Supporting Information:

Tailoring the mechanics of ultrathin carbon nanomembranes by molecular design

Xianghui Zhang, Christof Neumann, Polina Angelova, André Beyer, Armin Gölzhäuser*

Physics of Supramolecular Systems and Surfaces, University of Bielefeld, Bielefeld 33615, Germany

Contents

1. Experimental section

1.1 SAMs from different precursor molecules

Monolayers from 1,1' – biphenyl-4-thiol (BPT) and [1",4',1',1]-Terphenyl-4-thiol (TPT): A cleaned gold substrate was immersed in 1 mmol solution of BPT (or TPT) in dry and degassed dimethylformamide (DMF). For BPT the solution was kept under nitrogen at room temperature for 72 hours, while for TPT the solution was heated at 70°C under argon atmosphere for 24 hours. Then the samples were removed from solution, rinsed with DMF as well as ethanol (EtOH) and blown dry with nitrogen.

SAMs from hexa-peri-hexabenzocoronene (HBC) derivatives: 0.1 mg of the respective ethanethioate was dissolved in 0.2 ml tetrahydrofuran (THF) and 0.1 ml EtOH, and 20 µl NH_4OH were added. Then 5 ml dry DCM and 3 ml degassed and dry EtOH were added and a cleaned gold substrate was immersed. The sample was left for 96 hours at room temperature in a nitrogen atmosphere under exclusion of light. After removal from solution, it was rinsed with DCM and blown dry with nitrogen.

SAMs from S,S'-(3',4',5',6'-tetraphenyl-[1,1':2',1"-terphenyl]-4,4"-diyl)diethane-thioate (HPB): A cleaned gold substrate was immersed in 1 mmol solution of HPB in dry and degassed DMF. 20 µl NH_4OH were added and the mixture was left at room temperature under inert atmosphere and exclusion of light. After 72 hours the sample was removed from the solution, rinsed with DMF and dichloromethane (DCM) and blown dry with nitrogen.

Monolayers from naphthalene-2-thiol (NPTH): A cleaned gold substrate was immersed in 1 mmol solution of the respective compound in dry and degassed EtOH in a sealed flask at room

temperature under inert atmosphere and exclusion of light. After 24 hours the sample was removed from solution, rinsed with EtOH and dichloromethane and blown dry with nitrogen.

Monolayers from S-(pyren-2-ylmethyl) ethanethioate (2MP): A cleaned gold substrate was immersed in 1 mmol solution of the respective thioester in dry and degassed EtOH. 20 µl NH_4OH were added and the mixture was left at 68°C under an inert atmosphere. After 24 hours the sample was removed from the solution, rinsed with EtOH and DCM and blown dry with nitrogen.

