Electronic Supplementary Information for

Direct comparison between chemisorption and physisorption: a study of poly(ethylene glycol) by means of single-molecule force spectroscopy

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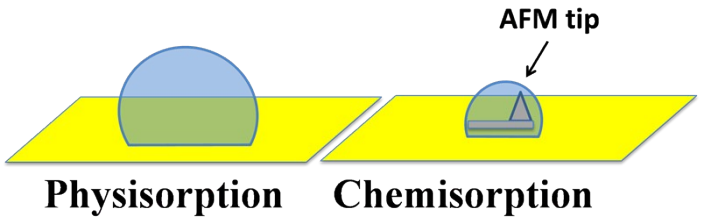

Fig. S1 Schematic drawing of the solution size for physisorption (~60 µl, left) and chemisorption (~15 µl, right). In a typical case, the chemisorption route would save ~97% of the raw material. The details are described as follows: 4 drops (~60 µl) of high concentration solution (1249 mg/ml) is needed for physisorption. However, only 1 drop (~15 µl) of dilute solution (131 mg/ml) is needed for chemisorption.

The details of QM calculations

The theoretical elasticity of single PEG chain is studied with quantum mechanics (QM) calculations. All QM calculations are carried out using the GAUSSIAN 09 program. EG trimer (as shown in Fig. S2) terminated with hydroxyl groups is used in the calculations.

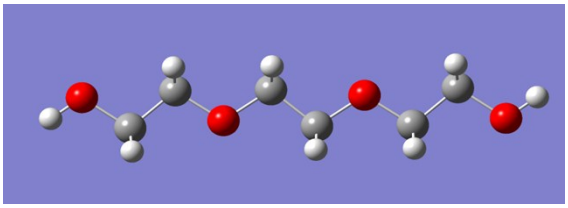

Fig. S2 EG trimer used in the QM calculation. Two hydroxyl groups are at both ends.

The distance between two ending oxygen atoms is fixed at different values in the calculations, while the positions of all other atoms are optimized to minimize the total energy. The calculations are performed at the MP2/TZV//B3LYP/TZV dual-level of theory. Fig. S3 presents the energy difference by stretching the model EG trimer at fixed distances between two ending oxygen atoms, taking the unstreched ground state as the energy reference. The solid line in Fig. S3 denotes polynomial fit according to

$$E = E_0 - a_0 \sum_{n=2}^{6} \gamma_{n-1} \left(a[E]/a_0 - 1 \right)^n / n \tag{S1}$$

where a0 is the length of the repeating unit at zero force, a[E] is the length at a given extension with energy E. γ1 is the linear elastic modulus of the repeating unit, other two coefficients are nonlinear corrections which become important at the higher force range. Fitting QM data to Eq. S1 gives values from $\gamma 1$ to $\gamma 5$ (see Table S1). The derivative of this equation leads to the force expression, which is actually measurable experimentally (e.g., by SMFS),

$$F = \frac{\partial E}{\partial a} = \sum_{n=1}^{5} \gamma_n \left(a[F] / a_0 - 1 \right)^n \tag{S2}$$

where a0 is the length at the given force, *F*.

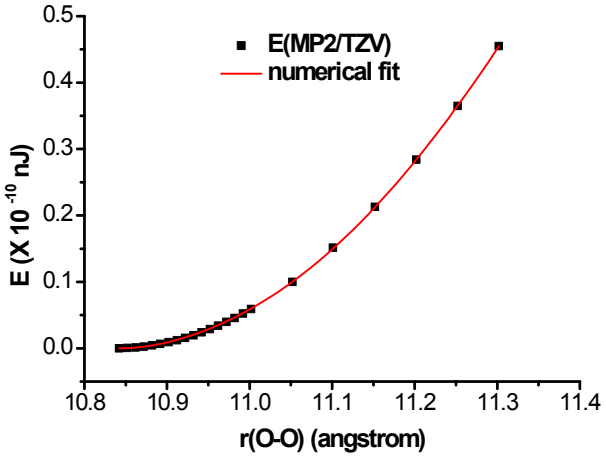

Fig. S3 The energies of stretched configurations at fixed distances at both ending oxygen atoms calculated at the MP2/TZV//B3LYP/TZV dual-level of theory. Solid line denotes the polynomial fit with Eq. S1.

Table S1. The elastic constants of PEG obtained from QM calculations.

