Supporting Information

Force Spectroscopy of Quadruple H-Bonded Dimers by AFM: Dynamic Bond Rupture and Molecular Time-Temperature Superposition

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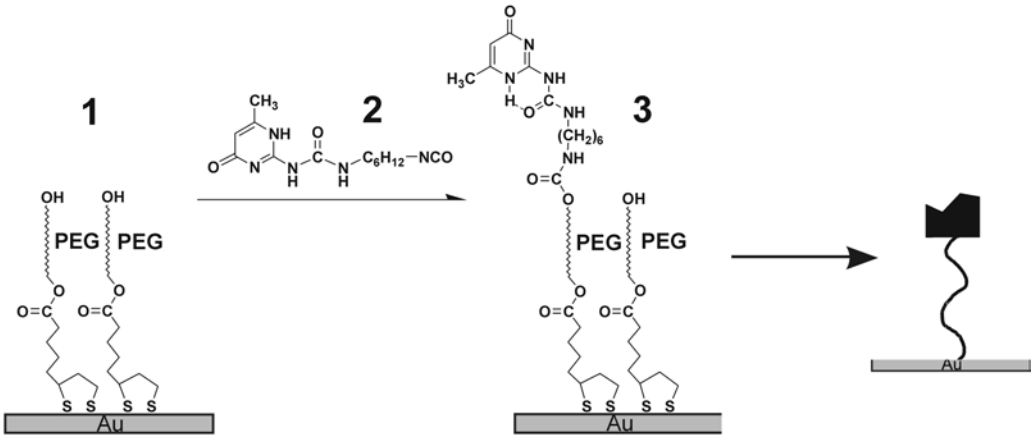
Experimental

Materials.[S1-S3]

For the synthesis of 1,2-dithiolane-3-pentyl-derivatized PEG **1**, UPy isocyanate **2**, and PEG-UPy disulfide **3** on Au (Scheme S1), see reference [S1].



Scheme S1. Formation of PEG linked 2-ureido-4[1H]-pyrimidinone moieties at Au(111) surfaces.

Preparation of Substrates and Self-assembled Layers.[S1,S2]

Gold substrates (11 × 11 mm^2, 250 nm Au on 2 nm Cr on borosilicate glass) for SMFS measurements were purchased from Metallhandel Schröer GmbH (Lienen, Germany). Au(111) samples were obtained by annealing these substrates in a high purity H_2 flame for 5 minutes [S1] Prior to use, these substrates were cleaned in piranha solution (3:1 H_2SO_4: H_2O_2 (30%) by volume), then rinsed with MilliQ water and ethanol and dried in a nitrogen stream***. Caution: Piranha solution should be handled with extreme caution: it has been reported to detonate unexpectedly.*** Self-assembled layers were formed, as described in ref. [S1] by immersing the

gold substrates into 1 mM solutions of **1** in CH_2Cl_2 for 10 hours. The surface reaction shown in Scheme S1 was carried out after rinsing with pure solvent as described in ref. [S1]. After rinsing with pure solvent and drying in an N_2 stream,[2] measurements were performed with minimal delay.

AFM and Tip Modification. The AFM measurements were carried out with a NanoScope IIIa multimode AFM (Veeco / Digital Instruments (DI), Santa Barbara, CA) in hexadecane (Aldrich) utilizing a liquid cell (DI). Triangular shaped silicon nitride cantilevers and silicon nitride tips (DI) coated with ca. 2 nm Ti and ca. 50 nm Au in high vacuum (SSENS b.v., Hengelo, the Netherlands) were functionalized as described above with **3**. The cantilever spring constants were calibrated by the thermal noise method as described in reference [S1]. The cantilever used in the experiment showen in Figures 1 and 2 had a spring constant of 0.094 ± 0.014 N/m.

The loading rate was directly determined from the slope of the force-extension curve near the rupture point. For instance, the force values for the last n data points (just before the rupture point) are easily measured on the force-extension curve. From the piezo ramp rate the corresponding time for each data point can be calculated. Thus, the force (in pN) of these n data points can be plotted against time (in seconds). A linear least squares fit of these data points affords the loading rate in pN/s.

