Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Intercalating cation specific self-repairing of vermiculite nanofluidic membrane

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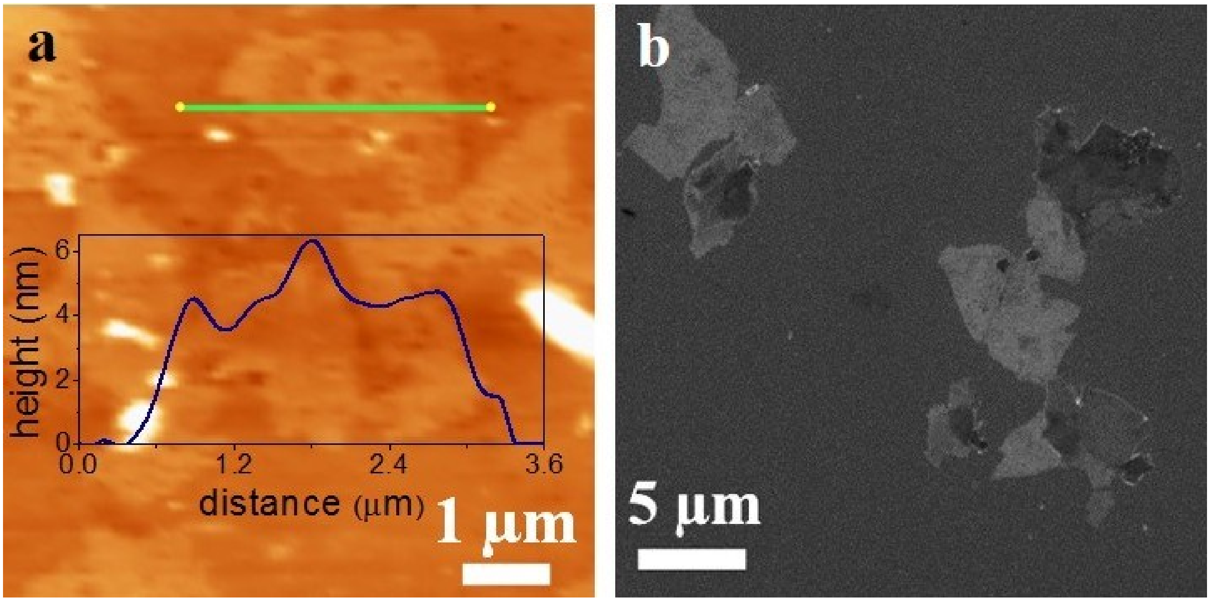

Figure S1: Microscopic images of exfoliated vermiculite layers. (a) AFM image with corresponding height profile (in the insert) and (b) FESEM image of exfoliated vermiculite layers.

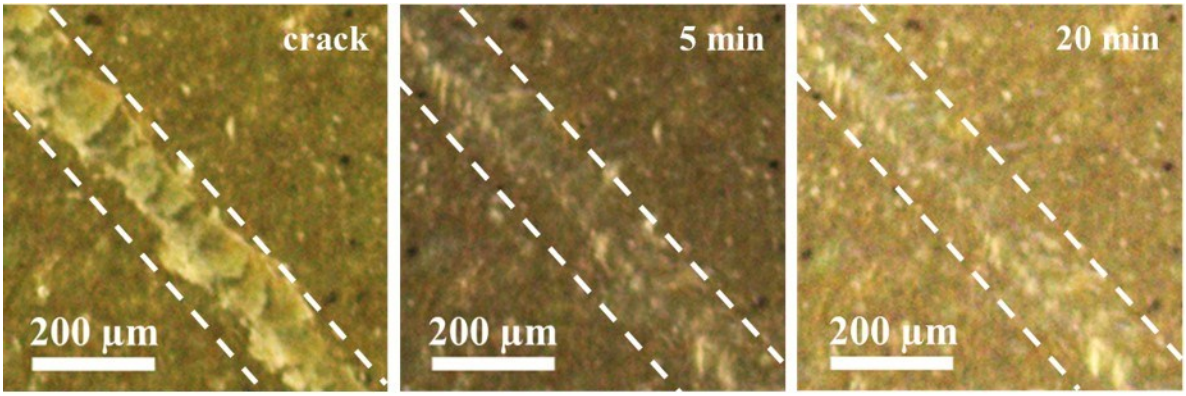

Figure S2: Healing of Li-vermiculite membrane: Optical microscopic images showing different stages of repairing of a sketch on the surface of Li-vermiculite membrane.

