## ELECTRONIC SUPPLEMENTARY INFORMATION.

## Shaping the molecular assemblies of native and alkali-modified agars in dilute and concentrated aqueous media *via* microwave-assisted extraction

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**Figure S1.** 2D <sup>1</sup>H- <sup>13</sup>C HSQC NMR spectrum of NA in D<sub>2</sub>O (data obtained at 80 °C with the following conditions: 0.19 s acquisition time, 1.5 s relaxation delay, a spectral width of (5000; 20000) Hz and an average of 128 scans).



**Figure S2.** 2D <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectrum of AA1 in D<sub>2</sub>O (data obtained at 80 °C with the following conditions: 0.19 s acquisition time, 1.5 s relaxation delay, a spectral width of (5000; 20000) Hz and an average of 128 scans).



**FIGURE S3.** 2D <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectrum of AA2 in D<sub>2</sub>O (data obtained at 80 °C with the following conditions: 0.19 s acquisition time, 1.5 s relaxation delay, a spectral width of (5000; 20000) Hz and an average of 128 scans).



**Figure S4.** 2D <sup>1</sup>H-<sup>13</sup>C HMBC NMR spectrum of AA2 in D<sub>2</sub>O (data obtained at 80 °C with the following conditions: 1.42 s acquisition time, 2.0 s relaxation delay, a spectral width of (5000; 23000) Hz and an average of 72 scans).



Figure S5. FTIR spectra of NA, AA and commercial agars. Bands assigned to total sulfate esters (1250 cm<sup>-1</sup>; a) and LA (930 cm<sup>-1</sup>; b) used in the  $A_{930}/A_{1250}$  calculation, are marked accordingly.



**Figure S6.** Topographical (**A**) and amplitude (**B**) AFM images of NA structures formed on the 50  $\mu$ g/mL dilute aqueous solutions when deposited onto mica and air dried. The image size is 5  $\mu$ m × 5  $\mu$ m. Examples of NA aggregates are identified by number 1.



Figure S7. Topographical (A) and amplitude (B) AFM images of AA1 structures formed on the 50  $\mu$ g/mL dilute aqueous solution deposited on mica and air dried. The image size is 5  $\mu$ m × 5  $\mu$ m. Examples of AA1 aggregates are identified by number 1.



**Figure S8.** Topographical (**A**) and amplitude (**B**) AFM images of AA2 structures formed on the 50  $\mu$ g/mL dilute aqueous solution deposited on mica and air dried. The image size is 5  $\mu$ m × 5  $\mu$ m. Example of AA2 aggregates are identified by number 1.



**Figure S9.** Height profile correponding to structures along the straight line over the topographic AFM image of NA for the 5  $\mu$ g/mL solution displayed in Figure 6A/B of the manuscript.



Figure S10. Height profile correponding to the structures along the straight line over the topographic AFM image of AA1 for the 5  $\mu$ g/mL solution displayed in 6C/D of the manuscript.



**Figure S11.** Height profile correponding to the structures along the straight line over the topographic AFM image of AA2 for the 5  $\mu$ g/mL solution displayed in Figure 6E/F of the manuscript.



Figure S12. Topographical (A) and amplitude (B) AFM images of NA structures formed on the 10  $\mu$ g/mL dilute aqueous solution when deposited on mica and air dried. The image size is 3  $\mu$ m  $\times$  3  $\mu$ m.



Figure S13. Topographical (A) and amplitude (B) AFM images of AA1 structures formed on the 10  $\mu$ g/mL dilute aqueous solution when deposited on mica and air dried. The image size is 3  $\mu$ m  $\times$  3  $\mu$ m.



Figure S14. Topographical (A) and amplitude (B) AFM images of NA structures formed on the 100  $\mu$ g/mL dilute aqueous solution when deposited on mica and air dried. The image size is 3  $\mu$ m  $\times$  3  $\mu$ m.



Figure S15. Topographical (A) and amplitude (B) AFM images of AA1 structures formed on the 100  $\mu$ g/mL dilute aqueous solution when deposited on mica and air dried. The image size is 3  $\mu$ m × 3  $\mu$ m.



Figure S16. Topographical (A) and amplitude (B) AFM images of AA2 structures formed on the 100  $\mu$ g/mL dilute aqueous solution deposited on mica and air dried. The image size is 3  $\mu$ m × 3  $\mu$ m.