1.2 AFM bulge test with the central point method

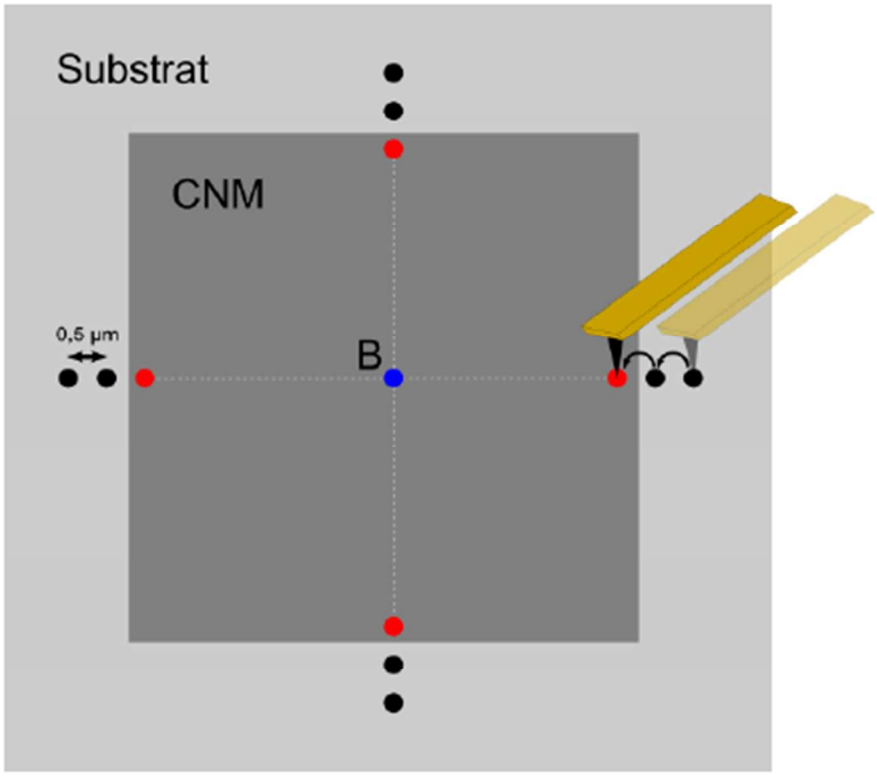

Figure S1 The scheme to determine the centre using AFM without scanning the whole membrane

In the central point method, the AFM tip is positioned on the membrane's center to detect the deflection of the membrane. The determination of the center of the membrane is done by the

stage positioning system of the AFM instrument assisted by a light microscope for coarse adjustment. Once the edge of the membrane is approximately determined with the microscope, the sample is moved in steps of typically 0.5 µm across the edge with the tip retracted. At each step, the AFM tip is lowered to measure the local sample height. A substantial change in the AFM height signal indicates the location of the edge of the membrane. After the positions of all four edges are determined, the sample is moved to the center B of the membrane.

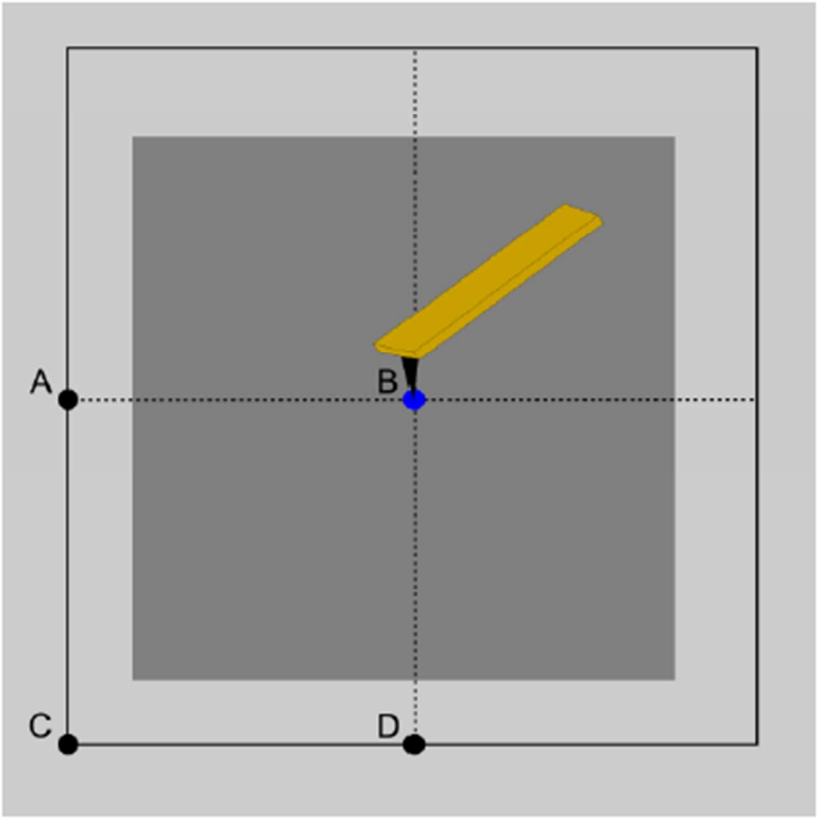

Figure S2 The scheme to determine the membrane deflection in the central point method

Due to the sample titling, one needs to determine the initial height h_B at point B by measuring additional three points on the substrate, i.e. A, C and D.

$$h_B = h_A + h_D - h_C \quad (1)$$

The membrane deflection $h(0)$ at zero applied pressure is given by

$$h(0) = h_{Measured}(0) - h_B \tag{2}$$

Due to the fact that there is a point load by AFM tip, the membrane deflection $h(0)$ is negative, usually in the range of tens of nanometer. Despite of that, the membrane is still under a tensile tension. Here we define an indentation depth $\delta(0)$ for a nonpressurized membrane as

$$\delta(0) = -h(0) \tag{3}$$

When applying a pressure p to the membrane, the whole substrate is also lifted up due to the deformation of PDMS support. Therefore, the height $h_A(p)$ of a reference point A on the substrate is always measured to give the true deflection $h(p)$ of the membrane center B,

$$h(p) = h_{Measured}(p) - h_A(p) + h_D - h_C \tag{4}$$

The indentation depth $\delta(p)$ for the membrane at an applied pressure p and pushed by the AFM tip with the same load can be estimated by considering the applied stress and the residual stress with the following equation:

$$\delta(p) = \delta(0)\frac{\sigma_0}{\sigma_0 + \frac{2\ E\ h^2}{3(1-\nu)a^2}} \tag{5}$$

