Supporting Information

Supramolecular Hydrogels with Properties Tunable by Calcium Ions: A Bio-Inspired Chemical System

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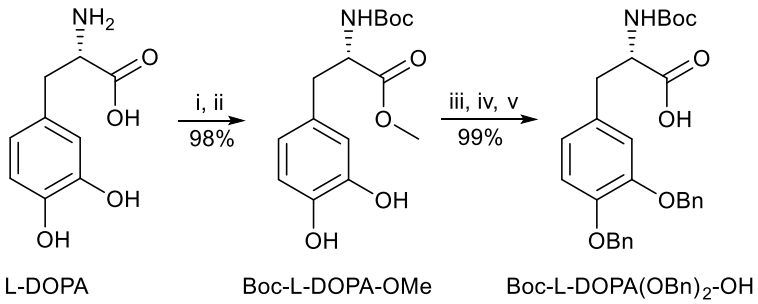


Scheme S1. Reagents and conditions: (i) $SOCl_2$ (excess), MeOH, 0 °C, 24 h; (ii) Boc_2O (2 equiv.), $NaHCO_3$ (2 equiv.), THF/H_2O, r.t., 18 h; (iii) BnBr (2.2 equiv.), K_2CO_3 (2.2 equiv.), TBAB (0.2 equiv.), NaI (0.2 equiv.), acetone, reflux, 4 h; (iv) 1M NaOH, MeOH/THF, r.t., 18 h; (v) 1M HCl.

References

Magoulas, G. E.; Rigopoulos, A.; Piperigkou, Z.; Gialeli, C.; Karamanos, N. K.; Takis, P. G.; Troganis, A. N.; Chrissanthopoulos, A.; Maroulis, G.; Papaioannou, D. Synthesis and Antiproliferative Activity of Two Diastereomeric Lignan Amides Serving as Dimeric Caffeic Acid-l-DOPA Hybrids. *Bioorg. Chem.* **2016**, *66*, 132–144.

Gaucher, A.; Dutot, L.; Barbeau, O.; Hamchaoui, W.; Wakselman, M.; Mazaleyrat, J. P. Synthesis of Terminally Protected (S)-B3-H-DOPA by Arndt-Eistert Homologation: An Approach to Crowned β-Peptides. *Tetrahedron Asymmetry* **2005**, *16*, 857–864.

