5 \cdot 10^{-8}$ m
λ_D	$4.3 \cdot 10^{-9}$ m
ψ_A	0.035 V
ψ_B	-0.0035V

We would like to note that quantitative interpretation of parameters shown in **Table S1** should be carried out with care (Particularly because the AFM-tip radius is unknown). However the main purpose of fitting DLVO theory is to demonstrate that primary adhesion as visible in **Figure 2A** can be explained by Van-der-Waals and electric double layer forces which act at a much different range than the observed single-molecular rupture forces which are the primary outcome of our measurements. Application of DLVO theory to small tip radii and AFM contact geometries is generally possible using geometrical correction factors.[4]

4) Worm-like-chain fit equation and parameters

The following WLC equation has been used to describe mechanics of single-molecular stretching:[5, 6]

$$\frac{FL_P}{k_B T} = \frac{1}{4} \left(1 - \frac{x}{L_C}\right)^{-2} - \frac{1}{4} + \frac{x}{L_C}$$

With F being the applied force, x the molecular extension, L_P the polymer's persistence length, k_B the Boltzmann constant, T the absolute temperature and L_C the polymer's contour length. **Table S2** shows the set of used model parameters for all fits.

Table S2:

parameter	value
k_B	$1.381 \cdot 10^{-23}$ J/K
T	298 K
L_C	$6.7 \cdot 10^{-9}$ m
L_P	$3.5 \cdot 10^{-10}$ m