The corrected membrane deflection $h(p)_{corrected}$ is given by

$$h(p)_{corrected} = h(p) + \delta(p) \tag{6}$$

2. **Deflection a BPT-CNM under constant pressure**

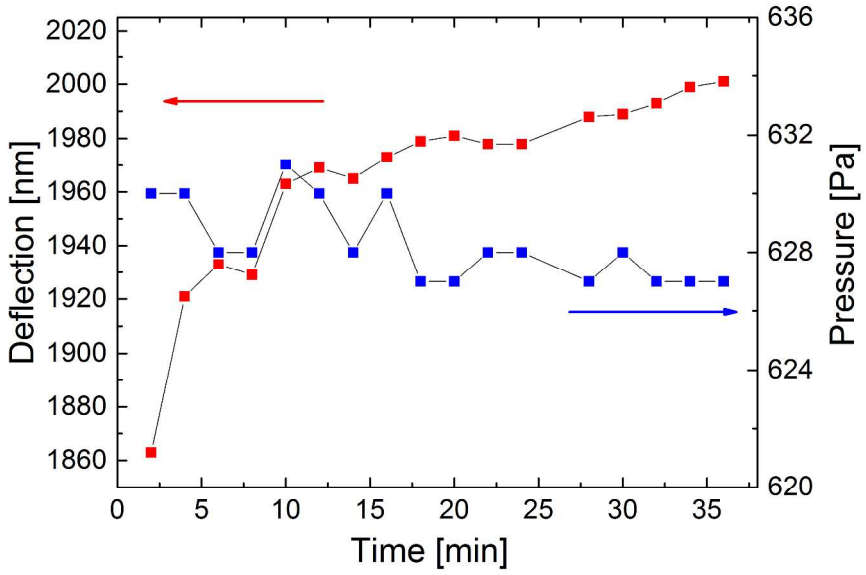

Figure S3 The creep deformation of a BPT CNM with a dimension of 47.3×46.4 μm^2: the deflection increases slowly from 1863 nm to 2001 nm within 34 minutes and the corresponding pressure only dropped slightly by 4 Pa.

3. **Indentation depth of a nonpressurized BPT-CNM over time**

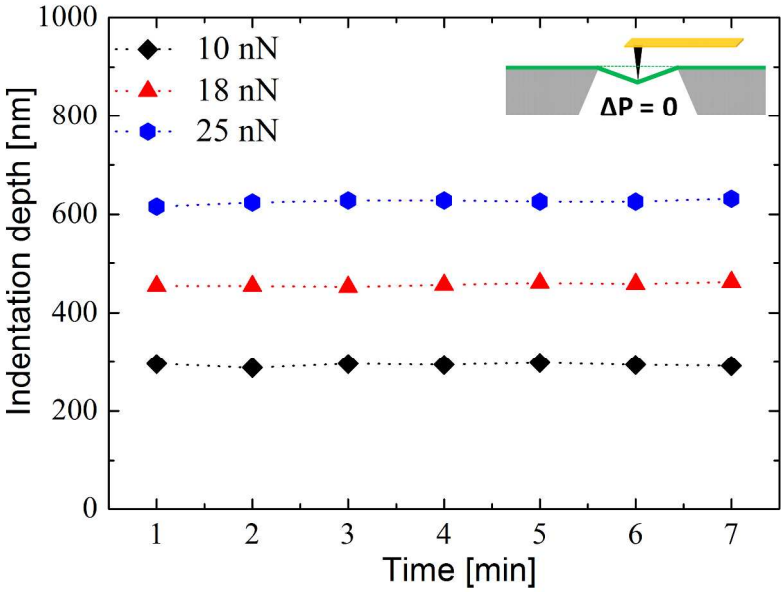

Figure S4 The indentation depths of a nonpressurized BPT-CNM were plotted over time for different point loads exerted by the AFM tip.