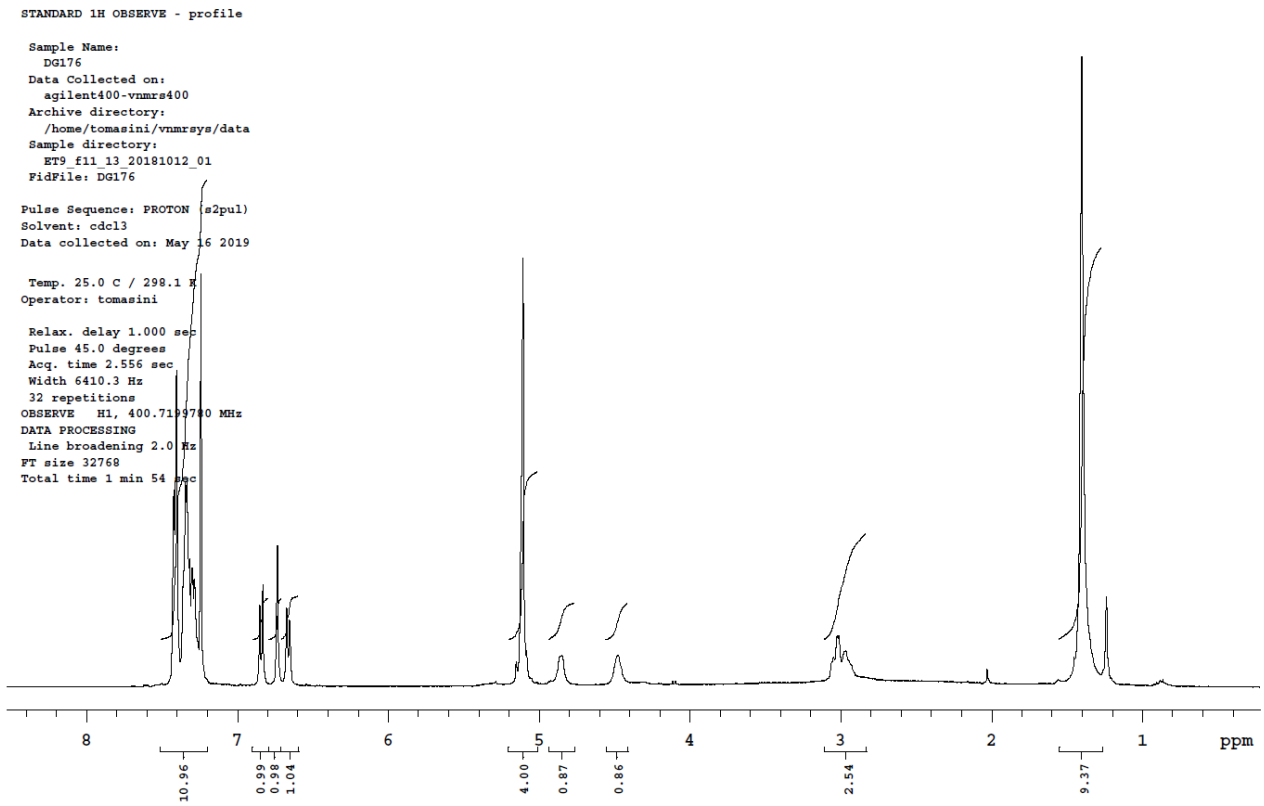


Figure S1. ^{1}H NMR spectrum of gelator **A**.

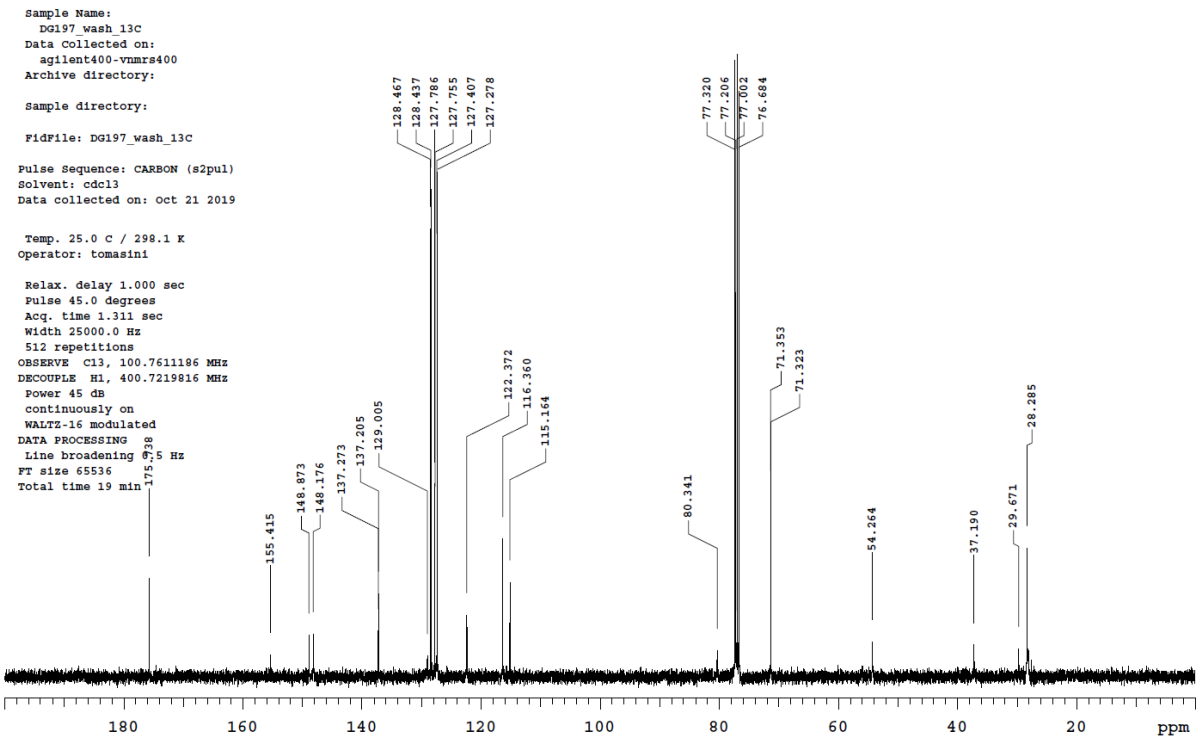
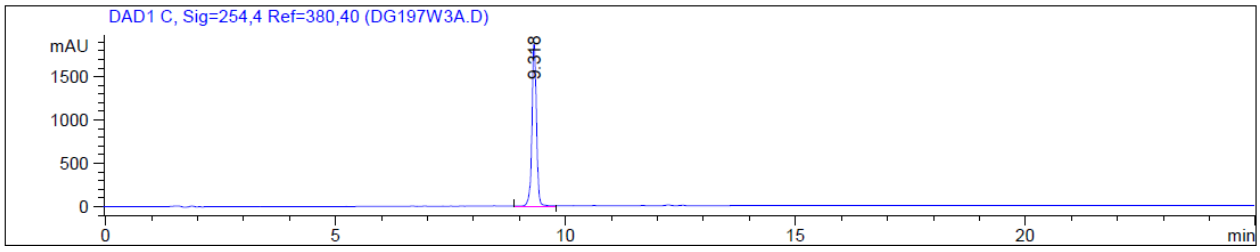


