Supplementary Information for

Single-molecule force-spectroscopic study on chiral recognition of cysteine derivatives immobilized on gold substrate by using AFM tips modified chemically with optically active crown ethers

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Contents

1) Preparation of crown-ether-unmodified tips.

The crown-ether-unmodified AFM tips were prepared according to Fig. S1.

(a) The AFM tips, which are commercially available: Si_3N_4 type coated with Au/Cr on both sides (spring constant 0.02 N m^{-1}, Olympus), were cleaned by soaking into a piranha solution (concentrated H_2SO_4/28% H_2O_2, 7/3, v/v). After being thoroughly rinsed with ion-exchange water, the tips were fully dried in the atmosphere. The cleaned tips were treated by immersion into an ethanol solution containing 1.0 mM 1-{[5-(1,2-dithiolan-3-yl)pentanoyl]oxy}-2,5-pyrrolidinedione at room temperature for 24 h. After being rinsed with ethanol, the tips were fully dried in the atmosphere.

(b) After the treatment of (a), the tips were treated by immersion into a DMF solution containing 0.20 mM α-aminopropyl-ω-aminopropoxy, polyoxyethylene (M_w = 3500, M_w/M_n = 1.4) and 5.0 mM *N*,*N*-dimethylaminopyridine (DMAP) at room temperature for 2 h. After being rinsed with DMF, the tips were fully dried in the atmosphere.

(c) After the treatment of (b), the tips were immersed into acetic anhydride at room temperature for 2 h for the capping of the remaining amino groups by nonpolarized functional groups. After being rinsed with ethanol, the tips were fully dried in the atmosphere.