	γ_1 [nN]	γ_2 [nN]	γ_3 [nN]	γ_4 [nN]	γ_5 [nN]
PEG	65.0	- 2.65×10^3	1.44×10^5	- 3.38×10^6	2.82×10^7

The details of QM-FRC model

In the freely-rotating chain (*FRC*) model (Eq. S3), the end-to-end distance of single polymer chain (*R*) at a given stretching force (*F*) can be written in a good approximation as:

$$R = L[F]\left[1 - k_B T/(2Fl_b)\right] \tag{S3}$$

where *L[F]* is the contour length of single polymer chain at a given stretching force, l_b is the rotating unit, k_B is the Boltzmann constant, and *T* is temperature in the Kelvin scale.

Note that *L[F]* is force dependent. It takes into account that the variations of bond angle and bond length append significantly to the purely entropy contributions of the *FRC* model at higher forces. Since the minor changes of bond length and bond angle are already considered in the calculations on one repeating unit, the formula can be easily rewritten to describe the whole polymer chain. The chain elasticity obtained by *QM* calculations (Table S1) is non-linear, which can be described in a polynomial expansion (Eq. S4) to provide the basis for a numerical fit of the experimental F-E curves:

$$F = \sum_{n=1}^{5} \gamma_n \left(L[F]/L_0 - 1 \right)^n \tag{S4}$$

where L_0 is the contour length of single polymer at zero force, γ_1 is the linear elastic modulus of one repeating unit, and other four coefficients are nonlinear corrections, which are important in the higher force region.

In Eq. S3, the *FRC* model has two free parameters for model fitting, i.e., *L[F]* and l_b. The singe polymer elasticity of PEG molecule (Table S1) can be integrated into the *FRC* model. The extension can be normalized as Eq. S5:

$$R/L_0 = \left(L[F]/L_0 \right) \cdot \left[1 - k_B T/(2F l_b) \right] \tag{S5}$$

R/L_0 is the normalized extension of a single polymer chain. During the elastic stretching of a single polymer chain, *L[F]* increases from L_0 to the breakage of the polymer bridge. Thus, the value of $L[F]/L_0$, starting from 1, is a monotonic increasing function of *F* and vice versa. During the elongation of PEG chain, $L[F]/L_0$ is an ergodic value ranging from 1 to 1.159, which corresponds the breakage of the C-S bond (2800 pN). Since $L[F]/L_0$ can be an ergodic value in the reasonable range, the model now has only one free parameter left (l_b). For a given value of l_b, the fitting curve can be obtained when the value of $L[F]/L_0$ is changed from 1 to 1.159; see the dotted lines in Fig. 2.

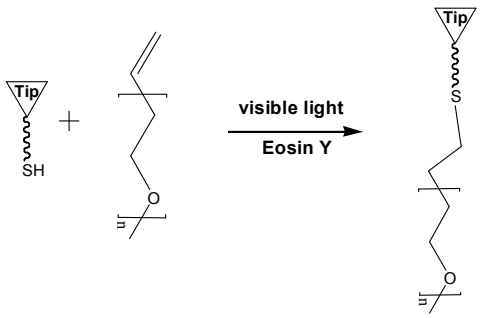

Fig. S4 PEG chain is covalently linked on the thiol-group modified AFM tip via thiol-ene click reaction.

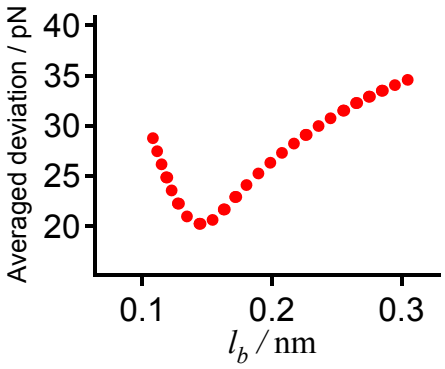

Fig. S5 Averaged deviation of force between the QM-FRC fitting curve and the experimental curve of PEG in the range of l_b = 0.1 - 0.3 nm. The minimum deviation is obtained at l_b = 0.147 nm.