Figure S2. ^{13}C NMR spectrum of gelator **A**.



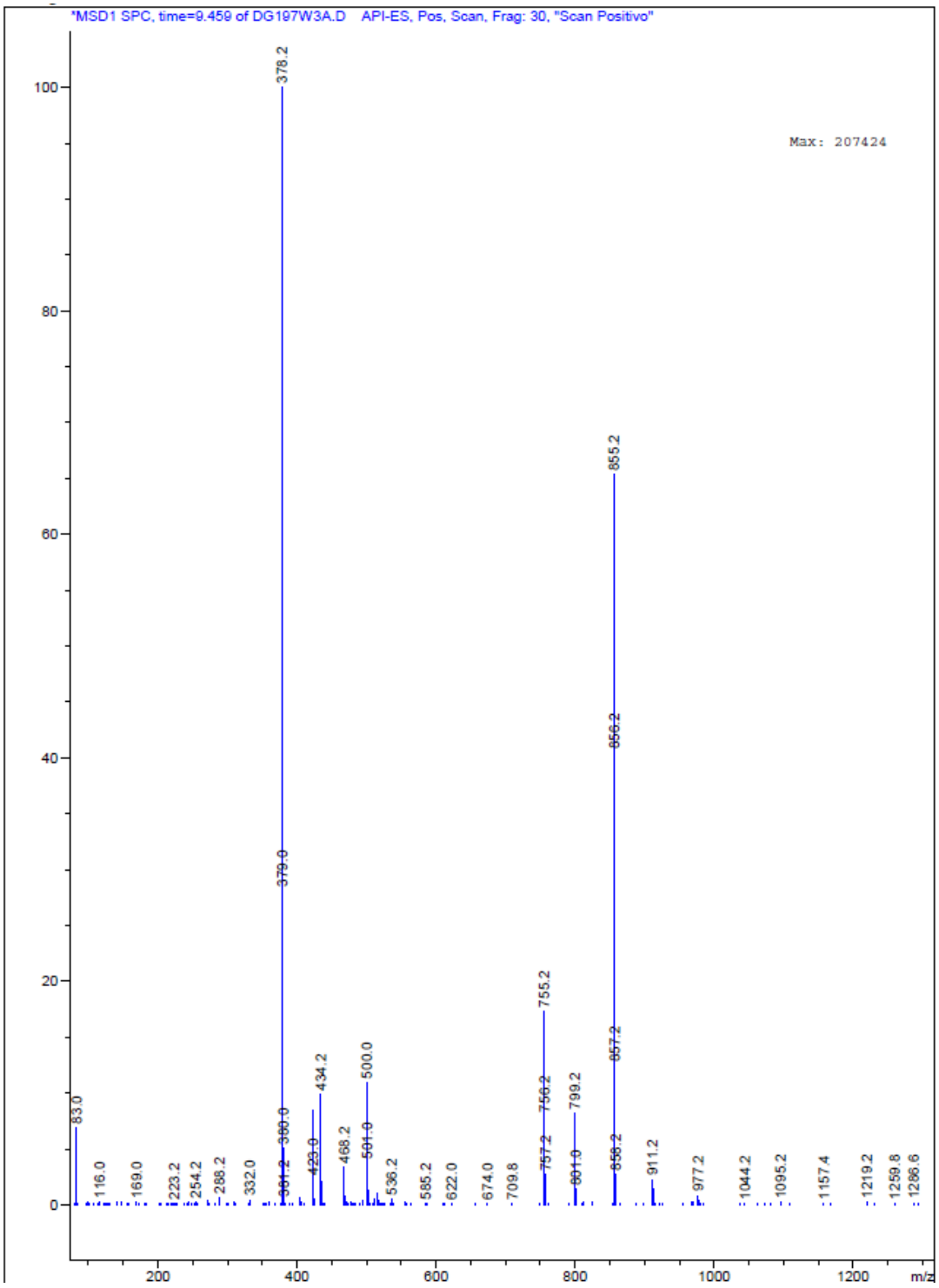


Figure S3. LC chromatogram and MS spectrum of gelator **A**.