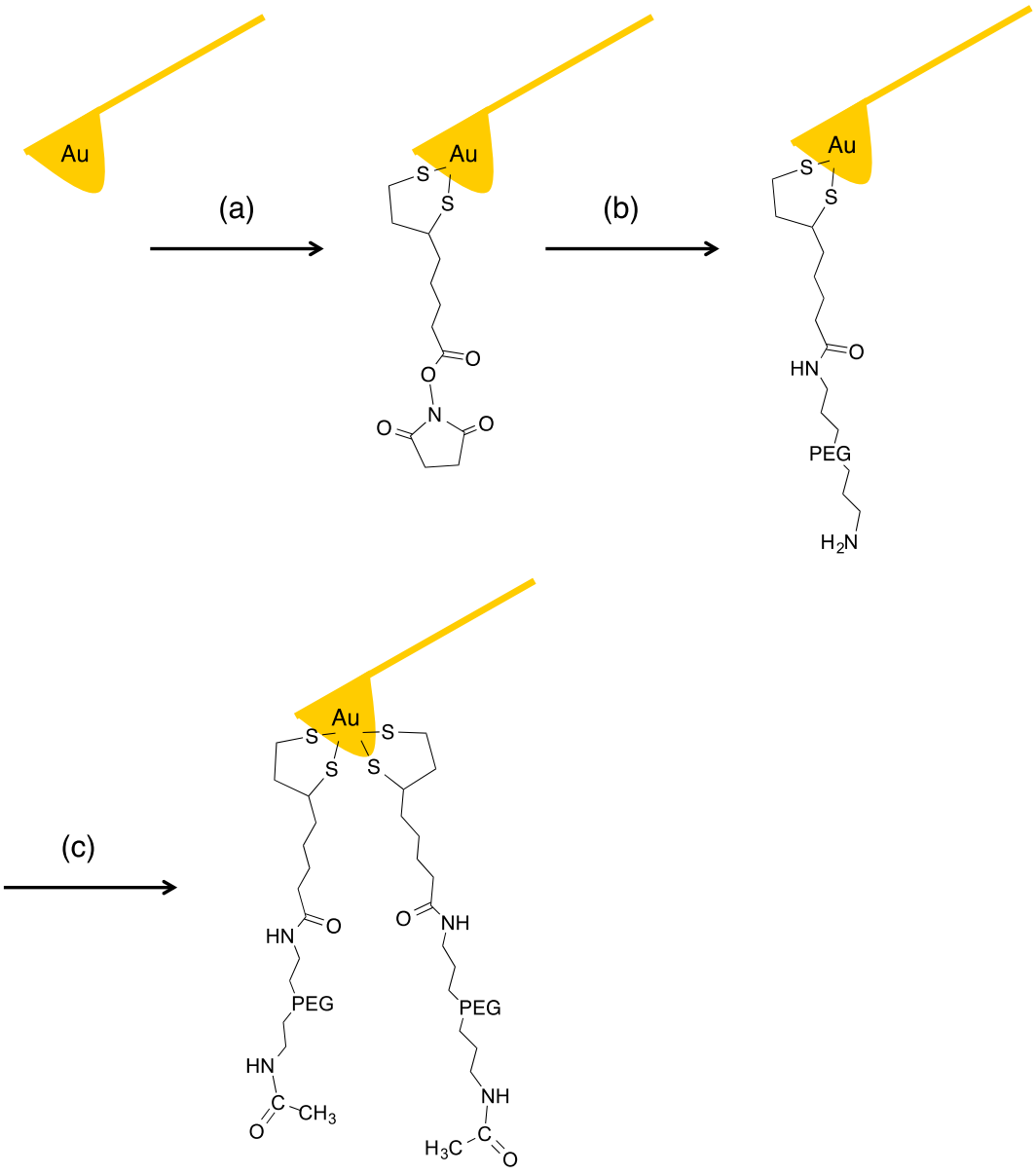

Fig. S1 Preparation of crown-ether-unmodified tips. Reagents and conditions: (a) 1-{[5-(1,2-dithiolan-3-yl)pentanoyl]oxy}-2,5-pyrrolidinedione, ethanol, rt, 24 h; (b) α-aminopropyl-ω-aminopropoxy, polyoxyethylene, DMAP, DMF, rt, 2 h; (c) acetic anhydride, rt, 2 h.

2) Representative force-extension curve except for the stretching of a single chain.

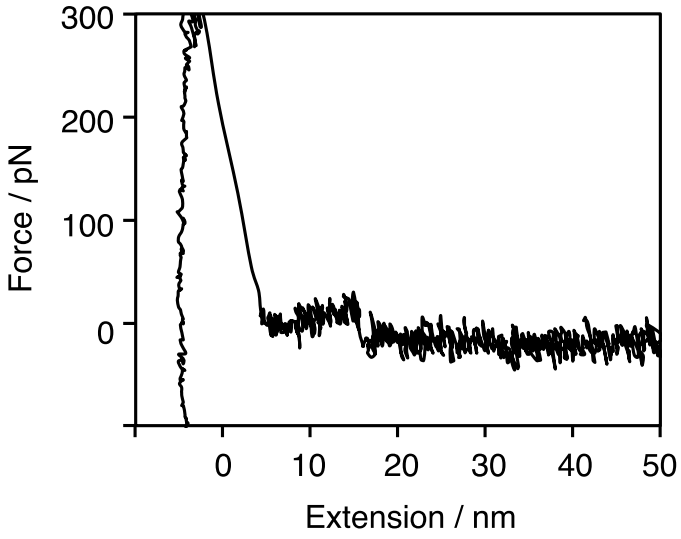

Fig. S2 Representative force-extension curve except for the stretching of a single chain.

3) Representative force-extension curves in the other combinations of the tips and substrates.