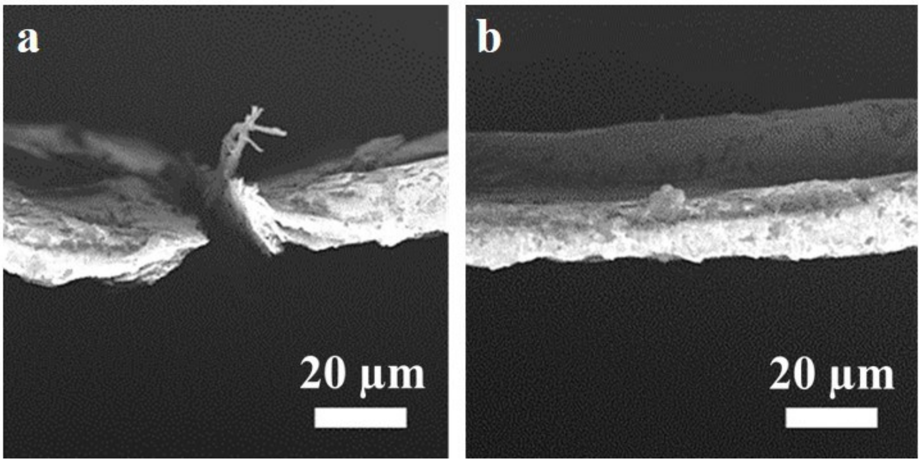

Figure S3: Cross-sectional FESEM images showing (a) cut and (b) repaired edge of a Li-vermiculite strip upon exposing to water droplet at room temperature.

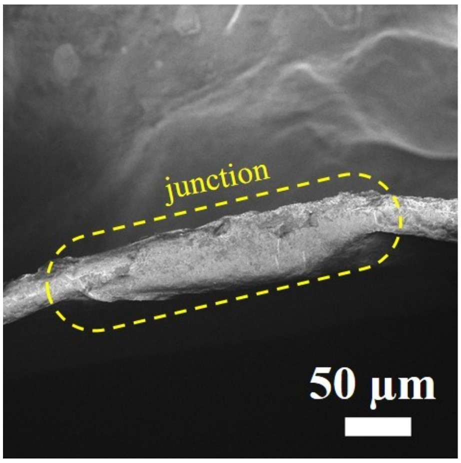

Figure S4: Cross-sectional FESEM image of the junction of two Li-vermiculite strips fused into a single piece by adding a water droplet (20 microliter).

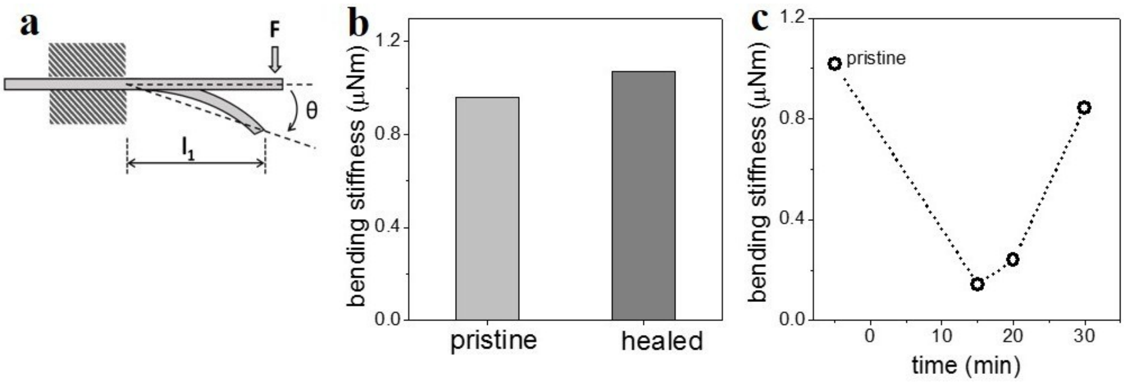

Figure S5: Bending stiffness: Schematic illustration of Lorentzen & Wettre two-point method bending stiffness measurement. (b) Bar diagrams comparing the bending stiffness of a pristine Li-vermiculite strip with the one healed at room temperature. (c) Plot showing time-dependent healing of bending stiffness of Li-vermiculite at 70 °C.