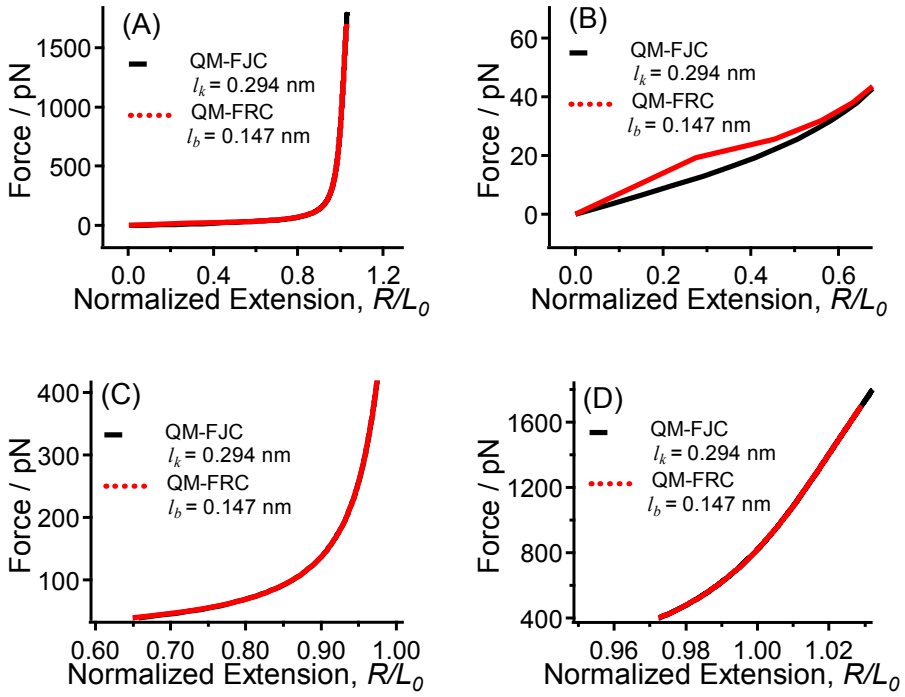

Fig. S6 The QM-FJC fitting curve with l_k = 0.294 nm (black solid line) and the QM-FRC fitting curve with l_b = 0.147 nm (red dotted line). The comparative of two kinds of fitting curves within whole region (A), low force region: 0~40 pN (B), low-mid force region: 40~400 pN (C), mid-high force region: 400~1700 pN (D).

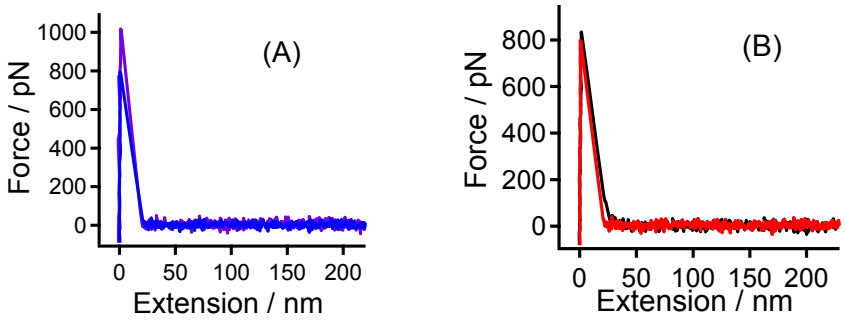

Fig. S7 The typical F-E curves obtained in the samples that prepared without visible-light irradiation (A), or without catalyst Eosin Y (B), respectively.

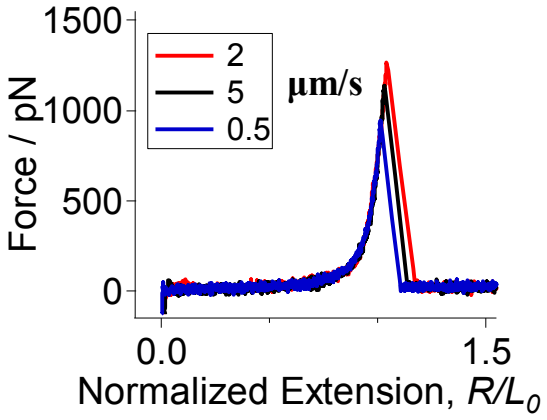

Fig. S8 Normalized F-E curves of PEG obtained in nonane at different stretching velocity.