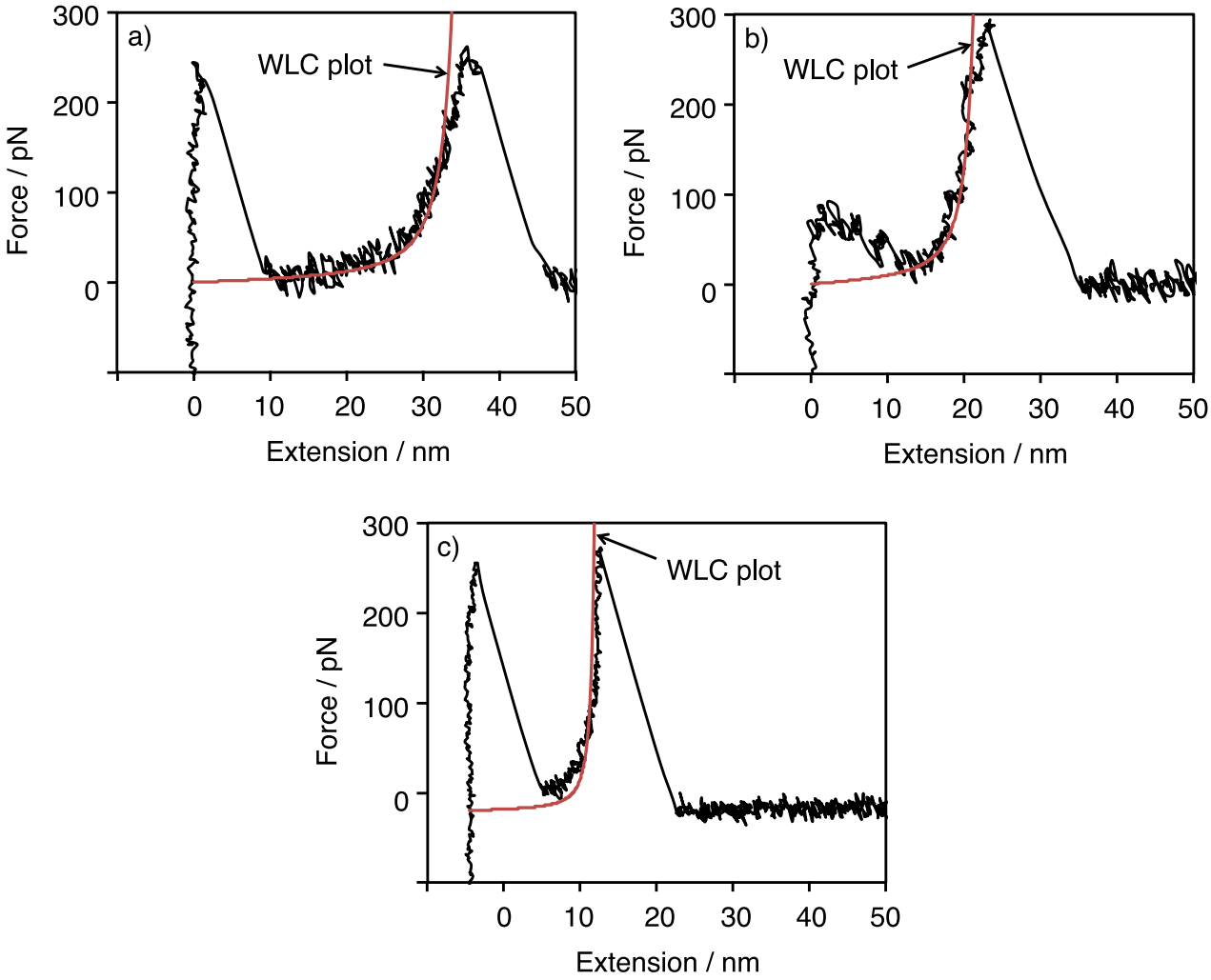

Fig. S3 Representative force-extension curves observed using (a) (*R*,*R*,*R*,*R*)-**1**-modified tip and (*S*)-**3**-modified substrate, (b) (*S*,*S*,*S*,*S*)-**1**-modified tip and (*R*)-**3**-modified substrate and (c) (*S*,*S*,*S*,*S*)-**1**-modified tip and (*S*)-**3**-modified substrate in ethanol.

4) Force-extension curve using (*R*,*R*,*R*,*R*)-1-modified tip and (*S*)-3-modified substrate in the presence of KSCN.

