

Stress dissipation in cucurbit[8]uril ternary complex small molecule adhesives

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S.1 Instrumentation and Materials

¹H and ¹³C NMR (400 MHz) spectra were recorded using an Avance QNP 400 (Bruker BioSpin GmbH, Rheinstetten, Germany). Chemical shifts were recorded in ppm (δ) in CHCl₃ with the internal reference set to δ 7.19 ppm for ¹H and 77.2 ppm for ¹³C. Extended ¹H and ¹³C NMR spectra were recorded on an AVANCE 500 Cryo FT-NMR spectrometer, all at 25 °C.

Gel permeation chromatography (GPC) was carried out in tetrahydrofuran (THF) on two Jordi 5 μ m DVB columns connected in series with a SPD-M20A prominence diode array detector and refractive index detector (both Shimadzu) calibrated relative to poly(styrene) standards. Samples were filtered over 0.45 μ m PVDF filters before injection using a 1.0 ml/min flow rate.

Dynamic light scattering (DLS) measurements were carried out on a Zetasizer nanoNS (Malvern Instruments, Malvern, UK) at 25°C.

Atomic force microscopy (AFM) topographical measurements were performed using a Digital Instruments cpII AFM in non-contact mode using RTESPA silicon tips (Bruker Nano Surface, Coventry, UK). Bulk force distance spectroscopy measurements and single molecule force spectroscopy were carried out on a MFP3D AFM (Asylum Research, Goleta, CA, USA) with iDrive cantilevers (Asylum Research) for bulk measurements and OMCL-TR400PSA cantilevers (Olympus, Japan) with a spring constant of approx. 0.08 N/m for single molecule experiments.

Unless otherwise stated, chemicals were used as received from Sigma-Aldrich Chemical Company (Dorset, UK) without further purification. AIBN (2,2'-azobis(isobutyronitrile)) was recrystallized twice from methanol. Dry solvents were obtained by passing over a column of activated alumina on a PureSolv MD7 solvent purification system from Inert Technology (Amesbury, MA, USA).

S.2 General Synthetic Protocols

S.2.1 Preparation of the relevant silane units

Synthesis of methyl viologen-(3-(triethoxysilyl)propyl)carbamate(bis)tetrafluoroborate, 2. Precursor **1**, was synthesized from a literature procedure. In brief, a monomethyl bipyridinium was refluxed with 2-bromoethanol overnight in acetonitrile and then precipitated as the PF_6^- salt from aqueous solution. Ion exchange with NaBF_4 resulted in the BF_4^- salt used in further manipulations. Compound **1** (Figure S1) (0.30 g, 0.80 mmol), was added to a solution of 3-isocyanatopropyl-triethoxysilane (0.18 g, 0.73 mmol) in anhydrous acetonitrile (20 ml). Di-*n*-butyltindilaurate (1-2 drops) was added to the solution and allowed to stir overnight (24 h). The solvent was removed under reduced pressure to yield 0.34 g (>99%) of product as a red solid without further purification.

Synthesis of azobenzene-(3-(triethoxysilyl)propyl)carbamate(bis)tetrafluoroborate, 3. 4-Phenylazophenol (1.92 g, 9.70 mmol) was added to a solution of 3-isocyanatopropyl-triethoxysilane (2.00 g, 8.06 mmol) in anhydrous DCM (50 ml). Di-*n*-butyltindilaurate (1-2 drops) was added to the solution and allowed to stir overnight (24 h). The solvent was removed under reduced pressure to yield 3.60 g (>99%) of product as a bright orange viscous liquid without further purification. Elemental analysis: $\text{C}_{22}\text{H}_{31}\text{N}_3\text{O}_5\text{Si}$; expected C, 59.30; H, 7.01; found C, 60.05; H, 7.22; ^1H NMR (400 MHz, CDCl_3) δ = 7.82 (4H, m, N=N-C-CH), 7.40 (3H, m, N=N-C-CH-CH-CH), 7.20 (2H, m, O-C-CH), 3.77 (6H, q, Si-O-CH₂-CH₃), 3.23 (2H, q, Si-CH₂-CH₂-CH₂-N), 1.67 (2H, q, Si-CH₂-CH₂-CH₂-N), 1.16 (9H, t, Si-O-CH₂-CH₃) ^{13}C NMR (400 MHz, CDCl_3) δ = 154.11, 156.26, 152.60, 149.76, 130.87, 129.04, 124.90, 122.79, 122.55, 122.00, 58.54, 43.57, 23.05, 12.84, 7.73.