5) Collected single molecule interaction curves

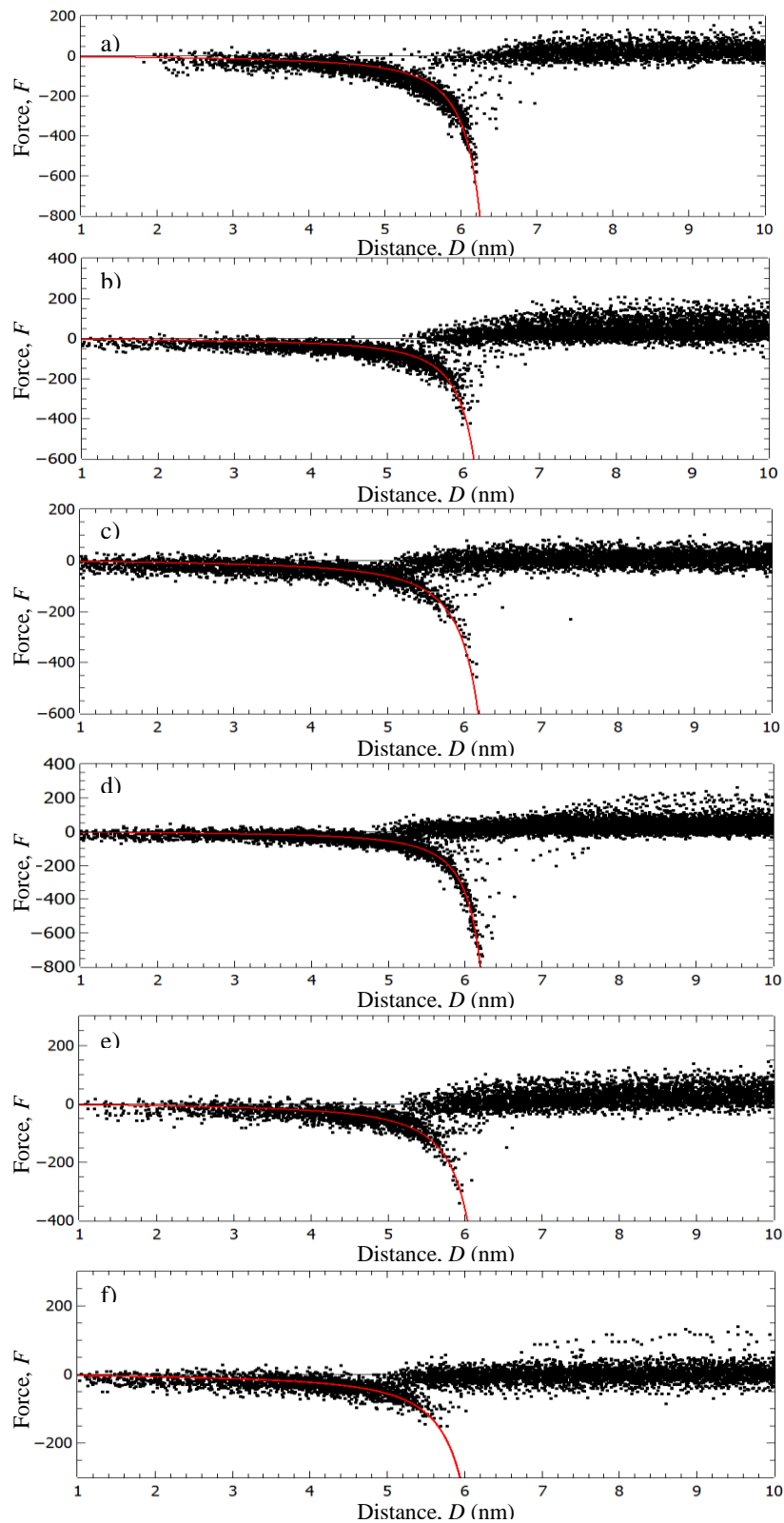


Figure S3: Alignment of all measured single-molecular events at a pulling speed of $0.5\mu\text{m/s}$ to the WLC-model (fitted master curve, red) for the interaction of Dopa with **a)** Titania **b)** OH-SAM **c)** NH₂-SAM **d)** COOH-SAM **e)** alkyl-SAM **f)** Gold.