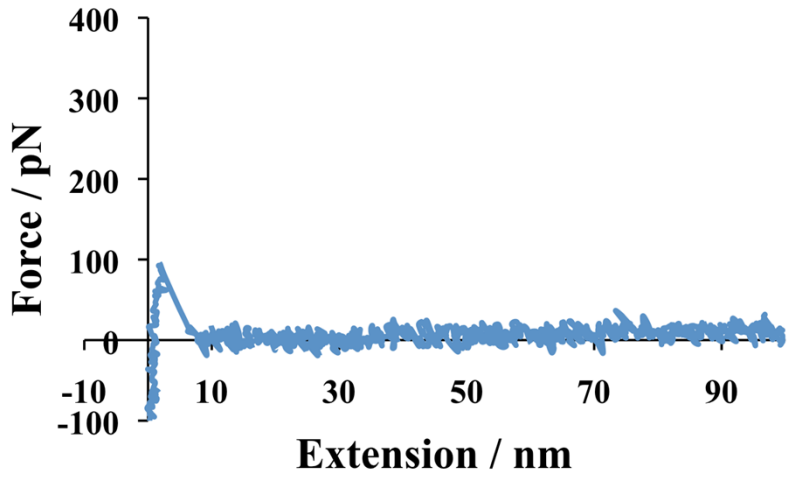

Fig. S4 Force-extension curve observed using (*R*,*R*,*R*,*R*)-**1**-modified tip and (*S*)-**3**-modified substrate in the presence of KSCN in ethanol.

5) Force-extension curve in the case using crown-ether-unmodified tip and (*S*)-3-modified substrate.

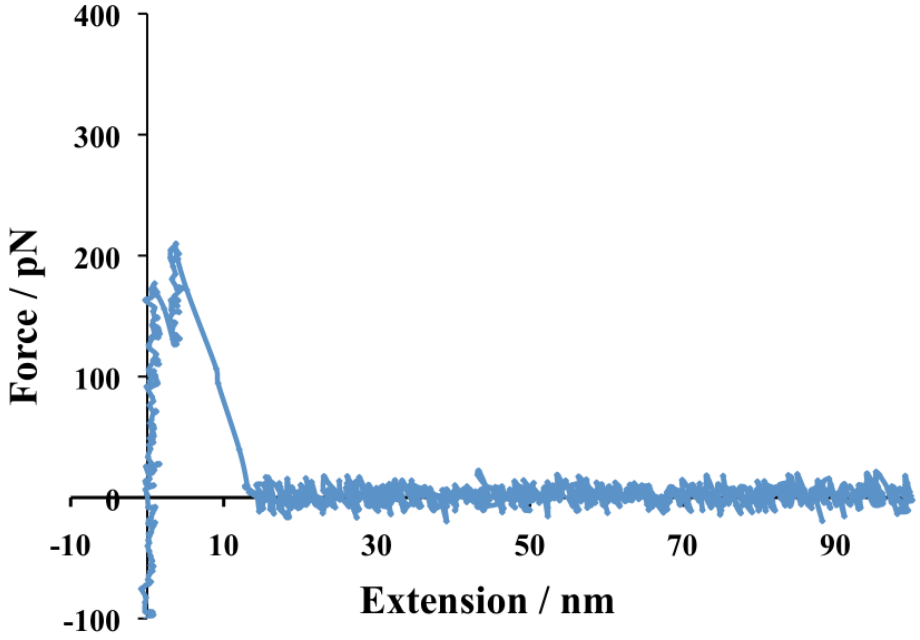

Fig. S5 Force-extension curve observed using crown-ether-unmodified tip and (*S*)-**3**-modified substrate in ethanol.

6) Typical force-extension curve badly fitting with WLC model plot.

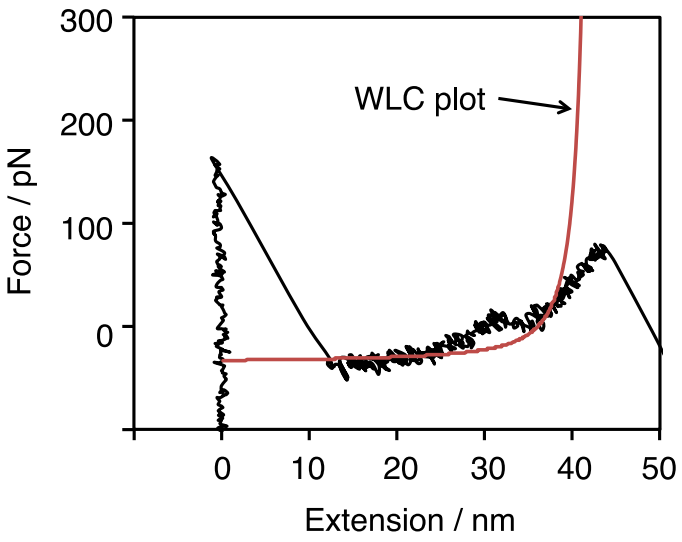

Fig. S6 Typical force-extension curve badly fitting with WLC model plot.