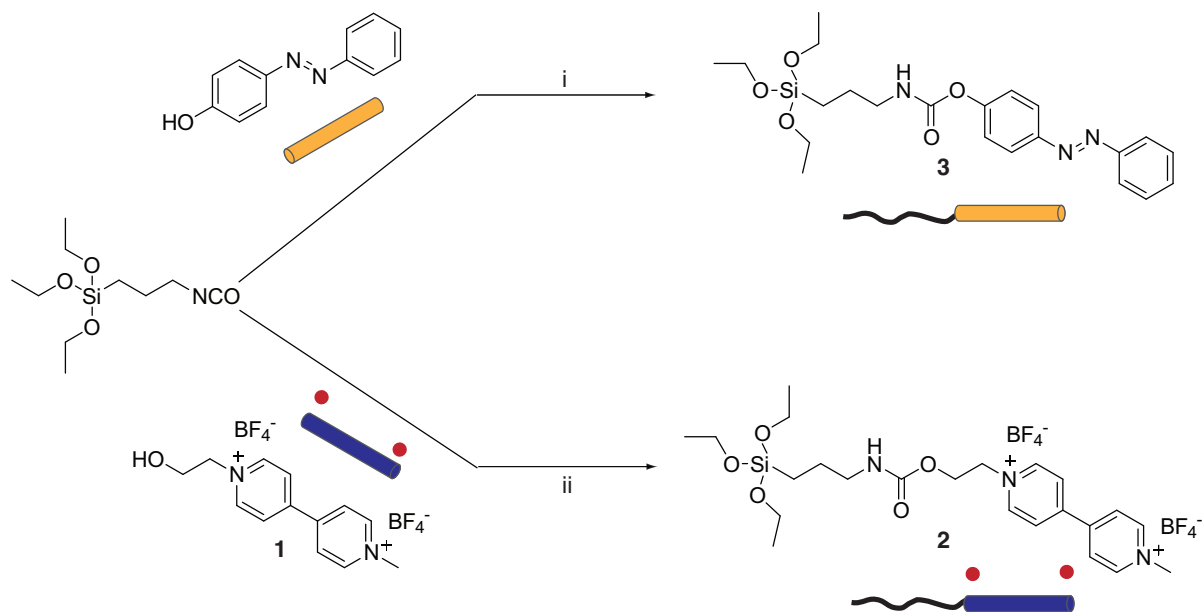


Figure S1: Schematic of the functionalization of azobenzene (yellow stick) and methyl viologen (blue stick) with silane groups to allow chemical modification of silica surfaces

S.2.2 Synthesis of dye-tagged azobenzene for visualization of surface assembly

Synthesis of azobenzene labeled rhodamine B. 4-Phenylazophenol (0.06 g, 0.03 mmol) was added to a solution of rhodamine B isothiocyanate (0.02 g, 0.04 mmol) in anhydrous acetonitrile (2 ml). Di-*n*-butyltindilaurate (1 drop) was added to the solution and allowed to stir overnight (24 h). The solvent was removed under reduced pressure to yield the final product without further purification and characterization.

S.2.3 Preparation of functionalized gold nanoparticles for visualization of surface assembly

Synthesis of tri(ethylene glycol)-1-butanethiol. First, tri(ethylene glycol)-1-butene was synthesized by reacting potassium hydroxide (1.61 g, 28.7 mmol) with triethylene glycol (4.63 ml, 33.9 mmol) and the mixture was stirred to aid dissolution. When all potassium hydroxide was dissolved the solution was cooled to -20 °C and 4-bromo-1-butene (2.5 ml, 24.6 mmol) was added drop-wise. The mixture was stirred at room temperature for 30 min and then at 60 °C for 3 h. After cooling, the mixture was partitioned between DCM/H₂O (1:1). The aqueous layer was collected, washed with DCM (2 x 75 ml) and dried with magnesium sulfate (MgSO₄). The crude product was collected and concentrated under reduced pressure before being purified by column chromatography (ethyl acetate/ethanol/H₂O, 25:2:1). The product was dried to give 0.26 g (5.1%). ¹H NMR (500 MHz, CDCl₃) δ = 5.27 (m, 1H), 5.00 (m, 2H), 3.60 (m, 12H), 3.46 (m, 2H), 2.40 (s, 1H), 2.38 (m, 2H) Tri(ethylene glycol)-1-butene (0.15 mg, 0.73 mmol) was then further reacted with azobisisobutyronitrile (AIBN) (0.02 g, 0.14 mmol) and thioacetic acid (0.20 g, 2.6 mmol) in toluene (3 ml). The solution was irradiated at 365 nm, under N₂, with a UV lamp for 5 h with gentle stirring. The resultant mixture was dissolved in DCM (50 ml) and washed with 1 M NaHCO₃ (50 ml). The organic layer was collected and washed with 1 M NH₄Cl (3 x 50 ml) before being concentrated under reduced pressure. The crude product was purified by column chromatography (ethyl acetate/ethanol/H₂O, 25:2:1) to give 128 mg (62.5%). ¹H NMR (500 MHz, CDCl₃) δ = 3.60 (m, 13H), 3.46 (m, 2H), 2.85 (m, 2H), 2.30 (s, 3H), 1.6 (m, 4H). Finally, the tri(ethylene glycol)-1-butanethioacetic acid (0.14 g, 0.50 mmol) was dissolved in methanol (1.5 ml) and added to 1.25 M HCl in methanol (1.5 ml). The mixture was refluxed for 5 h. The solvent was removed under reduced pressure to give pure tri(ethylene glycol)-1-butanethiol, 0.11 g (91.5%). ¹H NMR (500 MHz, CDCl₃) δ = 3.60 (m, 12H), 3.46 (m, 2H), 2.52 (s, 2H), 2.18 (s, 4H), 1.66 (t, 4H), 1.33 (s, 1H). ¹³C NMR (500 MHz, CDCl₃) δ = 72.5, 70.8, 70.8, 70.6, 70.6, 70.5, 70.3, 70.2, 70.1, 69.0, 61.8, 38.7, 30.7, 28.4, 28.3, 25.8, 25.8, 24.5. Mass Spec = 261.17 [M⁺⁺Na⁺]⁺.