4. **Parameters C_1 and C_2 as a function of membrane aspect ratio**

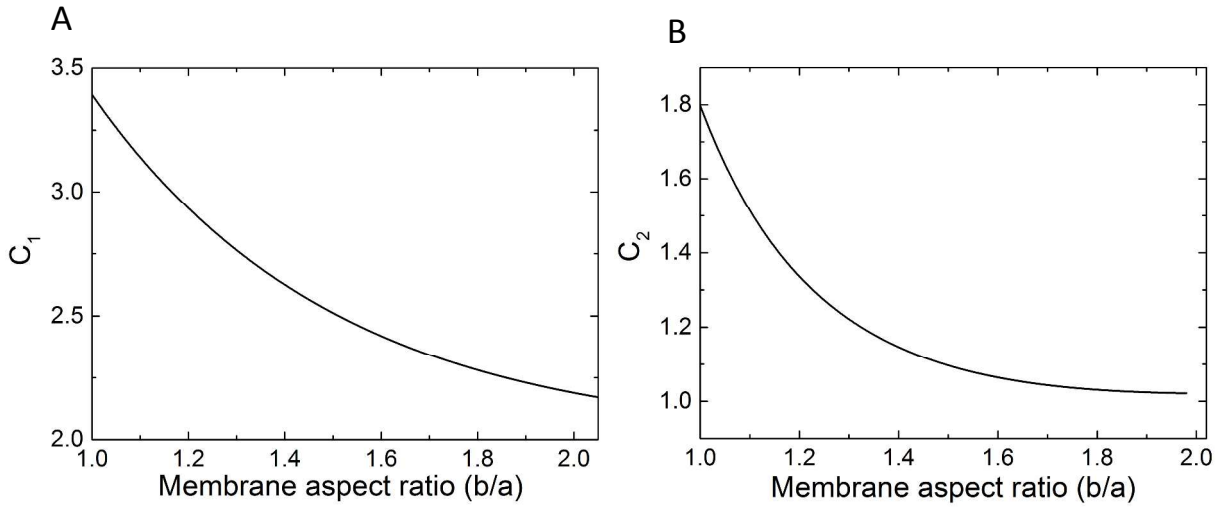

Figure S5 (A) The parameter C_1 as a function of membrane aspect ratio; (B) the parameter C_2 as a function of membrane aspect ratio for a Poisson's ratio of 0.35.

5. **Experimental results of CNMs**

Table S1 Experimental results of CNMs from different precursor molecules using AFM bulge tests

molecular precursor	thickness [Å]	sample	Dimension [μm^2]	load/ unload	E [GPa]	σ [MPa]	ε_{max} [%]	ϑ [%]
TPT	12	A2	65×65	load	7.4	14.0	1.24	26.3
				unload	11.0	32.6		
		B2	57×95	load	8.7	28.8	0.7	24.9
				unload	12.3	-0.7		
		C4	45x45	load	7.9	17.86	0.82	26.0
				unload	10.1	-9.1		
NPTH	6	B3	20x29	load	20.0	158.9	0.30	4.5
				unload	24.8	143.9		
		C1	39x80	load	16.1*	198.8*	0.52(1)	9.7(1)
				unload	22.1*	155.9*	0.71(2)	10.8(2)
2MP	8	A5	65x65	load	14.4*	86.9*	0.87(1)	16.2(1)
				unload	18.1*	38.5*	0.91(2)	19.1(2)
		D4	56x56	load	14.2	73.1	0.81	4.7
				unload	14.2	65.9		
HPB	8	D4	37x37	load	17.8	94.3	0.68	10.4
				unload	20.4	73.3		
		E2	26x34	load	14.1	50.4	0.65	18.6
				unload	18.7	16.9		
HBC	17	D1	37x55	load	13.8*	-2.2*	0.72(1)	10.9(1)
				unload	15.5*	15.1*	0.73(2)	8.4(2)
		D4	37x37	load	12.5	15.8	0.48	12.8
				unload	14.3	4.8		
		E4	27x27	load	10.2*	7.8*	0.44(1)	7.4(1)
				unload	12.2*	-0.6*	0.43(2)	10.9(2)

Notes: t is the thickness; E is the Young's modulus; σ is the residual stress; ε_{max} is the maximum applied strain; ϑ is the ratio of the dissipated energy to the stored mechanical energy; the mean value of two successive measurements is marked with an asterisk; the strain and specific damping capacity are given for each measurement marked by (1) or (2).