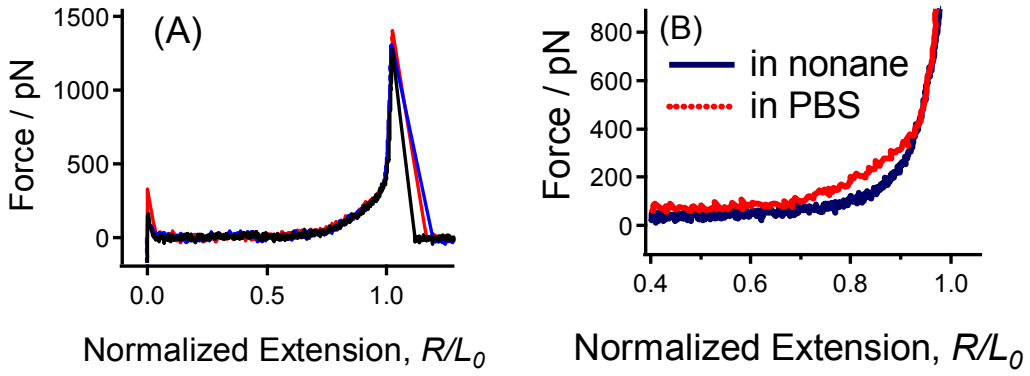

Fig. S9 (A) Normalized F-E curves of PEG obtained in PBS aqueous buffer. (B) The comparison of F-E curves of PEG obtained in PBS aqueous buffer and nonane.

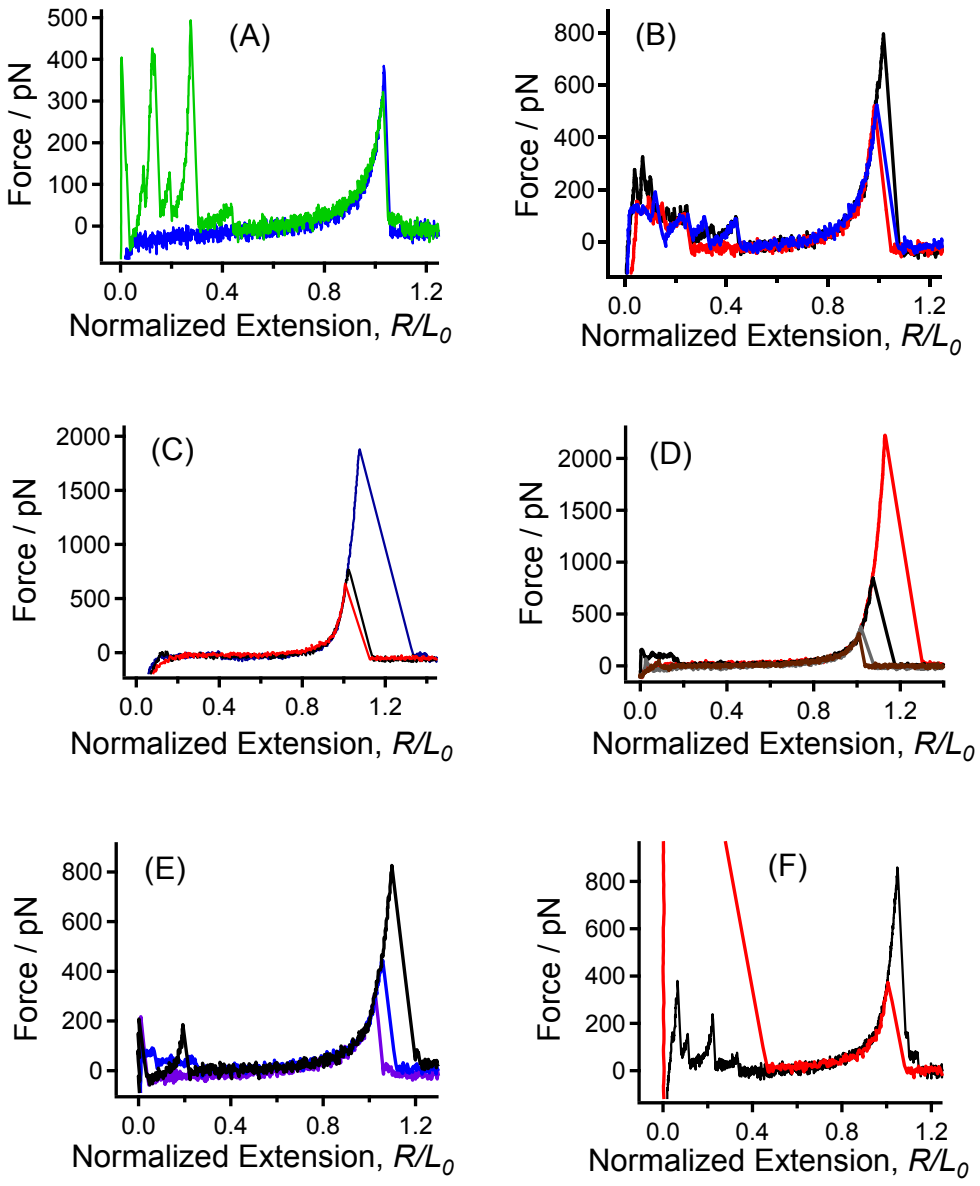

Fig. S10 The normalized F-E curves of chemisorbed PEG obtained in nonane with different concentrations: (A) 30 mg/L, (B) 50 mg/L, (C) 100 mg/L, (D) 150 mg/L, (E) 200 mg/L, and (F) 300 mg/L.