Synthesis of 11-(2-naphthoxy)-1-undecanethiol. First, 11-(2-naphthoxy)-1-undecene was prepared by adding potassium carbonate (0.726 g, 5.25 mmol) to a solution of 2-naphthol (0.50 g, 3.5 mmol), and 11-bromoundeca-1-ene (0.377 ml, 1.7 mmol) in acetonitrile (50 ml) in a dry, two-neck, round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser and a rubber septum. The mixture was refluxed overnight under N₂. Reaction progress was monitored by thin layer chromatography (TLC) (5% ethyl acetate in hexane). The solvent was removed under reduced pressure and the crude product washed with DCM (20 ml) and then H₂O (2 x 20 ml) to remove salts. The crude product was purified by column chromatography (5% EtOAc in petroleum ether) to give 0.40 g (78%) of analytically pure product. ¹H NMR (500 MHz, CDCl₃) δ = 7.70 (m, 3H), 7.40 (t, 1H), 7.38 (t, 1H), 7.13 (m, 2H), 5.81 (m, 1H), 4.96 (m, 2H), 2.04 (m, 2H), 1.84 (m, 2H), 1.50 (m, 2H), 1.34 (m, 10H). 11-(2-naphthoxy)-1-undecathioacetate was then prepared by reacting the 11-(2-naphthoxy)-undeca-1-ene (0.40 g, 1.3 mmol) with thioacetic acid (0.4 g, 5.2 mmol) in toluene (6 ml). To this solution freshly recrystallized AIBN (0.05 g, 0.26 mmol) was added and the solution irradiated at 365 nm, under nitrogen, with a UV lamp (5 h) with gentle stirring. The solvent was removed on a rotary evaporator and the crude product partitioned between DCM/1 M NaHCO₃ (1:1, 100 ml). The

organic phase was then washed with 1 M NH_4Cl solution (3 x 50 ml) and dried over MgSO_4 . The crude product was concentrated and then purified by column chromatography (10% EtOAc in petroleum spirits) to give 0.24 g (50%) of product. ^1H NMR (500 MHz, CDCl_3) δ = 7.70 (m, 3H), 7.40 (t, 1H), 7.38 (t, 1H), 7.13 (m, 2H), 4.5 (t, 2H), 2.83 (t, 2H), 2.30 (s, 3H), 1.82 (m, 2H), 1.53 (m, 2H), 1.47 (m, 2H), 1.30 (m, 12H). Finally, 11-(2-naphthoxy)-undeca-1-thioacetic acid (0.23 g, 0.68 mmol) was dissolved in methanol/ethanol (1:1, 1.5 ml). To this was added 1.25 M HCl in methanol (1.5 ml) and the mixture was refluxed for 5 h under N_2 . Solvent was evaporated on the rotary evaporator to give 0.18 g of product in a quantitative yield, with no further purification required. ^1H NMR (500 MHz, CDCl_3) δ = 7.70 (m, 3H), 7.40 (t, 1H), 7.38 (t, 1H), 7.13 (m, 2H), 4.05 (t, 2H), 2.50 (q, 2H), 1.82 (m, 2H), 1.58 (m, 2H), 1.47 (m, 2H), 1.30 (m, 14H). ^{13}C NMR (500 MHz, CDCl_3) δ = 157.0, 134.6, 129.3, 128.8, 127.6, 126.6, 126.2, 123.4, 119.0, 106.5, 68.0, 39.1, 34.0, 29.5, 29.5, 29.5, 29.3, 29.2, 29.1, 29.0, 28.5, 28.3, 26.0, 24.6. Mass Spec = 330.25

Synthesis of citrate-stabilized 20 nm gold nanoparticles (AuNPs). A 30 mM stock solution of HAuCl_4 (0.63 ml, 0.019 mmol) was added to a round-bottomed flask (RBF) and diluted with H_2O (48 ml), forming a pale yellow solution. The solution was heated to reflux with vigorous stirring. In a separate flask, sodium citrate (300 mg, 1.16 mmol) was dissolved in 6.7 ml H_2O . The resultant diameter of the AuNPs depends on the amount of sodium citrate solution added. Varying amounts of sodium citrate solution were injected into the boiling HAuCl_4 solution (injection time approx. 1 s). The solution immediately changed color and within 10 min the color of the solution became red, purple or blue depending on the diameter of the resulting NPs. [THIS IS INCOMPLETE]