In Lorentzen & Wettre two-point method bending stiffness measurement method one end of the strip is clamped to a glass slide and force of known weight is applied to the other end. The bending stiffness (S_b) was calculated using equation below

$$S_b = \frac{60 \times F \times l^2}{\pi \times \theta \times b}$$

Where, bending force (F) = weight x gravitational constant, l = distance between the clamp and the free end, θ = defection, and b = width of the strip. The bending stiffness of a strip (30 micron, thickness).

Time-dependent healing of the mechanical properties; After measuring bending stiffness, a pristine Li-vermiculite strips was cut into two pieces such a way that one piece remains hanging to the glass slide. The edges of the broken pieces were than placed in contact with each other (supported by a glass slide), and a droplet of water (20 µl) was added to the junction. The atmospheric temperature was maintained at 70 °C to facilitate faster repairing of the strips. Stiffness values were recorded at a regular interval of time by removing the support. Figure S5c shows the variation in stiffness of healing strip as function of time.

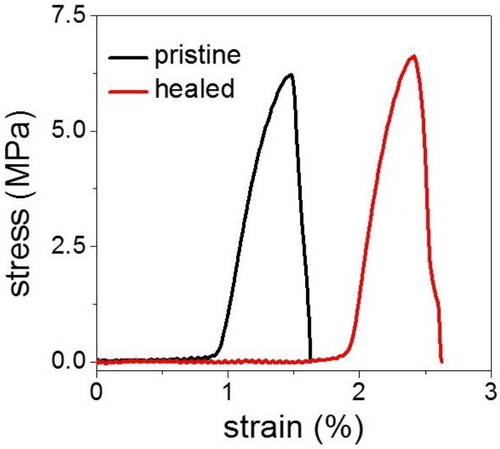

Figure S6: Stress-stain curve. Stress-stain curves of pristine and healed strips.

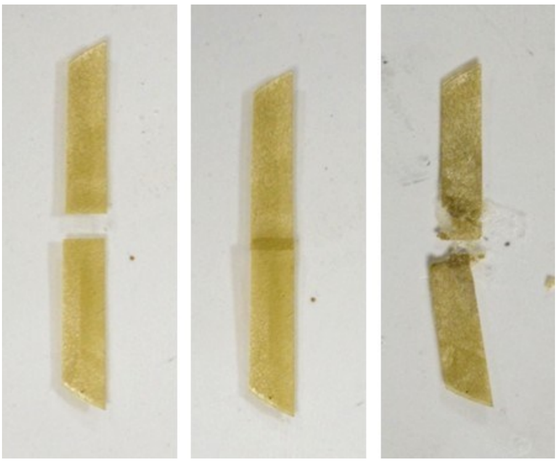

Figure S7: Photos showing damage of Li-vermiculite strips upon on addition of water droplet at 160 °C.