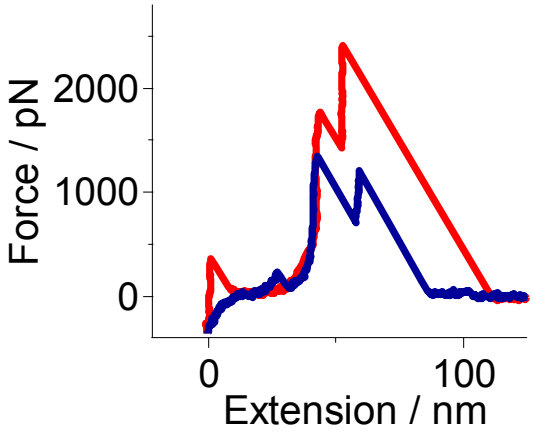

Fig. S11 (C) Multiple-chain F-E curves of PEG by physisorption obtained in nonane.

Scheme S1. An schematic drawing of the sample of substrate-CS (A) and tip-PS (B).

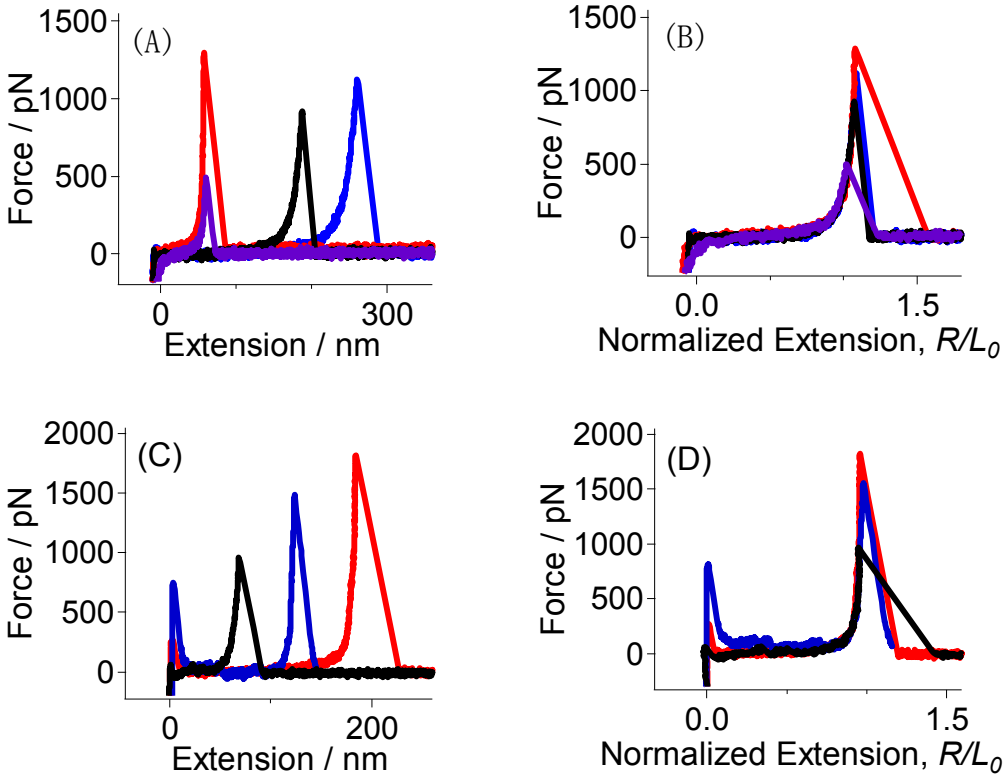

Fig. S12 Typical F-E curves of substrate-CS samples (A) and tip-PS samples (C) obtained in nonane. (B) and (D) show the normalized F-E curves of those shown in (A) and (C).