Functionalization of 20nm AuNPs. Once prepared, the 20 nm AuNPs (5 ml) were combined with a surfactant (Tween 20, 15% wt.%, 100 μl) and incubated for 30 min, followed by the addition of the desired ratio of ligands (triethylene glycol-1-butanethiol and 11-(2-naphthoxy)-1-undecanethiol). 11-(2-naphthoxy)-1-undecanethiol was dissolved in 50:50 DMF/water and the ligands were mixed before adding to the AuNP solution. The mixture was incubated for 48 h and the pure NPs separated by three centrifuge washes against Millipore water.

General procedure for mica surface functionalization. Mica (11 mm x 11 mm x 0.5 mm) was washed with hexane, acetone, water and methanol, respectively, and dried under N_2 . The cleaned surfaces were then plasma oxidized (10 min) to create silanol functionalities on the surface. The treated surfaces were immediately placed into a solution of either methyl viologen-(3-(triethoxysilyl)propyl)carbamate(*bis*)tetrafluoroborate or azobenzene-(3-(triethoxysilyl)propyl)carbamate(*bis*)tetrafluoroborate and stirred on an automatic stirrer (48 h). Solutions consisted of methyl viologen-(3-(triethoxysilyl)propyl)carbamate(*bis*)tetrafluoroborate (5 mg, 0.01 mmol) in anhydrous 1-methyl-2-pyrrolidinone (2 ml) or azobenzene-(3-(triethoxysilyl)propyl)carbamate(*bis*)tetrafluoroborate (5 mg, 0.01 mmol) in anhydrous toluene (2 ml). Functionalized surfaces were cleaned with hexane, acetone, water and methanol, respectively, and dried under N_2 .

S.3 Characterization of surface functionalization and assembly with contact angle measurements

Surface functionalization was verified using contact angle measurements carried out on a First Ten Ångströms FTA2000 contact angle instrument (Portsmouth, VA, USA). Images of the contact angle measurement alongside the graphical representation of the surface are shown in Figure S2. The exchange of the methyl viologen counterion from BF_4^- to Cl^- results in a more hydrophilic surface and a drop in the surface contact angle from 31° to 24° , Figure S2B and C. The switching of the azobenzene from the *trans* to the *cis* configuration and back with the application of UV and visible light, respectively, produces no significant change in the hydrophobicity of the surface, Figure S2D and E.

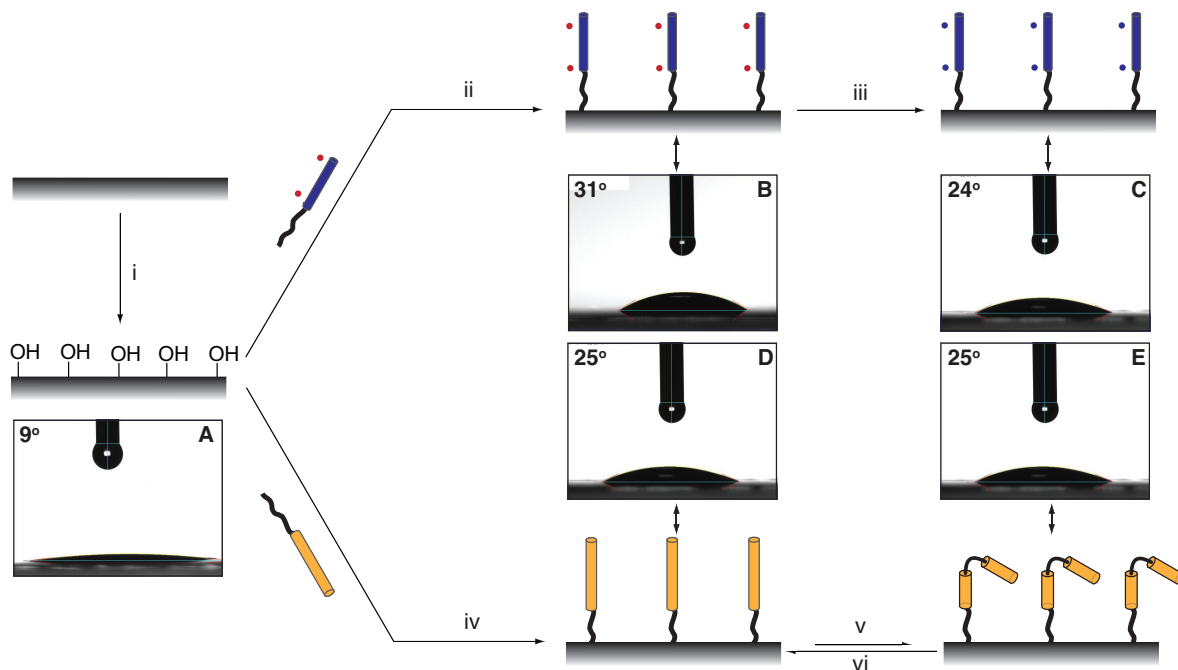


Figure S2: Contact angle measurements of (A) a bare mica surface after plasma oxidation (i) to expose surface silanol groups, (B) a methyl viologen silane–functionalized mica surface directly after preparation (ii) with BF_4^- counterions, (C) a methyl viologen silane–functionalized mica surface after counterion exchange (iii) from BF_4^- to Cl^- , (D) an azobenzene silane–functionalized (iv) mica surface under visible light (vi) and (E) under UV light (v).

