S1. Additional information about the CDI method

N,N’-carbonyldiimidazole (CDI) is a commonly used reagent for preparation of different peptides (amino acid coupling) and in other chemical reactions in which mild conditions have to be used due to the presence of labile molecules. In our study, CDI was used to activate the carboxyl group of CMC, which was then ready to bind to the surface of the AFM tip without use of any additional external force (for example, shaking or stirring) or increase in temperature. The tips (with previously attached amino groups) were simply dipped inside the solution of such activated CMC. After 24 hours the tips were functionalized. The reaction was carried out in a similar fashion as described in (R. Paul, and G. W. Anderson, J. Am. Chem. Soc, 1960, 82(17), 4596-4600). The concentrations of the reagents were adjusted to 10 mmol, as proposed in that article.

S2. Monitoring of pH during tip functionalization

Figure S2. Scheme of the pH monitoring during the tip functionalization procedures.
S3. SEM imaging of functionalized tips

Figure S3. SEM image proving successful and reasonably tip-selective functionalization.

Before starting the AFM measurements, one needs to be sure that the functionalization of the tip was successful. For that purpose we used electronic microscopy, which proved reasonably fast (the fresh tip can easily be imaged) and reliable enough a technique to evaluate the success of CMC binding. Although it does not provide any quantitative information about the type of bonding, microscopic examination can distinguish between different loci of binding such as the tip, the surface of the chip etc. In our case we wanted to avoid binding on the surface of chip because this would result in a lower sensitivity of the force measurement - due to changes in laser reflection and consecutive deflection measurement.

In our case, the chip surface was usually not as clean as should be in the ideal case, but one could clearly observe that the polymer preferentially bound to the tip. A possible explanation for the unexpected appearance of “dirt” on the surface of chip is that it was deposited after the functionalization and mainly in the connection with SEM imaging. Namely, as-prepared tips were first put into an argon flooded desiccator and kept there until immediately before the measurement. The preparation of the samples observed under SEM, however, proceeded partly in air, where there was additional possibility for deposition of dirt on the chip surface. In any case, whereas for quantitative measurements a strong confidence in the cleanness of the sample is necessary, qualitative comparison of different samples does not require perfectly clean chip surface as the deflection changes due to possible dirt are indeed minimal.