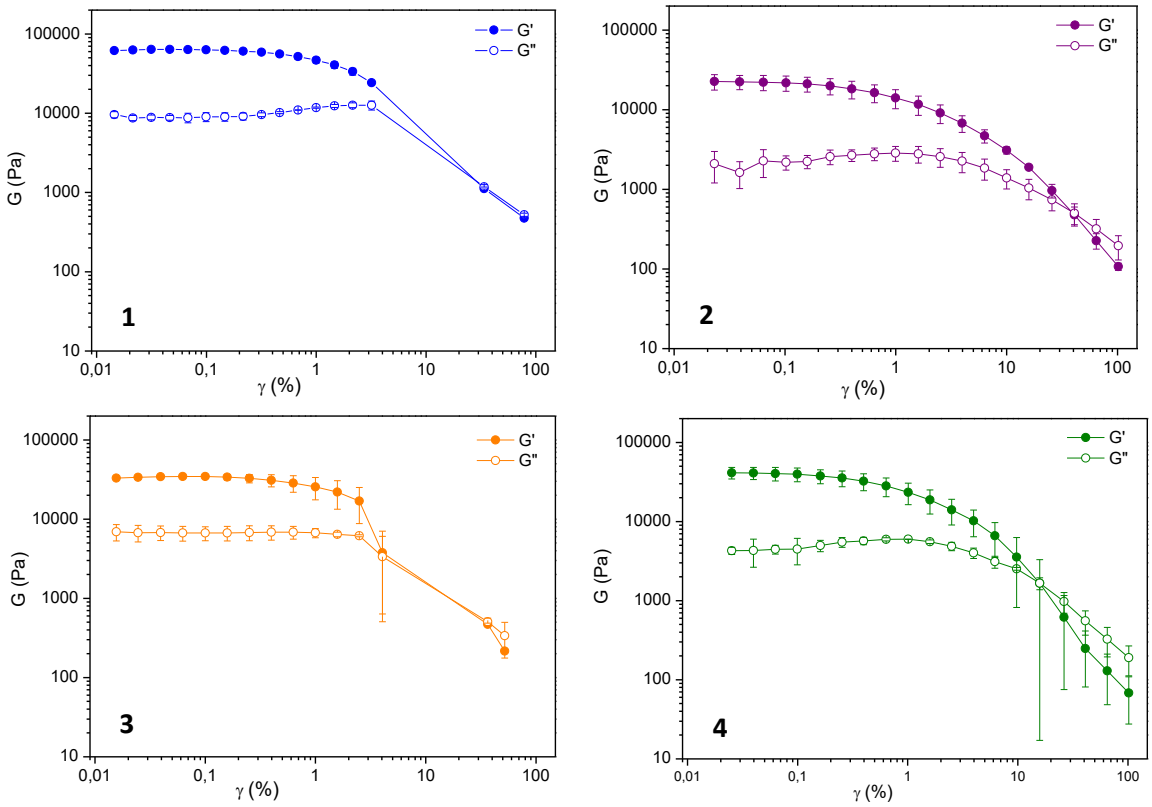


Figure S4. Amplitude sweep experiments of the hydrogels **1**, **2**, **3** and **4**, made with 1% w/w gelator concentration of gelator **A**. The analyses were performed on the gels about 20 hours after the gelation begun. (Storage modulus (solid circles) and loss modulus (empty circles).

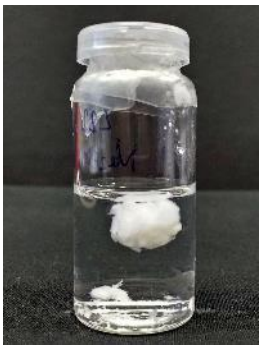


Figure S5. Photograph of a hydrogel **2** sample suspended into a 0.05 M EDTA solution.