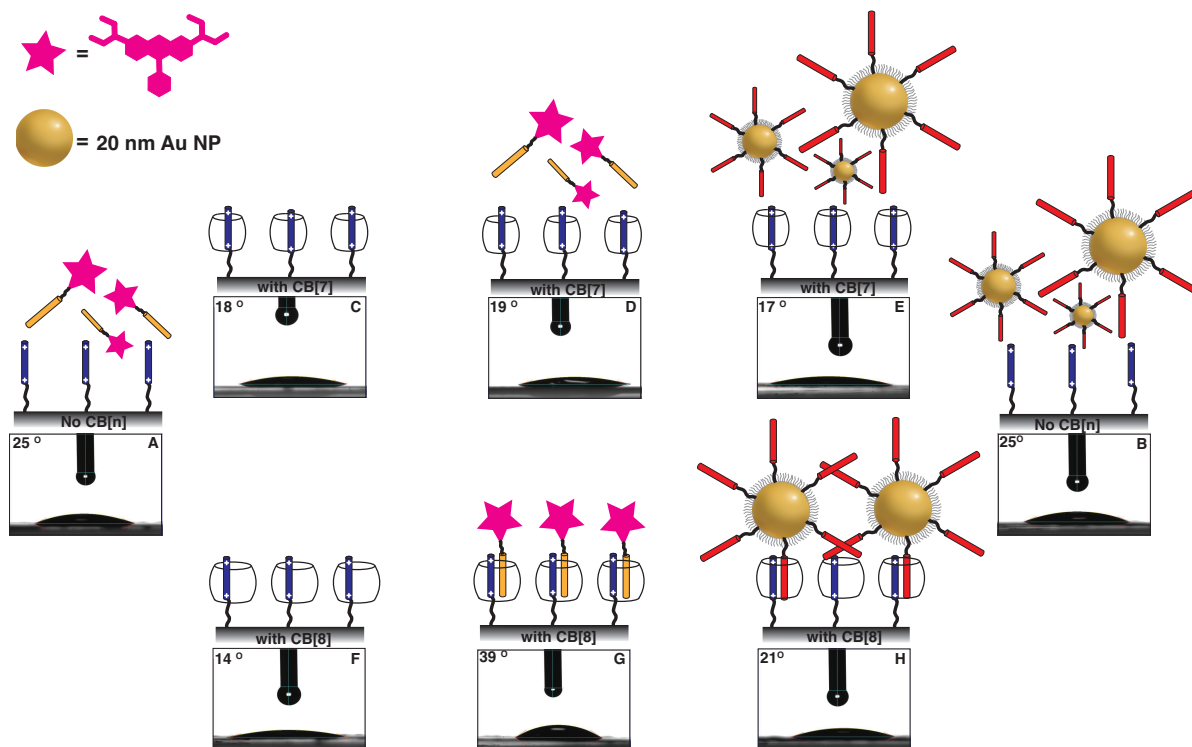


Figure S3: Contact angle measurements of mica-1 in the presence of (F) a rhodamine-tagged azobenzene (Rh-Azo), (G) 20 nm naphthol-modified Au nanoparticles (Np-AuNP), (H) a 0.2 mM solution of CB[7], (I) Rh-Azo and a 0.2 mM solution of CB[7], (J) Np-AuNP and a 0.2 mM solution of CB[7], (K) a 0.2 mM solution of CB[8], (L) Rh-Azo and a 0.2 mM solution of CB[8] and (M) Np-AuNP and a 0.2 mM solution of CB[8].

S.4 Quantification of binding sites on mica surfaces using AFM topographical images