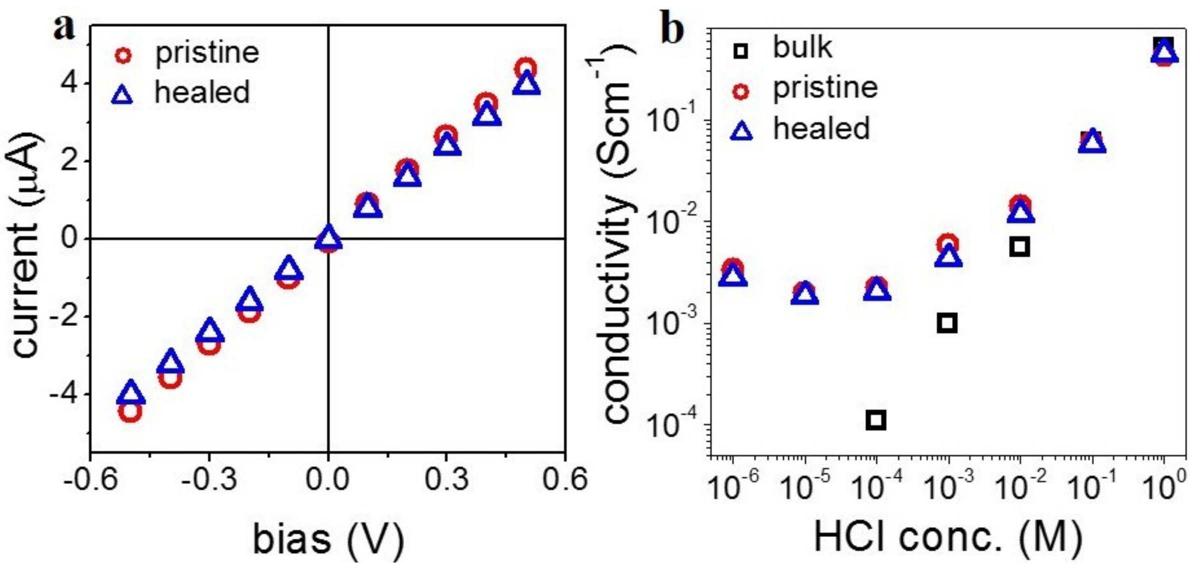

Figure S8: Surface-charged-governed proton transport of vermiculite nanofluidic devices: (a) *I-V* curves of pristine and healed nanofluidic devices at 10^{-2} M HCl as electrolyte. (b) Comparison of conductivity of as a function of HCl concentration of pristine and healed devices.

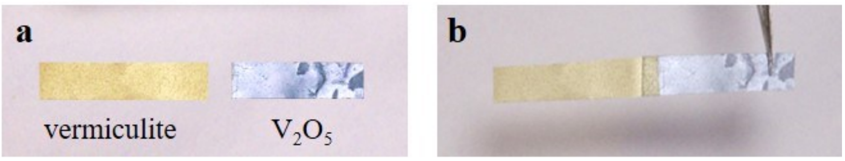

Figure S9: Photo of vermiculite strip fused with a strip of vanadium pentoxide lamellar membrane.