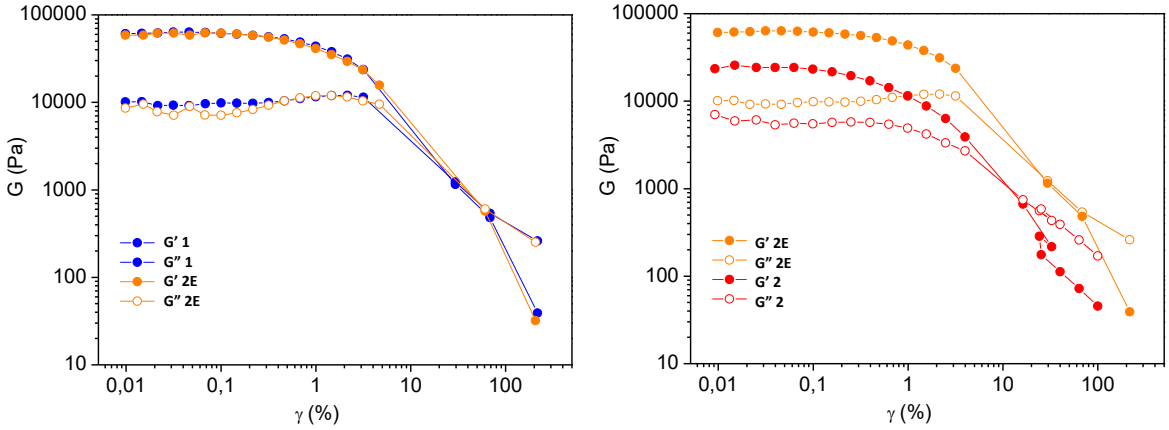


Figure S6. Amplitude sweep experiments performed on the 1 wt.% hydrogels. The results obtained for **2E** were compared with **1** (left) and **2** (right).

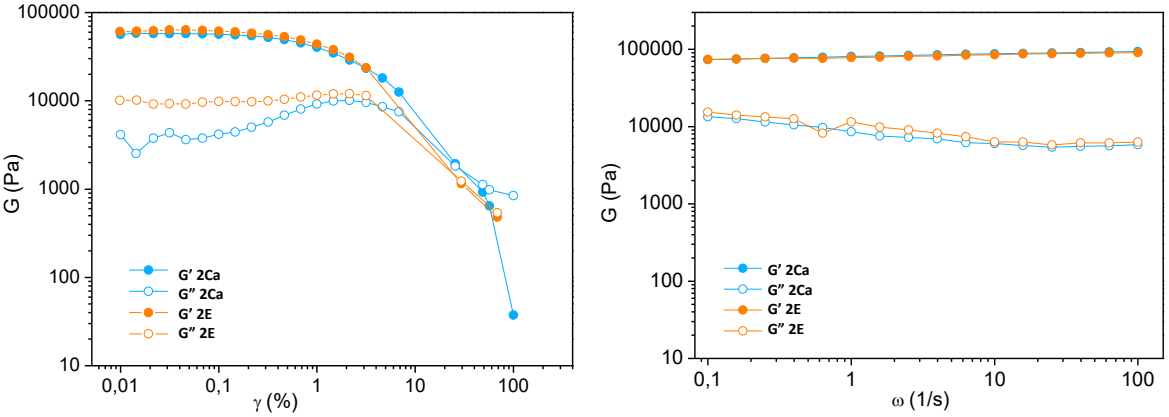


Figure S7. Amplitude sweep experiments (left) and frequency sweep experiments (constant γ = 0.04%, right) performed on the 1 wt.% hydrogels. The results obtained for **2Ca** were compared with **2E**.