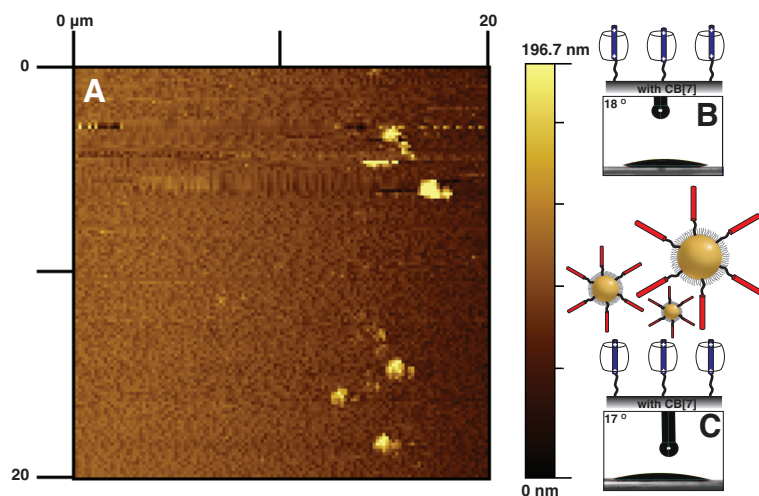


Figure S4: (A) Atomic force microscopy images of a mica-1 surface immersed in a 0.2 mM solution of CB[7] followed by a concentrated solution of Np-AuNPs. Contact angle measurements of a mica-1 surface after immersion in (B) a 0.2 mM solution of CB[7] and (C) a 0.2 mM solution of CB[7] followed by a concentrated solution of Np-AuNPs.

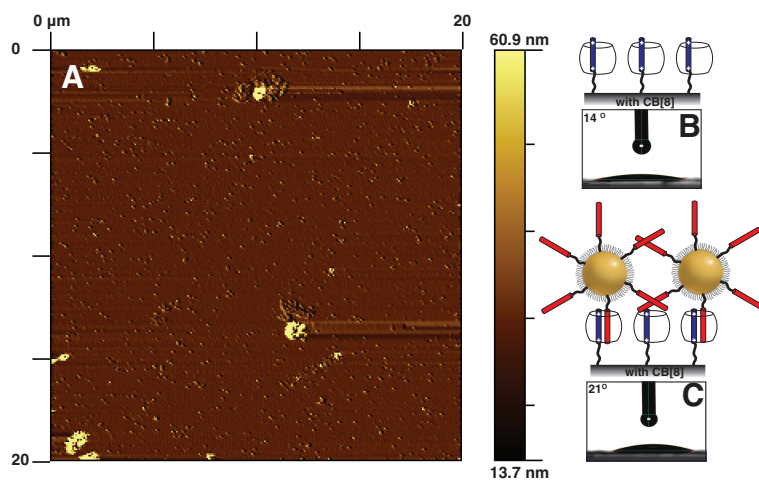


Figure S5: (A) Atomic force microscopy images of a mica-1 surface immersed in a 0.2 mM solution of CB[8] followed by a concentrated solution of Np-AuNPs. Contact angle measurements of a mica-1 surface after immersion in (B) a 0.2 mM solution of CB[8] and (C) a 0.2 mM solution of CB[8] followed by a concentrated solution of Np-AuNPs.

S.5 Quantification of force of interaction of the methyl viologen · CB[8] · azobenzene heteroternary complex by single molecule force spectroscopy

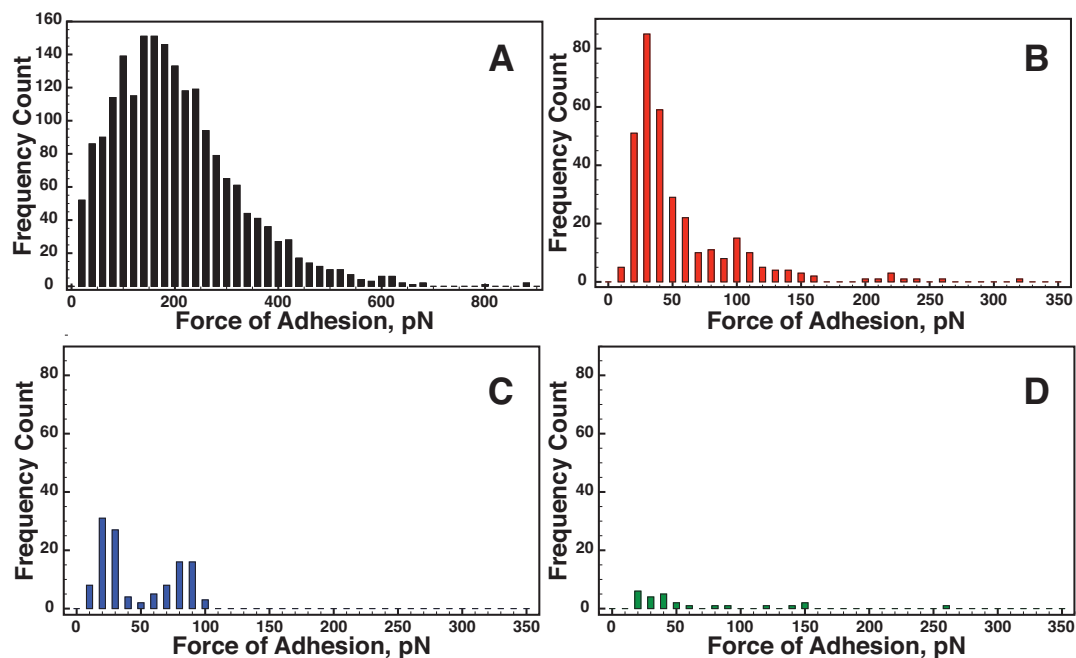


Figure S6: Frequency plots obtained from force spectroscopy data showing the force and frequency of (A) non-specific tip-surface interactions, (B) specific tip-surface interactions of the ternary complex, (C) specific tip-surface hydrophobic interactions, and (D) specific tip-surface portal interactions.