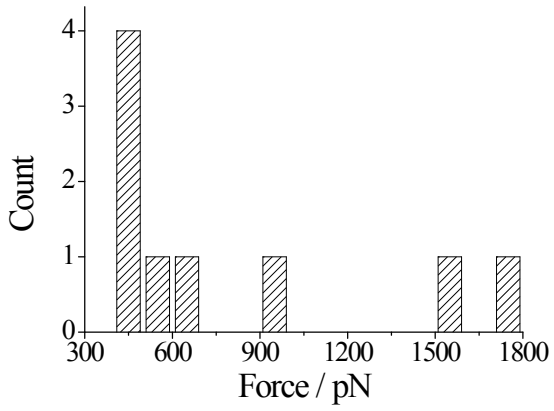

Fig. S13 The statistics of the rupture force observed on the tip-PS sample.

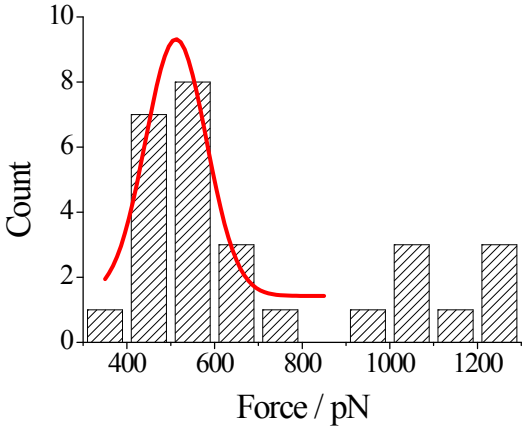

Fig. S14 The statistics of the rupture force observed on the substrate-CS sample.

Monte Carlo (MC) Simulations

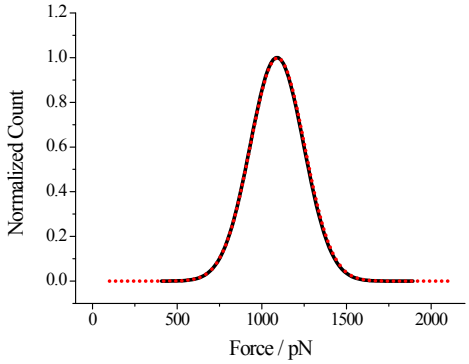

Fig. S15 The distribution of the desorption force of the physisorbed part from the substrate. The other end is covalently bonded to the AFM tip. The red dash line is the result from experiments (μ = 1092 pN and σ = 160 pN), while the black curve is the result from MC simulations (μ = 1092 pN and σ = 160 pN).

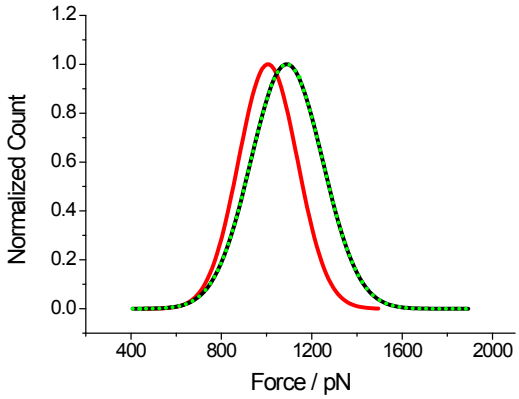

Fig. S16 The distribution of the desorption force of the chain that both of two ends are physisorbed to the solid surfaces (substrate and AFM tip). The black curve (X_1) and green dotted line (X_2) are the results of MC simulations assuming that the desorption force of both of the two ends from the solid surfaces (substrate or AFM tip) follow the same Gaussian distribution of μ = 1092 pN and σ = 160 pN. The red

curve is the result by selecting a smaller value from a pair of values of the desorption force (X_1 and X_2), which also follows a Gaussian distribution (μ = 1006 pN and σ = 130 pN).

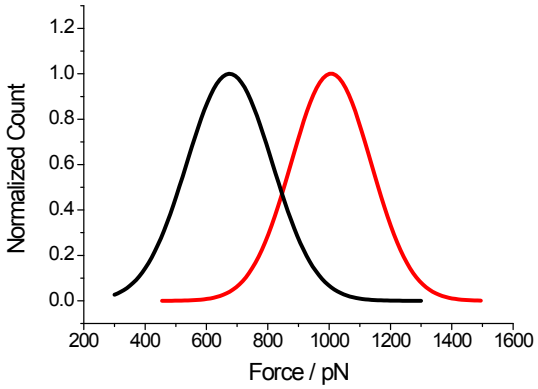

Fig. S17 The distribution of the desorption force of the chain that both of two ends are physisorbed to the solid surfaces (substrate and AFM tip). The black curve is the result from experiments (μ = 675 pN and σ = 140 pN), while the red curve is the result from MC simulations (μ = 1006 pN and σ = 130 pN). The red curve here is same to the red one shown in Fig. S11.