

# Single-molecule force spectroscopy quantification of adhesive forces in cucurbit[8]uril host-guest ternary complexes

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## S1. General Experimental

### S1.1. Materials

4,4'-azobis(4-cyanopentanoic acid) (APCA), *N,N'*-dimethyl acrylamide, 1,4-dioxane, dichloromethane, diethyl ether, methanol, 1 N hydrochloric acid and dibutyltindilaurate were purchased from Sigma-Aldrich Chemical (Dorset, UK) and used as received with the exception of *N,N'*-dimethyl acrylamide, which was passed through a plug of silica prior to use. Naphthol-

isocyanate was purchased from Fluka. Hydroxyl terminated chain transfer agents (CTA-OH) for reversible addition-fragmentation chain-transfer (RAFT) polymerization were synthesized in-house according to the procedure described by Williams *et al.*<sup>1</sup> 4,4'-bipyridine was purchased from Sigma-Aldrich Chemical and then further modified to give a MV-silane, which was used to functionalize mica surfaces. Cucurbit[7]uril and cucurbit[8]uril were synthesized and purified in-house using procedures described by Jiao *et al.*<sup>2</sup> Water used in experiments was either deionized water from a Milli-Q water filtration system (Millipore, Livingston, UK) or purified water from Huangzhou Wahaha Group, Ltd (Huangzhou, China).

## S1.2. Instrumentation

<sup>1</sup>H spectra were recorded using a Bruker Avance QNP 400. Chemical shifts are recorded in ppm ( $\delta$ ) in CHCl<sub>3</sub> with the internal reference set to  $\delta$  7.19 ppm for <sup>1</sup>H. Gel permeation chromatography (GPC) was carried out in tetrahydrofuran (THF) on two Jordi 5 $\mu$ m DVB columns connected in series with a SPD-M20A Prominence diode array detector and refractive index detector (both Shimadzu) calibrated with respect to poly(styrene) standards. Samples were filtered over 0.45  $\mu$ m PVDF filters before injection using a 1.0 mL/min flow rate.

## S1.3. Contact angle measurements

To verify the change in counterion on the MV<sup>2+</sup> 2(X<sup>-</sup>) surface, dynamic contact angle measurements with water were measured on each freshly prepared surface using a FTÅ2000 optical contact angle instrument (First Ten Ångstroms, Portsmouth, VA, USA). Examples of the contact angles measured for unfunctionalized mica, MV<sup>2+</sup> 2(Cl<sup>-</sup>), MV<sup>2+</sup> 2(Br<sup>-</sup>) and MV<sup>2+</sup> 2(BF<sub>4</sub><sup>-</sup>) are shown in Figure 1.