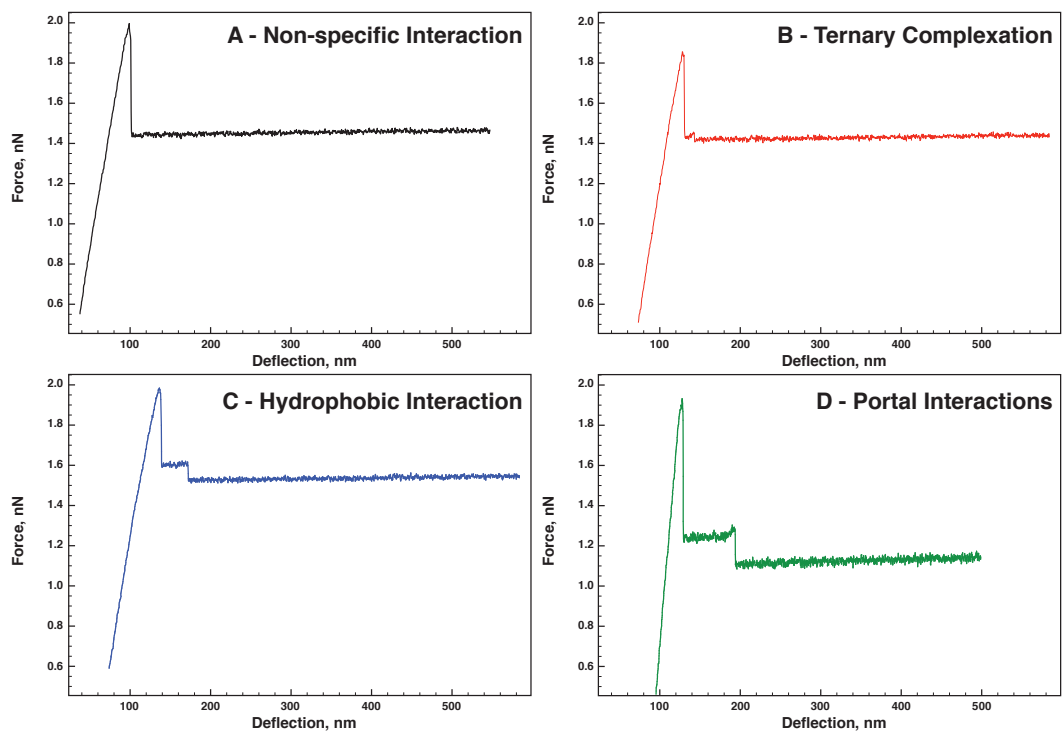


Figure S7: Examples of single molecule force spectra taken on the retraction of the tip from the surface showing (A) non-specific tip-surface interactions, (B) specific tip-surface interactions of the ternary complex, (C) specific tip-surface hydrophobic interactions, and (D) specific tip-surface portal interactions.

S.6 Calculation of approximate adhesive forces from macroscale adhesion of functionalized surfaces and bulk force distance spectroscopy experiments

Macroscale adhesion of functionalized surfaces Experiments are carried out on functionalized mica surfaces with a surface area (a) of 2.5 cm x 2.5 cm, that is;

$$a = 0.025 \text{ m} \times 0.025 \text{ m} = 6.25 \times 10^{-4} \text{ m}^2 \quad (\text{S1})$$

A 100 g weight is applied to each pair of surfaces, thus the force (F) applied to each individual surface can be calculated by

$$F = m.a \quad (\text{S2})$$

where a is acceleration due to gravity, $9.81 \text{ m}^2.\text{s}^{-1}$, and m is 0.1 kg, thus

$$F = 0.1 \text{ kg} \times 9.81 \text{ m}^2.\text{s}^{-1} \quad (\text{S3})$$

$$F = 0.981 \text{ kg}.\text{m}^2.\text{s}^{-1} \quad (\text{S4})$$

or

$$F = 0.981 \text{ N} \quad (\text{S5})$$

A force of 0.981 N over a surface area of $6.25 \times 10^{-4} \text{ m}^2$ equates to $1569.6 \text{ N}.\text{m}^{-2}$

From the AFM experiments carried out in Section S5 above it is known that each surface contains 1×10^9 MV units per mm^2 or 1×10^{15} per m^2 , thus the total force per binding site (Force of adhesion, F_{adh}) is

$$F_{adh} = 1569.6 \text{ N}.\text{m}^{-2} \div 1 \times 10^{15} \text{ m}^2 F_{adh} = 1.57 \times 10^{-12} \text{ N} F_{adh} = 1.57 \text{ nN} (\text{S6})$$

Bulk force distance spectroscopy As shown in Figure 3 of the main article, the approximate F_{adh} for the ternary complex on the bulk surface is in the order of 40 nN.