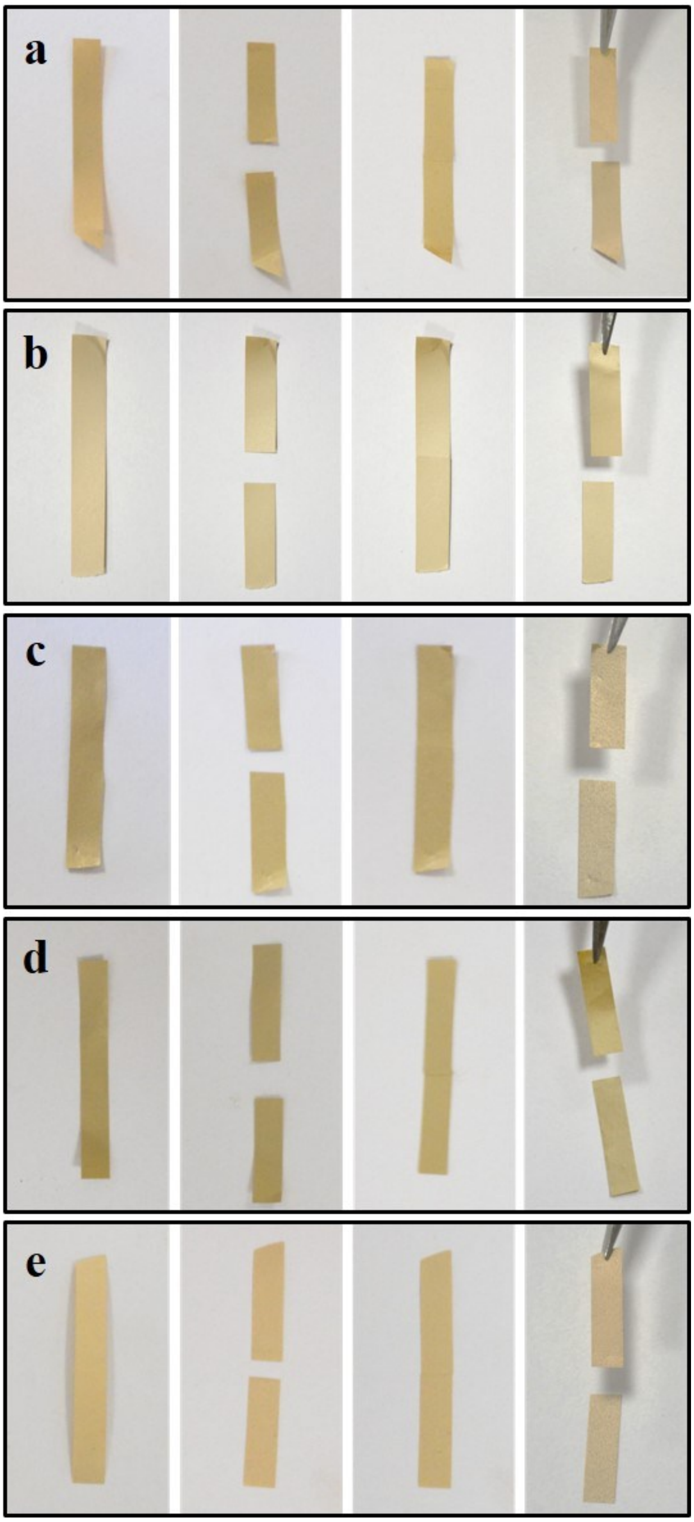

Figure S10: The water assisted healing process was repeated to re-connect broken strips made-up of vermiculite flakes charge balanced with (a) K^+, (b) Na^+, (c) Mg^{2+}, (d) Ca^{2+}, and (e) H^+ ions. Surprising, except Li-exchanged vermiculite, none of the clay strips shown water assisted healing capability.

Table 1: Expansion of vermiculite in presence of water.

Samples	Dry (nm)	Wet (nm)	Expansions (nm)
Li-vermiculite	1.35	1.65	0.30
K- vermiculite	1.54	1.58	0.04
Na- vermiculite	1.08	1.10	0.02
Mg- vermiculite	1.51	1.58	0.07
Ba- vermiculite	1.53	1.60	0.07
H- vermiculite	1.22	1.30	0.08
Li(Ba)- vermiculite	1.33	1.61	0.28

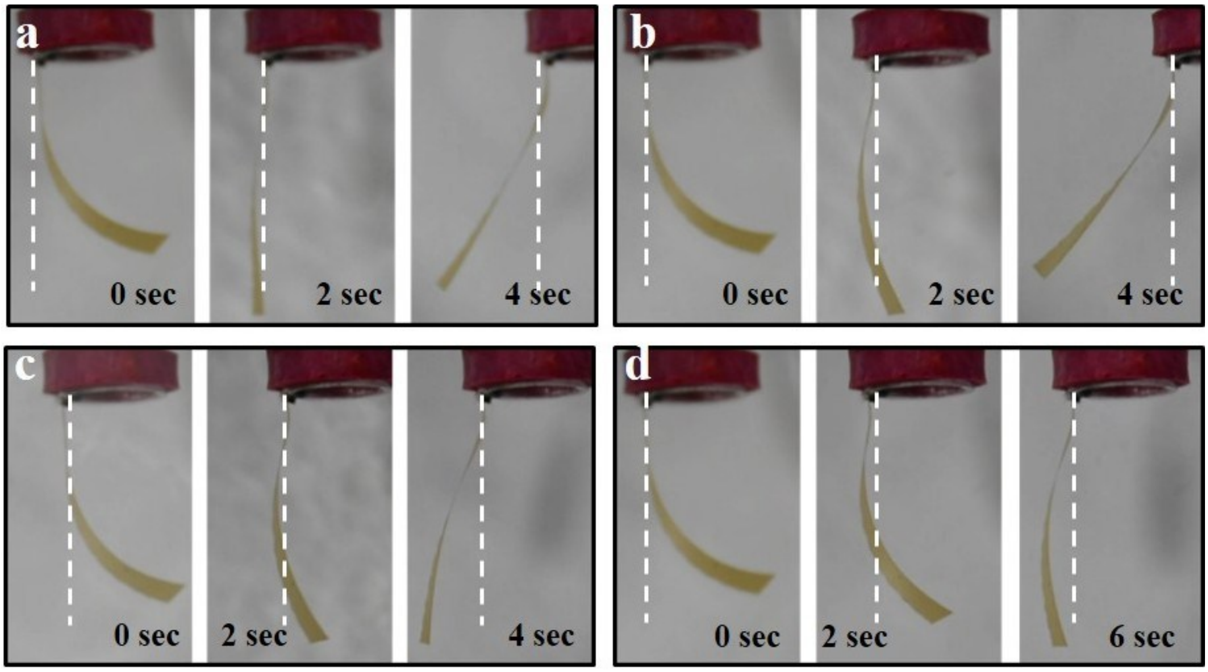

Figure S11: Bending movement of pristine bilayer vermiculite strip on exposure to (a) methanol, (b) ethanol, (c) THF and (d) 2-propanol vapours.