6) Work-histograms and convergence-plots for all measured interactions

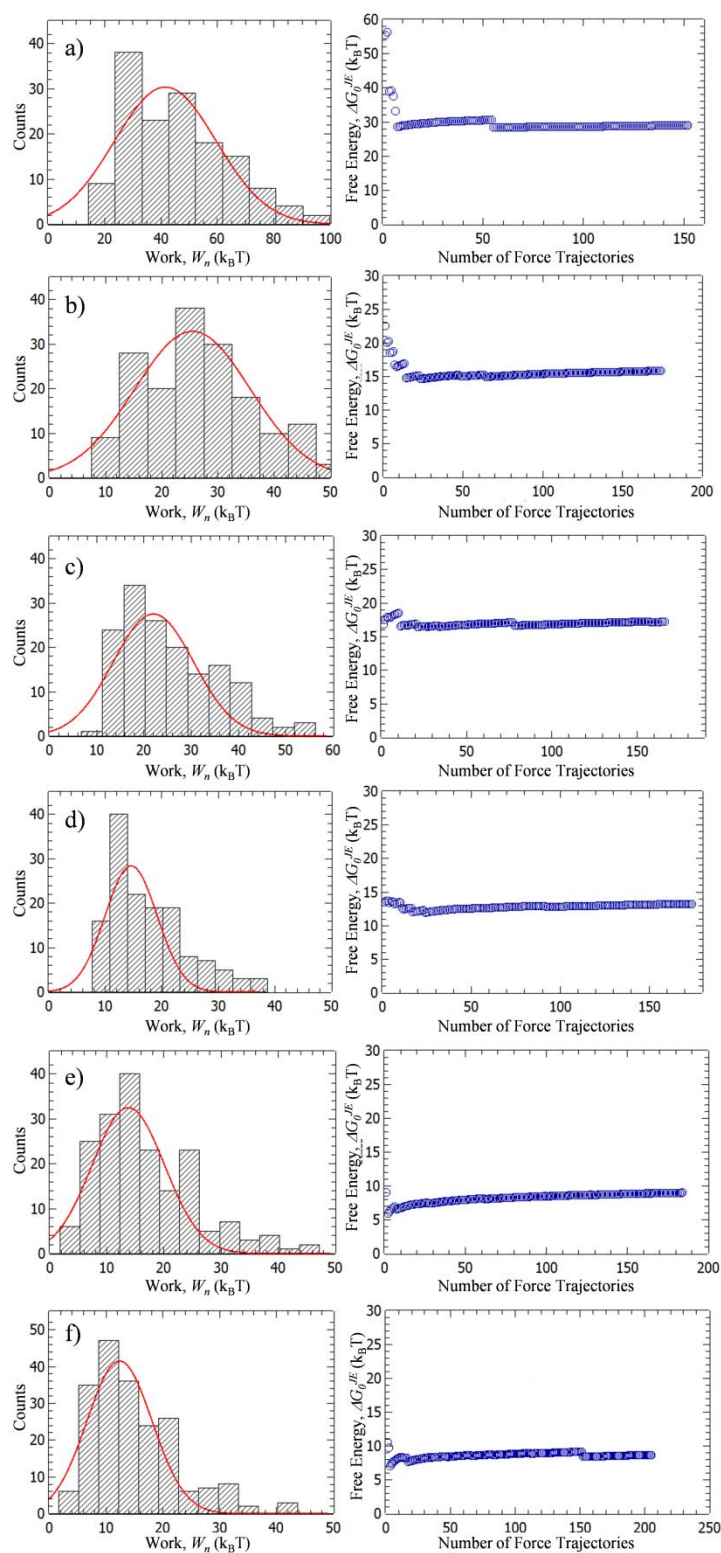


Figure S4: Work histograms (left) and convergence of the calculated binding energies (right) of Dopa interacting with a) Titania b) OH-terminated SAM c) NH_2 -terminated SAM d) COOH-terminated SAM e) alkyl-SAM f) Gold.