From the tip specifications, the tip radius is 20 nm, thus the surface area of the tip can be calculated by the area of a circle,

$$\pi r^2 = \pi \times 20 \times 10^{-9} \text{ m}^2 = 1.26 \times 10^{-15} \text{ m}^2 \quad (\text{S7})$$

Each gold atom on the tip surface is capable of binding an thiolated azobenzene unit through the S-H bond. The atomic radius of gold is 166 pm, thus the area of each Au atom is

$$\pi r^2 = \pi \times 166 \times 10^{-12} \text{ m}^2 = 8.66 \times 10^{-20} \text{ m}^2 \quad (\text{S8})$$

Thus, the number of potential binding sites on the surface can be calculated by

$$1.26 \times 10^{-15} \text{ m}^2 \div 8.66 \times 10^{-20} \text{ m}^2 = 14549.65 \quad (\text{S9})$$

or 14,550 potential sites.

The interaction force of 1 tip–surface interaction was estimated from bulk force distance experiments to be 40 nN, from single molecule experiments the actual value appears closer to 30 pN (Figure S5B). If this is the case, then 1333 ternary complexes must interact simultaneously to produce a force of 40 nN per tip–surface contact, this equates to approx. 9.2% of the available binding sites on the tip. Non-specific interactions must also be taken into account as they abound in such complex systems. Figure S5A suggests this interaction force to be in the region of 150 pN for this system, thus a combined force of approximately 180 pN is a result of 1 ternary complexation at the surface. This would equate to 222 simultaneous interactions or just 1.5% of the total available interaction sites, assuming all were filled with a methyl viologen unit. From the macroscopic experiments the value for each individual interaction appears to be in the region of 1.597 nN, bringing the actual number of simultaneous interactions to just 25 or 0.17% of the available sites on the tip surface.

S.7 Visualization of the photo-switchable adhesive properties of the functionalized surfaces

Further detail can be seen in the supplementary videos.

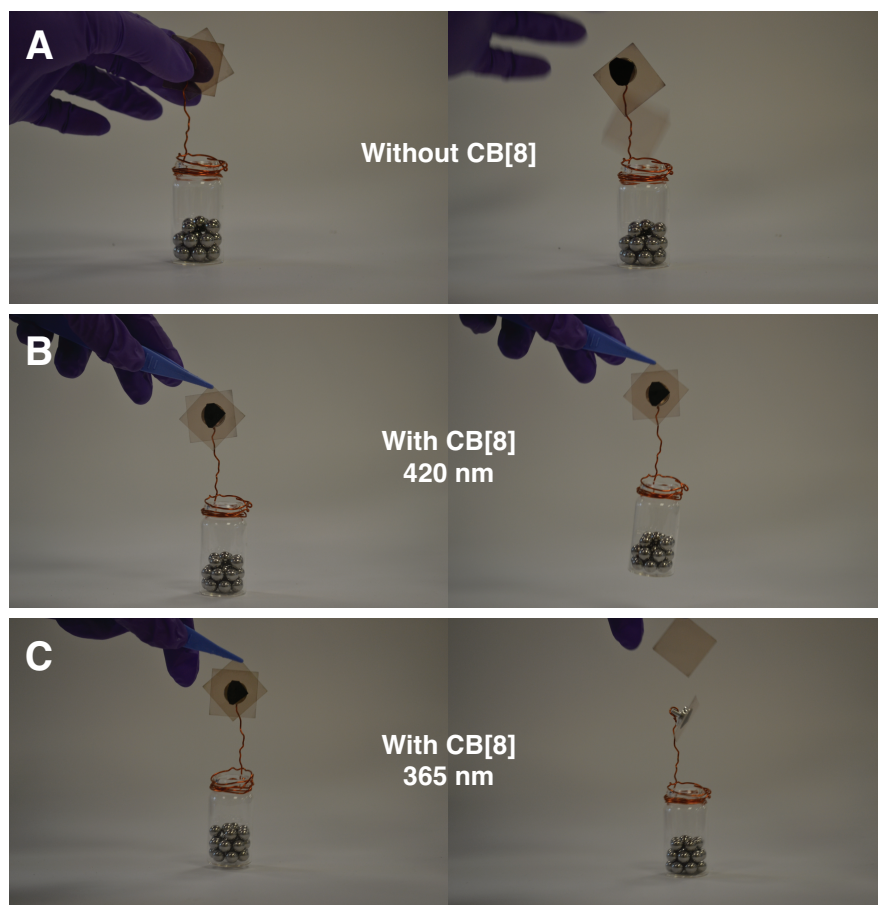


Figure S8: Photographic images of a mica-1 surface with a 100 g weight attached brought in contact with a mica-2 surface (A) in the presence of pure H₂O, (B) in the presence of a 0.2 mM solution of CB[8] under irradiation at 420 nm, and (C) in the presence of a 0.2 mM solution of CB[8] under irradiation at 365 nm.