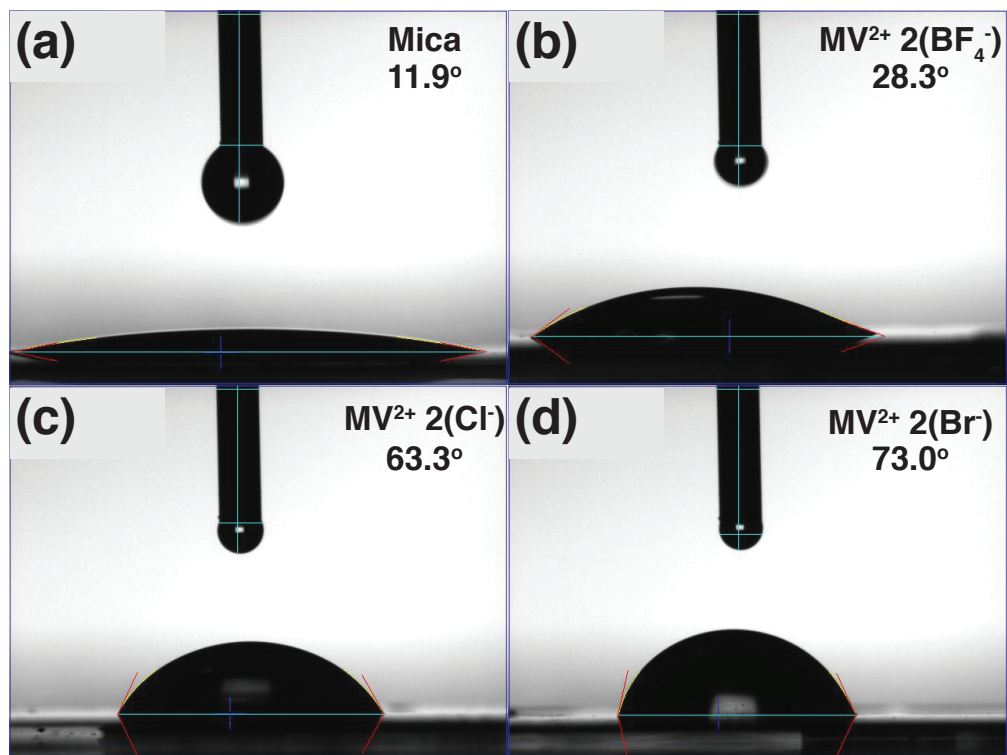


Figure 1: Images of dynamic contact angle measurements on (a) unfunctionalized mica, (b)  $MV^{2+} 2(BF_4^-)$  functionalized mica, (c)  $MV^{2+} 2(Cl^-)$  functionalized mica and (d)  $MV^{2+} 2(Br^-)$  functionalized mica.

## S2. Control experiments testing the interactions of the short thiol linker with functional surfaces

Single-molecule force spectroscopy is an extremely sensitive technique and as such it is possible to interpret many different interactions of the tip as binding events of a specific complex, although that might not be the case. In order to properly understand the presence of specific binding events a series of control experiments were carried out to determine the reaction of the system to non-specific interactions so that specific binding events would be easier to interpret. In order to limit the number of long chains on the surface of the AFM tip, a short thiol (2-mercaptoethanol) was used to coat the surface and limit the space available for the long poly(DMA) chains to attach. The first control was then to understand the interactions between the short thiol functionalized surface, with and without the presence of CB[8], this

can be seen in Figure 2.