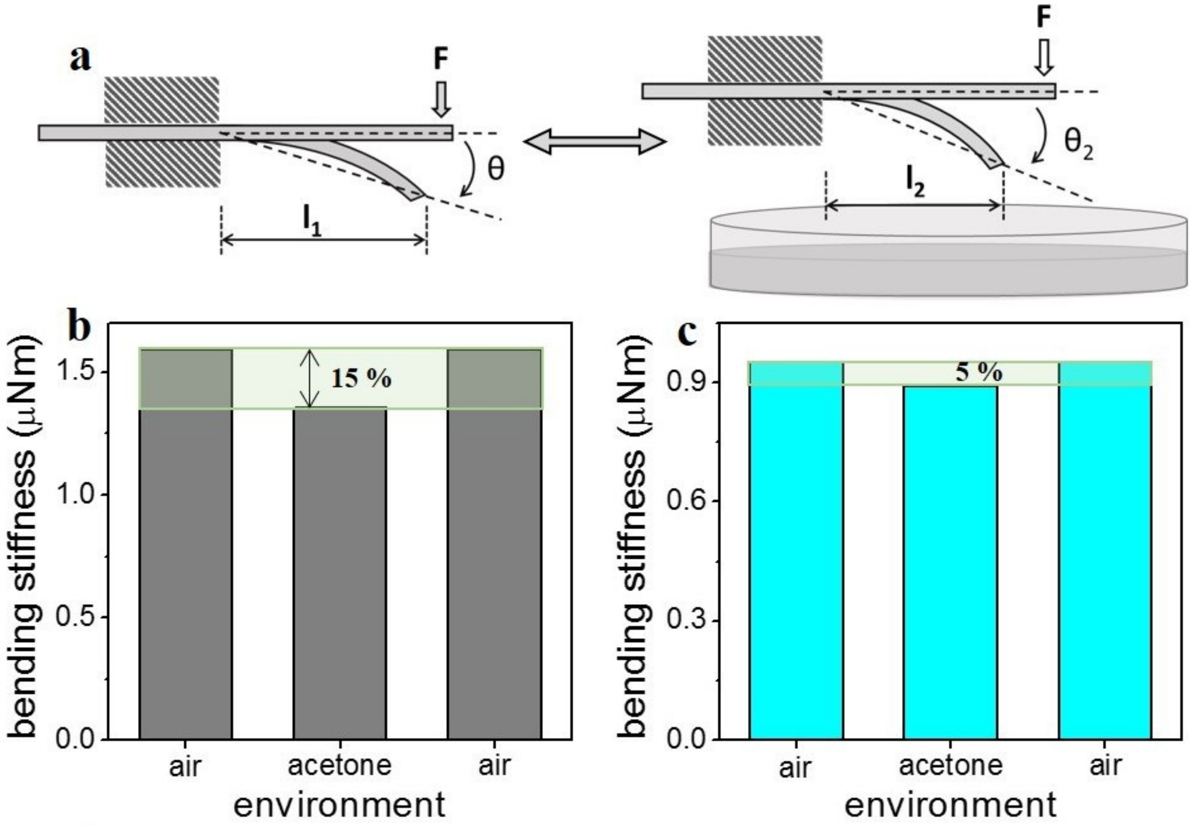

Figure S12: Mechanism of responsiveness of vermiculite bilayer membrane. (a) Schematic illustration of the experiment done for measuring environment dependence on bending stiffness. Bar diagrams compare the stiffness of (b) H-vermiculite and (c) Li-vermiculite in different atmospheric conditions.

Under ambient condition, the stiffness of H- and Li-exchanged strips (30 microns each) were calculated as 1.59 x 10^{-6} Nm and 9.52 x 10^{-7} Nm, respectively. Exposure to acetone vapors reduced the stiffness of the H-exchanged strip by 15 % and that of Li-exchanged strip by 5 %.