7) Loading rate dependence of the measured interaction free energies

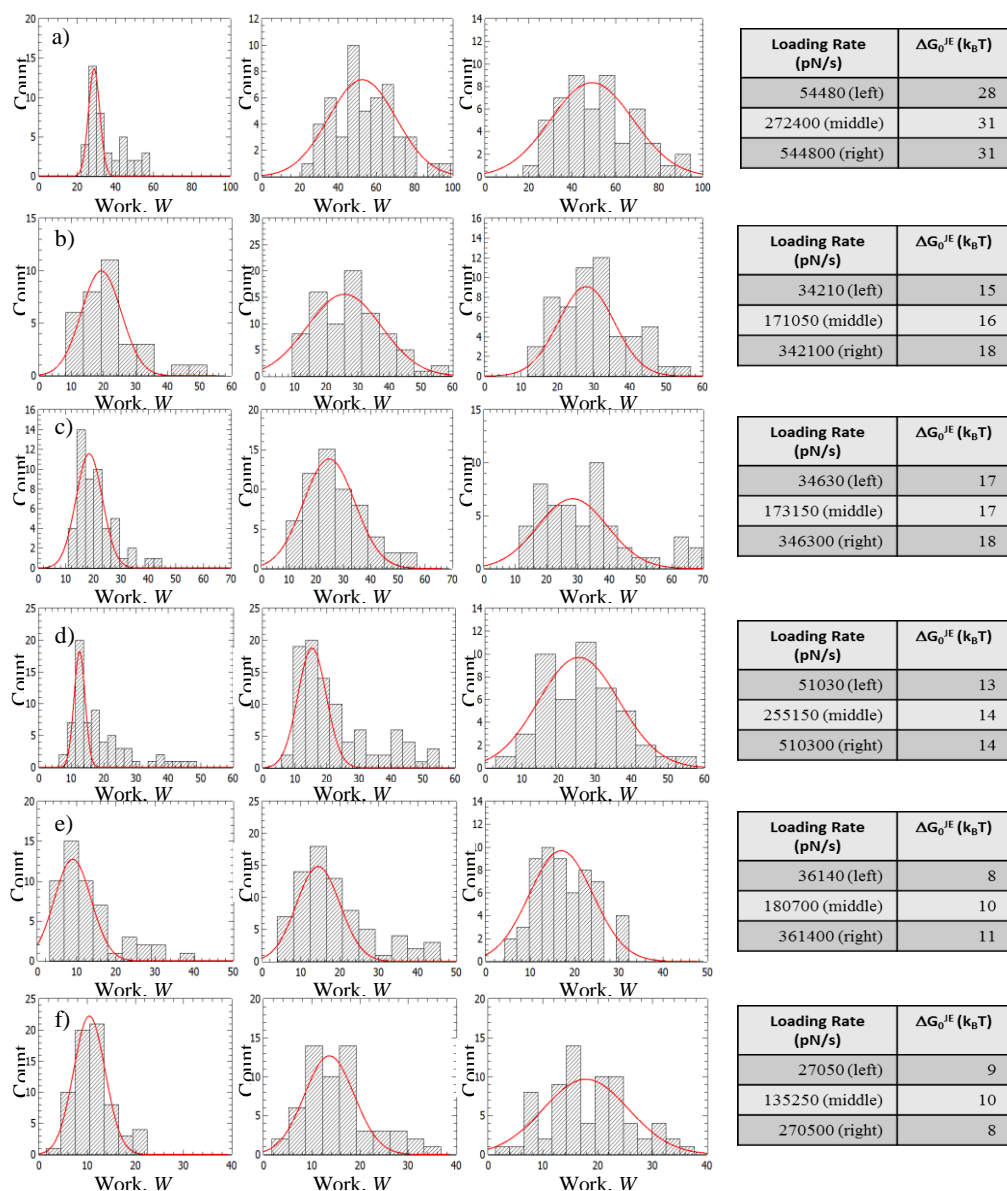


Figure S5: Loading Rate Dependence of the measured interaction free energy. The plotted histograms show all measured work values at three particular loading rates and the corresponding interaction free energy (listed in the tables). Dopa interacts with **a)** Titania **b)** OH-terminated SAM **c)** NH₂-terminated SAM **d)** COOH-terminated SAM **e)** alkyl-SAM **f)** Gold.

8) Data analysis in the framework of Bell-Evans theory for all measured interactions

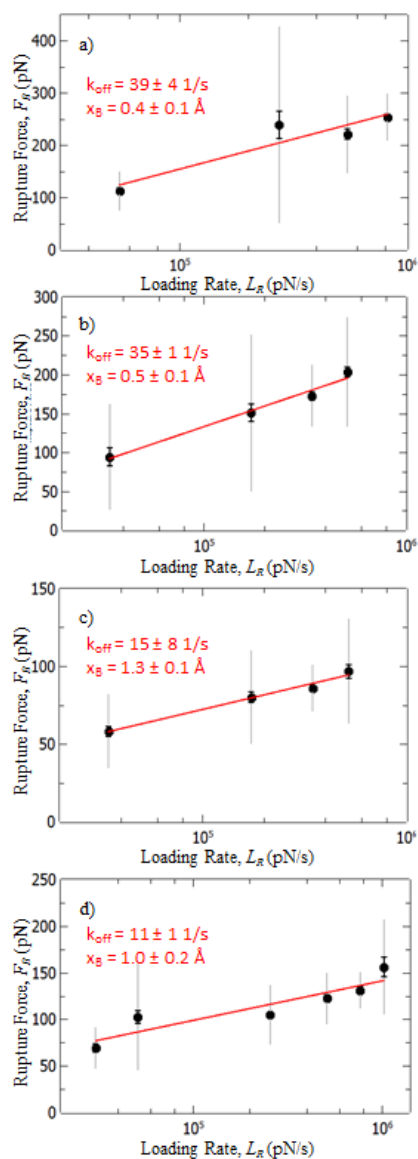


Figure S6: Loading rate dependence of the most probable rupture force for the interaction of Dopa with **a)** Titania **b)** OH-SAM **c)** NH₂-SAM and **d)** COOH-SAM. The solid red lines represent fits to Bell-Evans model. The extracted parameters k_{off} and x_B characterize the unbinding kinetics. The loading rate dependence of the interaction of Dopa with gold and with alkyl-SAMs is shown in **Figure 3** of the main text.

References

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- (2) Stock, P.; Utzig, T.; Valtiner, M., Manuscript in preparation.
- (3) Burnham, N. A.; Chen, X.; Hodges, C. S.; Matei, G. A.; Thoreson, E. J.; Roberts, C. J.; Davies, M. C.; Tandler, S. J. B., Comparison of calibration methods for atomic-force microscopy cantilevers. *Nanotechnology* **2003**, *14* (1), 1-6.
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