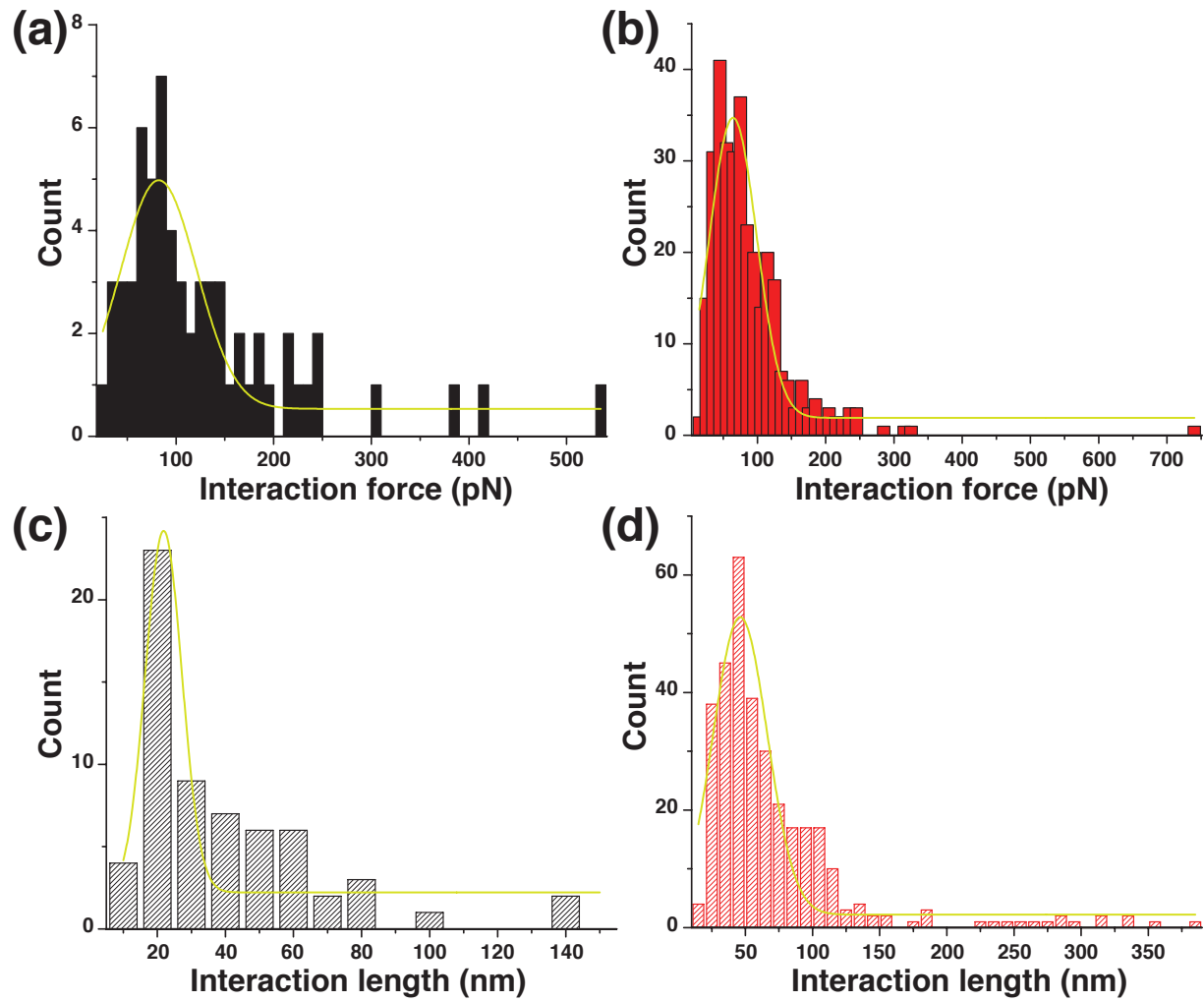


Figure 2: Histograms showing the distribution of interaction forces for a short thiol functionalized AFM tip with the  $MV^{2+} 2(BF_4^-)$  surface in (a) pure water and (b) CB[8] and the corresponding interaction lengths in (c) pure water and (d) CB[8].

Although the number of interactions increases when the CB[8] is present, there is always a monomodal distribution to the interactions with negligible observed peak formations in the spectra. We can conclude that there is no specific interaction between the tip and the surface, rather interactions appear to be non-specific hydrophobic interactions, which is to be expected.

Once it was clear that the short thiol does not introduce any specific interactions between the tip and the surface, the interaction between the polymer functionalized tips and a functionalized mica surface without CB[8] was also controlled. An example of such a control is shown for the Np-DMA<sub>12k</sub> polymer functionalized tip and the MV<sup>2+</sup> 2(Cl<sup>-</sup>) functionalized mica in the presence of pure water in Figure 3.

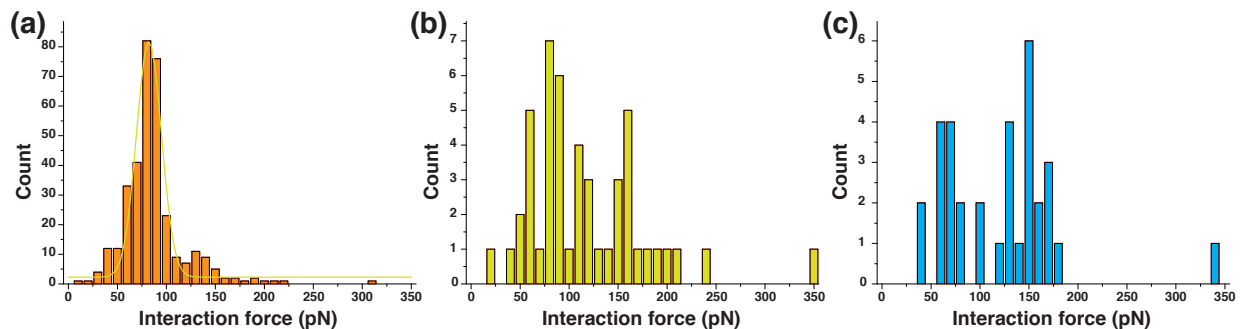


Figure 3: Histograms showing the distribution of interaction forces for the Np-DMA<sub>12k</sub> functionalised AFM tip with MV<sup>2+</sup> 2(Cl<sup>-</sup>) functionalized mica in pure water, showing the occurrence of (a) plateau (b) peaks and (c) plateau-peaks.

### S3. Effects of the polymer linker in the system

In order to illustrate the relative ease or difficulty in the analysis of the spectra corresponding to an individual functionalised tip examples of force spectra, extracted from the AFM software are shown in Figure 4.

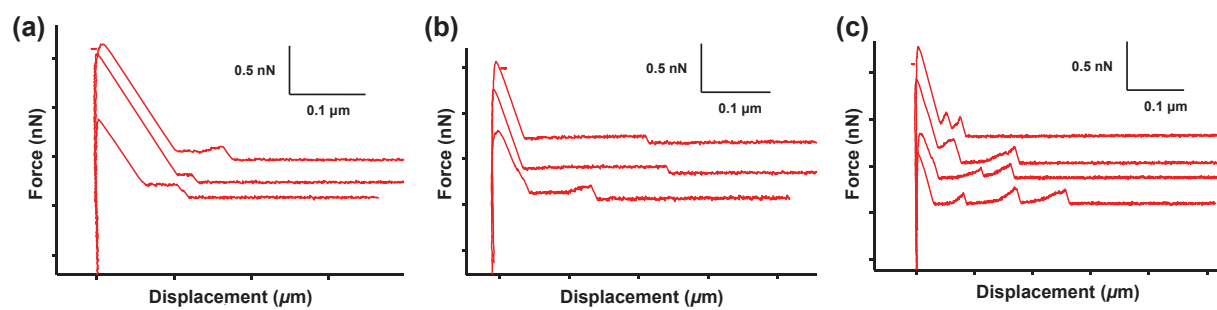


Figure 4: Representative force spectra extracted from the AFM software for (a) Np-DMA<sub>5k</sub>, (b) Np-DMA<sub>12k</sub> and (c) Np-DMA<sub>19k</sub>.