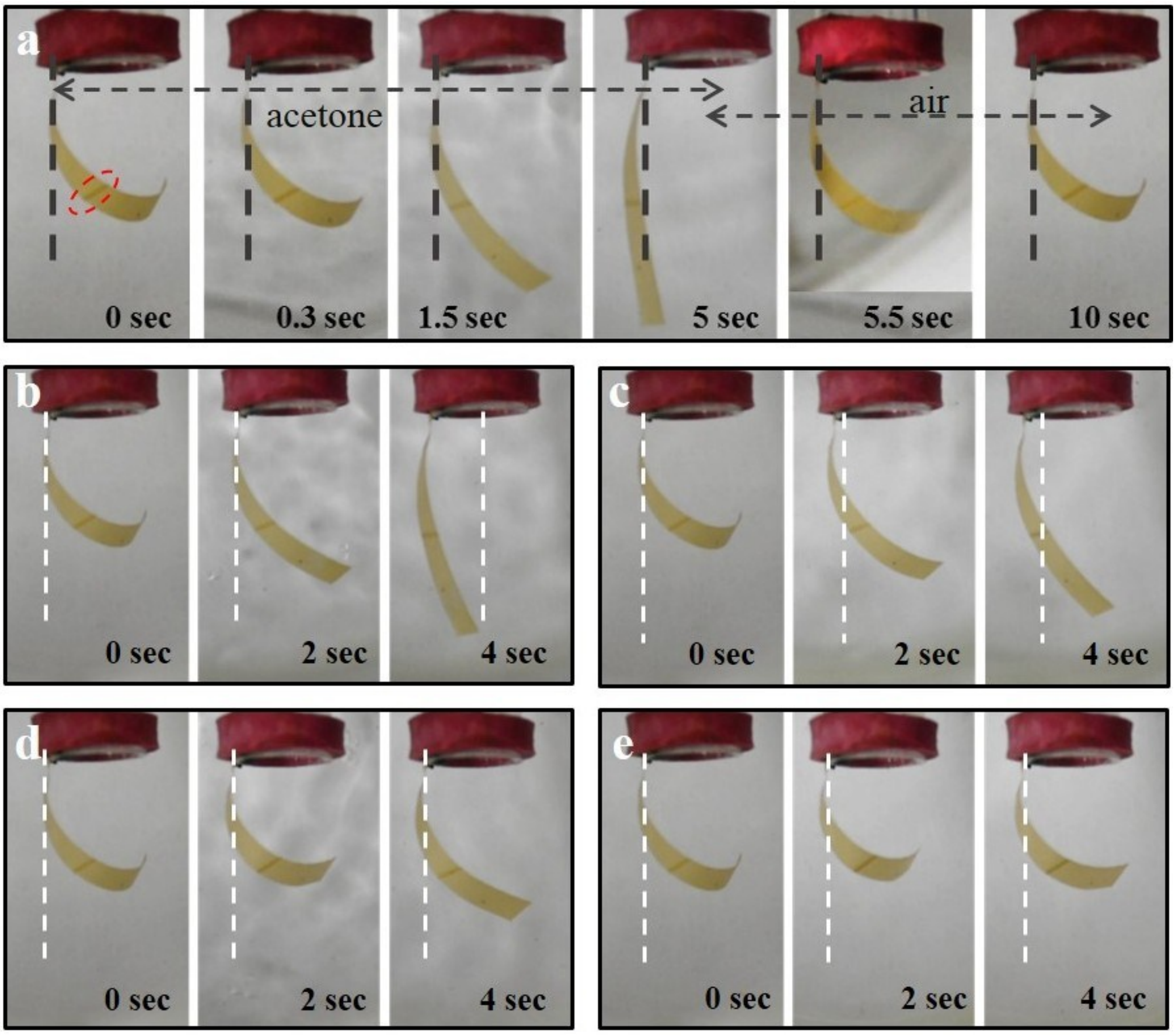

Figure S13: Bending movement of healed bilayer vermiculite strip upon exposure to (a) acetone (along with recovery), (b) methanol, (c) ethanol and (d) THF and (e) 2-propanol vapours.