The temperature of the liquid inside the liquid cell was controlled by a custom-made heating device [S4]. This heating device is based on a Peltier element (type TEC1 C-24.0-5.0-23/78-xy; size 6 × 6 mm^2; Eureca Messtechnik GmbH, Germany) attached with epoxy glue (thermal conductivity 0.0002 W/cm K) onto an AFM sample disk. Gold substrates were attached directly over the Peltier element by paper glue (Pritt type Glue-it, Henkel, Germany). The Peltier was connected to a DC power supply (Delta Elektronika) and a Fluke 52 II Thermometer using a K type thermocouple probe (Fluke). The electrical and temperature measurements were performed using a DMM 3020 Digital Multimeter (Kontron Electronic). The temperature calibration of the heating device in air was performed using n-alkanoic acids (decanoic, dodecanoic, tetradecanoic and hexadecanoic acid, Aldrich) with known melting points. The temperature calibrations in hexadecane for the liquid cell AFM set-up were performed by measuring the respective temperature for different applied currents using a thermocouple.

Analysis of Rupture Forces of Quadruple Hydrogen Bonds[S1]

Quadruple H-bonding interactions in individual $(UPy)_2$ complexes were probed by SMFS between PEG linked UPy (**3**) immobilized both on Au(111) and gold-coated AFM tips

functionalized with **3**. The force - extension data were fitted with the m-FJC model (Equation S1), for details see reference S1:

$$x(F) = [\coth(\frac{FI_K}{k_BT}) - \frac{k_BT}{FI_K}][L_{contour} + \frac{n}{K_{segment}}F] \quad \textbf{(S1)}$$

where x is the extension of the polymer chain; F is the applied force; I_K (Kuhn length) is the length of the statistically independent segment; n is the number of segments, which equals $L_{contour} / I_K$; K_{segment} is the segment elasticity, which characterizes the deformability of the segment; k_B is the Boltzmann constant; and T is the temperature.