To illustrate the difference in the observed length of the polymer linkers with respect to the estimated contour length, histograms of the interaction lengths with their respective frequency for each of the Np-DMA<sub>*x*</sub> polymers is shown in Figure 5. The apparent length estimated by the AFM is consistently different from that calculated from the chain length of the polymers.

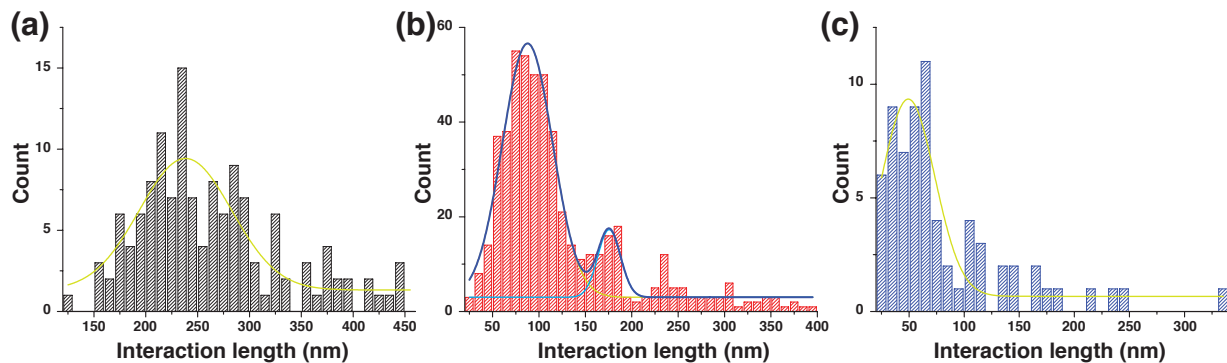


Figure 5: Histograms showing the distribution of interaction lengths for (a) Np-DMA<sub>5k</sub>, (b) Np-DMA<sub>12k</sub> and (c) Np-DMA<sub>19k</sub>.

## S4. Varying the counterion on the surface

The counterion on the methyl viologen functionalized mica was varied between  $MV^{2+} 2(BF_4^-)$  and  $MV^{2+} 2(Cl^-)$  to understand the effect on adhesive forces. A histogram of the interaction length frequencies for the  $MV^{2+} 2(Cl^-)$  surface is shown in Figure 6 and the representative spectra extracted from the AFM software for both the  $MV^{2+} 2(BF_4^-)$  and  $MV^{2+} 2(Cl^-)$  surfaces are shown in Figure 7.

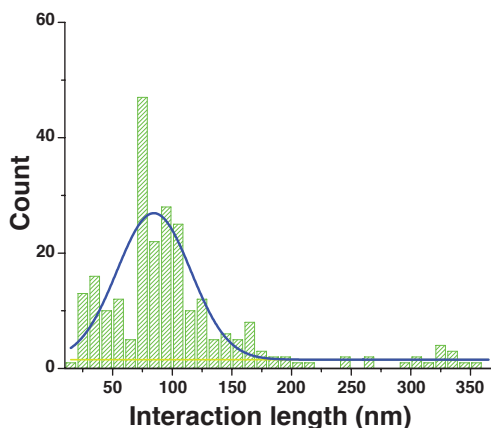


Figure 6: Histogram showing the distribution of interaction lengths for Np-DMA<sub>12k</sub> against the  $MV^{2+} 2(Cl^-)$  surface.

