# SUPPORTING INFORMATION

**Sample Preparation.** The anchor spicule of the *M. chuni* collected in New Caledonia, was cut into a 5 mm thick disks with a diamond circular saw and then embedded into polymethyl methacrylate (PMMA). The samples were then polished with water suspended alumina particles down to a particle size of 300 nm.

**Modulus Mapping.** Modulus mapping across organic layers was performed by Hysitron Triboindenter TI950 equipped with a nano-DMA-II measurement system. Tip radius, as calibrated with fused quartz sample, was $R$ = 140 nm. Maps were collected from a 1 $\mu m^2$ surface area at frequency of 210 Hz. The scan rate and time constant of the low-pass filter were set appropriately for resolving a 35 nm thin spatial features[26]. In all measurements, the phase shift and, then, viscoelastic response was negligible.

**TEM and HAADF-STEM measurements.** Preliminary TEM examinations of the samples were performed by using a Jeol JEM 4010 microscope at acceleration voltage of 400 kV. STEM measurements were carried out by the aid of a FEI TITAN 80/300 S/TEM microscope operated at 300 kV. The STEM micrographs in Figs.1c and 1d were recorded in the high-angle annular dark-field mode (HAADF), which provides pure atomic number (Z) contrast. Correspondingly, in the collected images, the low-Z organic layer appears darker on the background of bright silica matrix (higher Z-value). All TEM/STEM samples were prepared from the spicule by focused ion beam (FIB) technique, using a FEO Nano 600 NanoLab instrument.

**Finite element analysis.** Finite element analysis (FEA) was performed using ABAQUS Standard 6.11. In this model, a tip with a radius of 140 nm was displaced into the structure and the resulting reaction forces were recorded. The structure was constructed using an exact surface topography measured by tapping mode AFM. Diamond tip was modeled as analytically rigid. Elastic modulus and Poisson's ratio of biosilica were 37 GPa and 0.3, respectively. The thickness of the organic layer based on STEM results was estimated to be

36 nm. Poisson's ratio of the organic layer was assumed to be 0.499 and its elastic modulus was varied to achieve best fit to experimental results. Modulus gradient at the interface was introduced to the model as a four-step function following the averaged compositional gradation at the interface (from organic layer to biosilica): 8 nm with elastic modulus of 10 GPa, 5 nm with elastic modulus of 20 GPa, 5 nm with elastic modulus of 30 GPa and 30 nm with elastic modulus of 35 GPa.

To obtain stiffness profiles across the structure, the procedure was repeated for different distances from the center of the organic layer. Only one side of the structure was scanned (from 0 to 300 nm).

Due to the mentioned composition and topography features, the load, $F$, is expected to deviate from the well-known Hertz equation:

$$F = \frac{4}{3} E_r R^{1/2} u^{3/2} \qquad (1)$$

where $u$ is the tip displacement, $E_r$ is the sample-tip reduced modulus, and $R$ is again the tip radius. In order to overcome this difficulty, the load, $F$, as a function of the displacement, $u$, was fitted to a power function:

$$F = au^b + c \qquad (2)$$

with a, $b$, and $c$ being the fitting parameters. The contact stiffness was calculated as the slope, $K$:

$$K = \frac{dF}{du} = abu^{b-1} \qquad (3)$$

This approach allowed us to extract the local stiffness at experimental load $F = F_{DC} = 3$ μN. By using this procedure, the regression coefficient, of the fit at each measurement position was higher than 0.99.