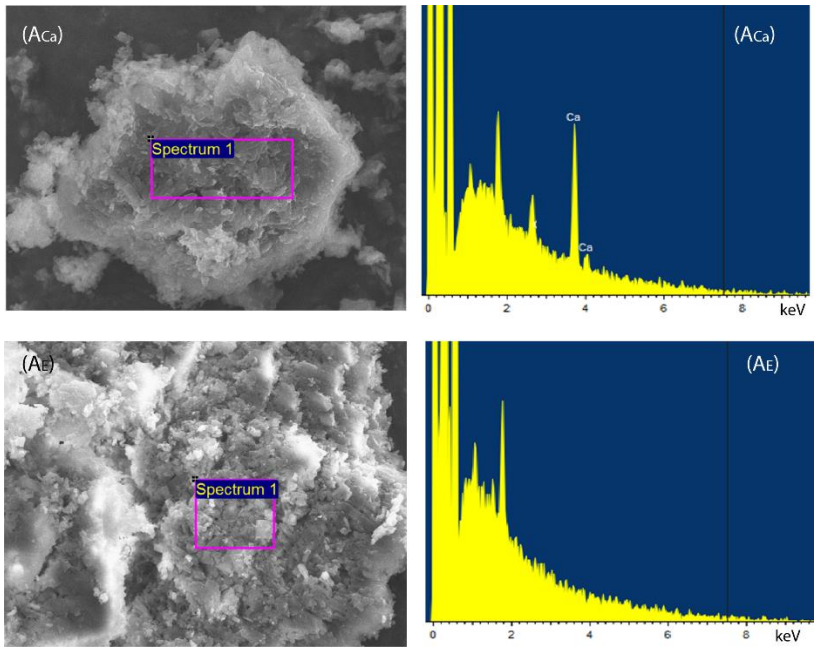


Figure S8. EDX spectrum of the **xero-2Ca** (A_{Ca}) and **xero-2E** (A_E) samples. The area of collection of the EDX spectrum is the one inside the purple colored quadrilateral. Only the sample **xero-2Ca** show the peaks due to the presence of Ca.

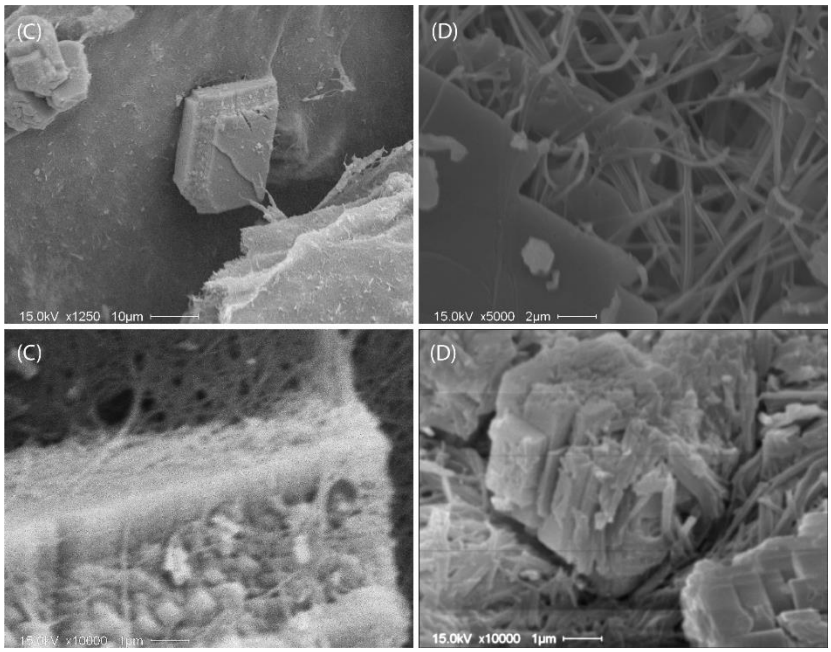


Figure S9. SEM images of the xerogel samples **xero-3** (C) and **xero-4** (D).

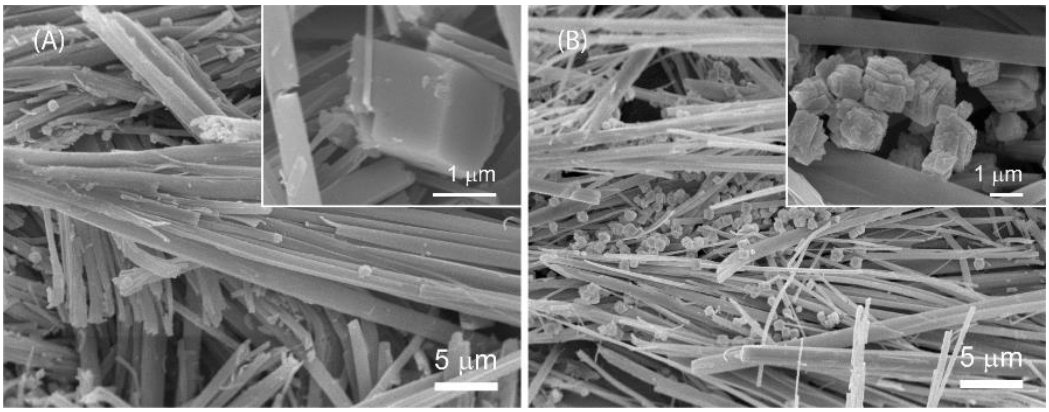


Figure S10. SEM images of the xerogel samples **xero-3#** (A) and **xero-4#** (B).