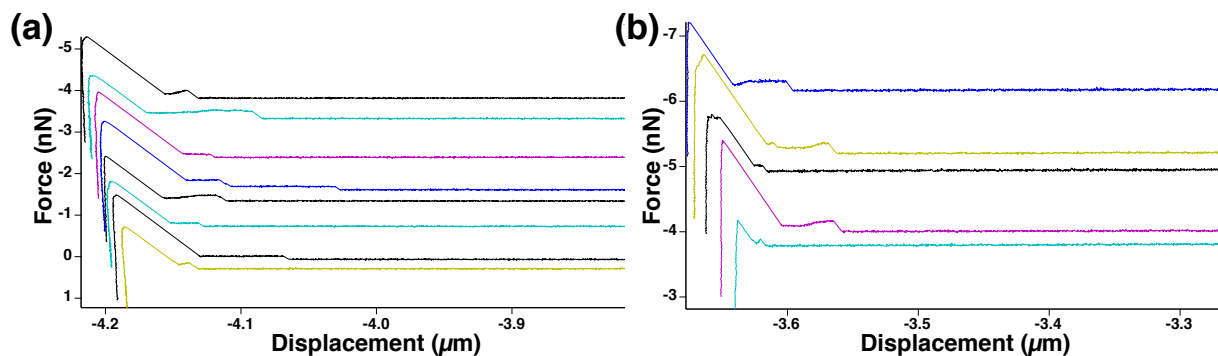


Figure 7: Force spectra extracted from the AFM analysis software (Igor) for the interactions of the  $MV^{2+} 2(BF_4^-)$  surface (a) and the  $MV^{2+} 2(Cl^-)$  surface (b) with a Np-DMA<sub>12k</sub> functionalized tip in the presence of CB[8].



## S5. Understanding the various peak formations (Manipulation of the surface)

In order to validate the provenance of the plateau-peak force, spectra were obtained for the Np-DMA<sub>12k</sub> tip and MV<sup>2+</sup> 2(BF<sub>4</sub><sup>-</sup>) surface in the presence of CB[7], the histograms of interaction forces and interaction lengths are shown in Figure 8.

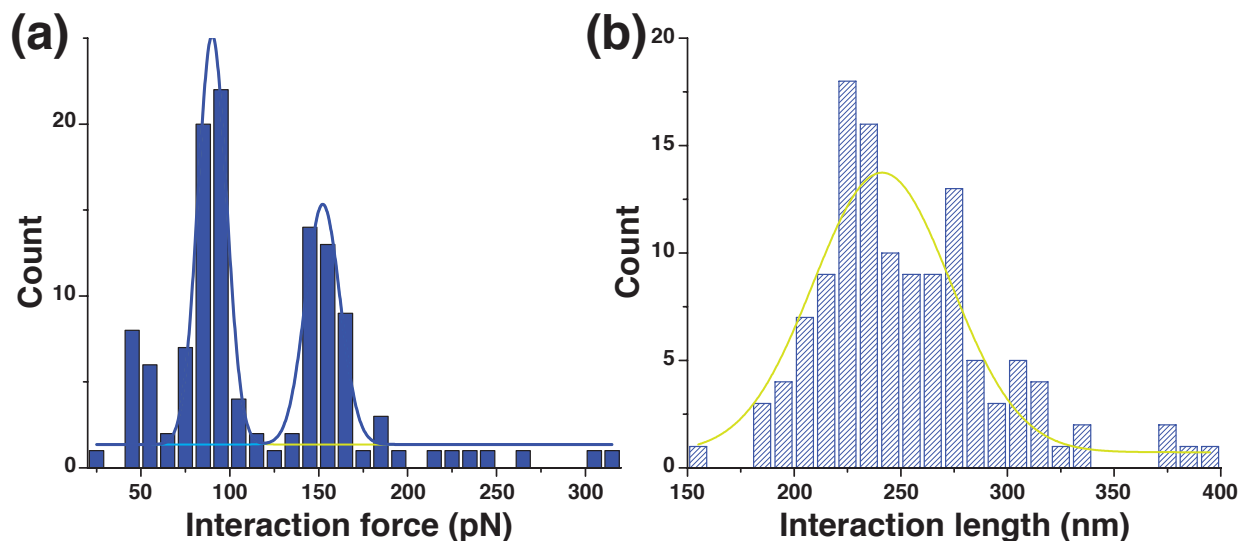


Figure 8: Histograms showing the distribution of interaction forces (a) and interaction lengths (b) for MV<sup>2+</sup> 2(BF<sub>4</sub><sup>-</sup>) · CB[7] · Np-DMA<sub>12k</sub>.

## References

- (1) Williams, P. E. Synthesis of conducting polymer-metal nanoparticle hybrids exploiting RAFT polymerization. Ph.D. thesis, Department of Chemistry, University of Cambridge, 2012.
- (2) Jiao, D.; Scherman, O. A. Isolation of cucurbit[n]uril homologues with imidazolium salts in a recyclable manner. *Green Chem.* **2012**, *4614*, 2445–2449.