Rupture Forces at 301 K

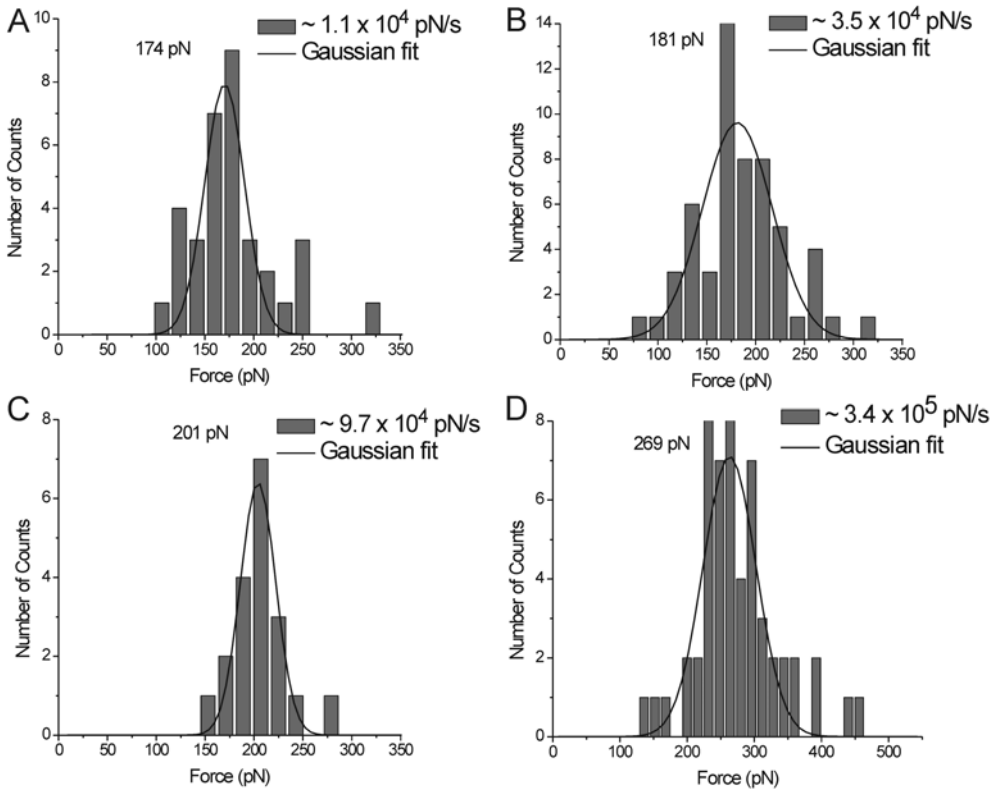


Figure S1. Histograms of pull-off forces of individual $(UPy)_2$ complexes at loading rates of (A) 1.1 (± 0.2) × 10^4 pN/s, (B) 3.5 (± 0.7) × 10^4 pN/s, (C) 9.7 (± 1.9) × 10^4 pN/s, and (D) 3.4 (± 0.7) × 10^5 pN/s at 301 K in hexadecane. The solid lines in (A) – (D) are Gaussian fits to the corresponding histograms.

Rupture Forces at 330 K

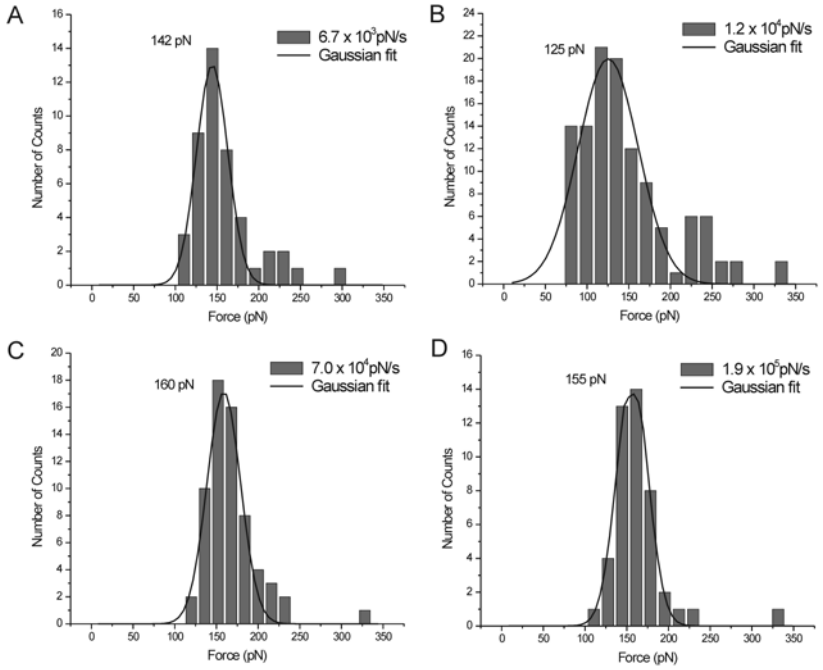


Figure S2. Histograms of rupture forces of individual $(UPy)_2$ complexes determined at 330 K in hexadecane at loading rates of (A) 6.7 (± 1.3) × 10^3 pN/s, (B) 1.2 (± 0.2) × 10^4 pN/s, (C) 6.9 (± 1.4) × 10^4 pN/s, and (D) 1.9 (± 0.4) × 10^5 pN/s. The solid lines are Gaussian fits to the corresponding histograms.

References

[S1] Zou, S.; Schönherr, H.; Vancso, G. J. *Angew. Chem. Int. Ed.* **2005**, *44*, 956-959.

[S2] Zou, S.; Zhang, Z. H.; Förch, R.; Knoll, W.; Schönherr, H.; Vancso, G. J. *Langmuir* **2003**, *19*, 8618-8621.

[S3] Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 874-878.

[S4] Zou, S.; Vera Marún, I. J.; Schönherr, H.; Vancso, G. J. *manuscript in preparation*.