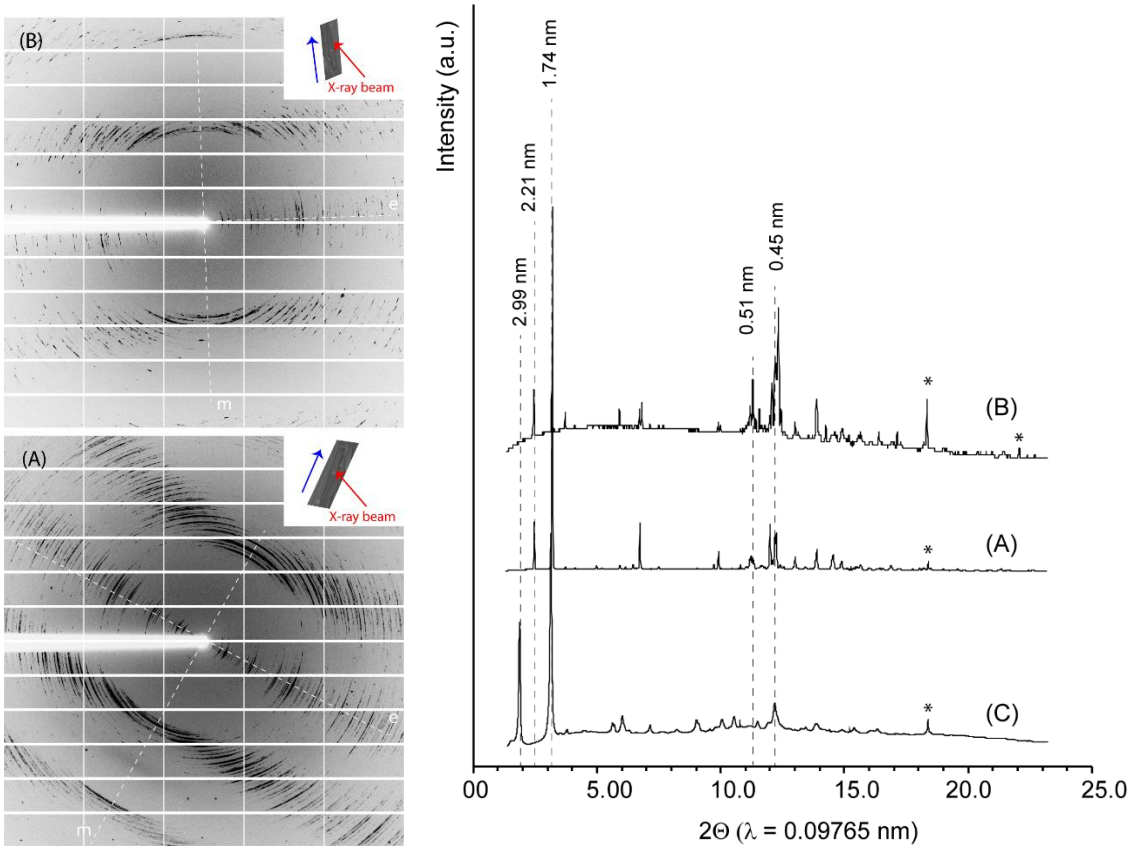


Figure S11. (left) Synchrotron X-ray fiber diffraction image from a bundle of fibers from the samples **xero-3#** (A) and **xero-4#** (B). The fiber orientation is indicated by the blue arrow in the image insets, where also the direction of the X-ray beam is illustrated by the red arrow. In the X-ray diffraction image, the meridional (i.e. fiber) axis is indicated by a dashed line marked with m. The equatorial axis is indicated by a dashed line marked with e. (right) Powder diffraction profiles of the samples **xero-3#** (A) and **xero-4#** (B) obtained by integration of the intensities along the 2Θ angle. The powder diffraction profile of the sample **xero-3** (C) is shown for comparison. The main diffraction peaks from the xerogel structure are indicated with their associated periodicities. The diffraction peaks of calcite are marked by an asteriscus.