

Supporting Information

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

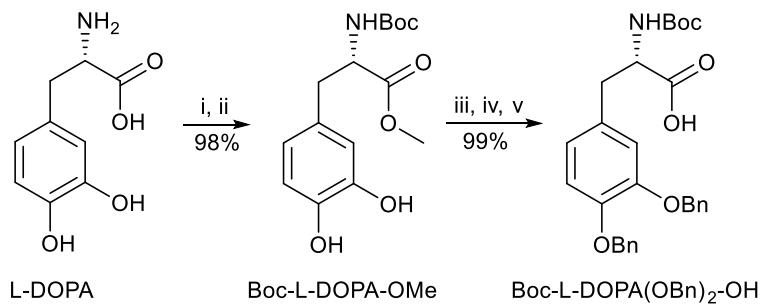
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Scheme S1. Reagents and conditions: (i) SOCl_2 (excess), MeOH , $0\text{ }^\circ\text{C}$, 24 h; (ii) Boc_2O (2 equiv.), NaHCO_3 (2 equiv.), $\text{THF}/\text{H}_2\text{O}$, r.t., 18 h; (iii) BnBr (2.2 equiv.), K_2CO_3 (2.2 equiv.), TBAB (0.2 equiv.), 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.

STANDARD 1H OBSERVE - profile

Sample Name:
DG176
Data Collected on:
agilent400-vnmrs400
Archive directory:
/home/tomasini/vnmrsys/data
Sample directory:
ET9 fil1_13_20181012_01
Fidfile: DG176

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 16 2019

Temp. 25.0 C / 298.1 K
Operator: tomasini

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
32 repetitions
OBSERVE H1, 400.7199780 MHz
DATA PROCESSING
Line broadening 2.0 Hz
FT size 32768
Total time 1 min 54 sec

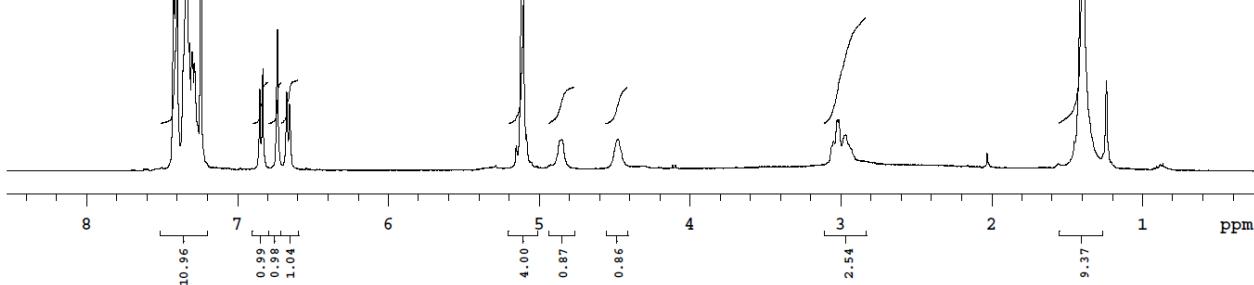


Figure S1. ^1H NMR spectrum of gelator A.

Sample Name:
DG197 wash_13C
Data Collected on:
agilent400-vnmrs400
Archive directory:

Sample directory:
Fidfile: DG197_wash_13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: oct 21 2019

Temp. 25.0 C / 298.1 K
operator: tomasini

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions
OBSERVE C13, 100.7611186 MHz
DECOUPLE H1, 400.7219816 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536
Total time 19 min

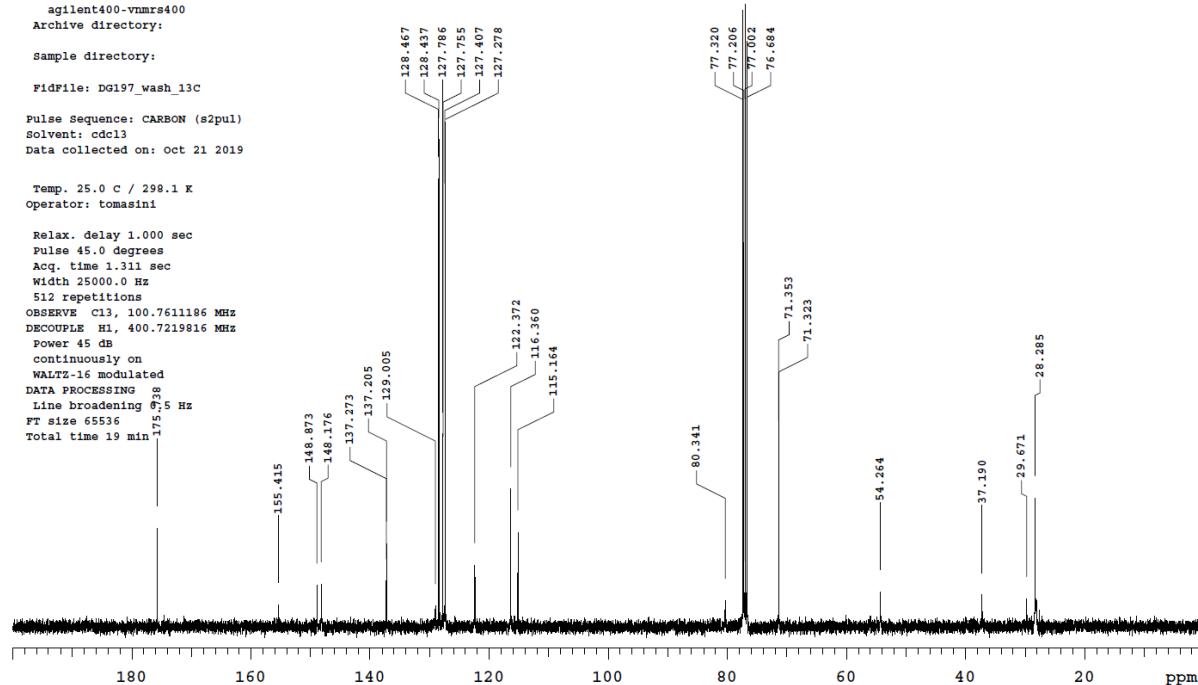


Figure S2. ^{13}C NMR spectrum of gelator A.

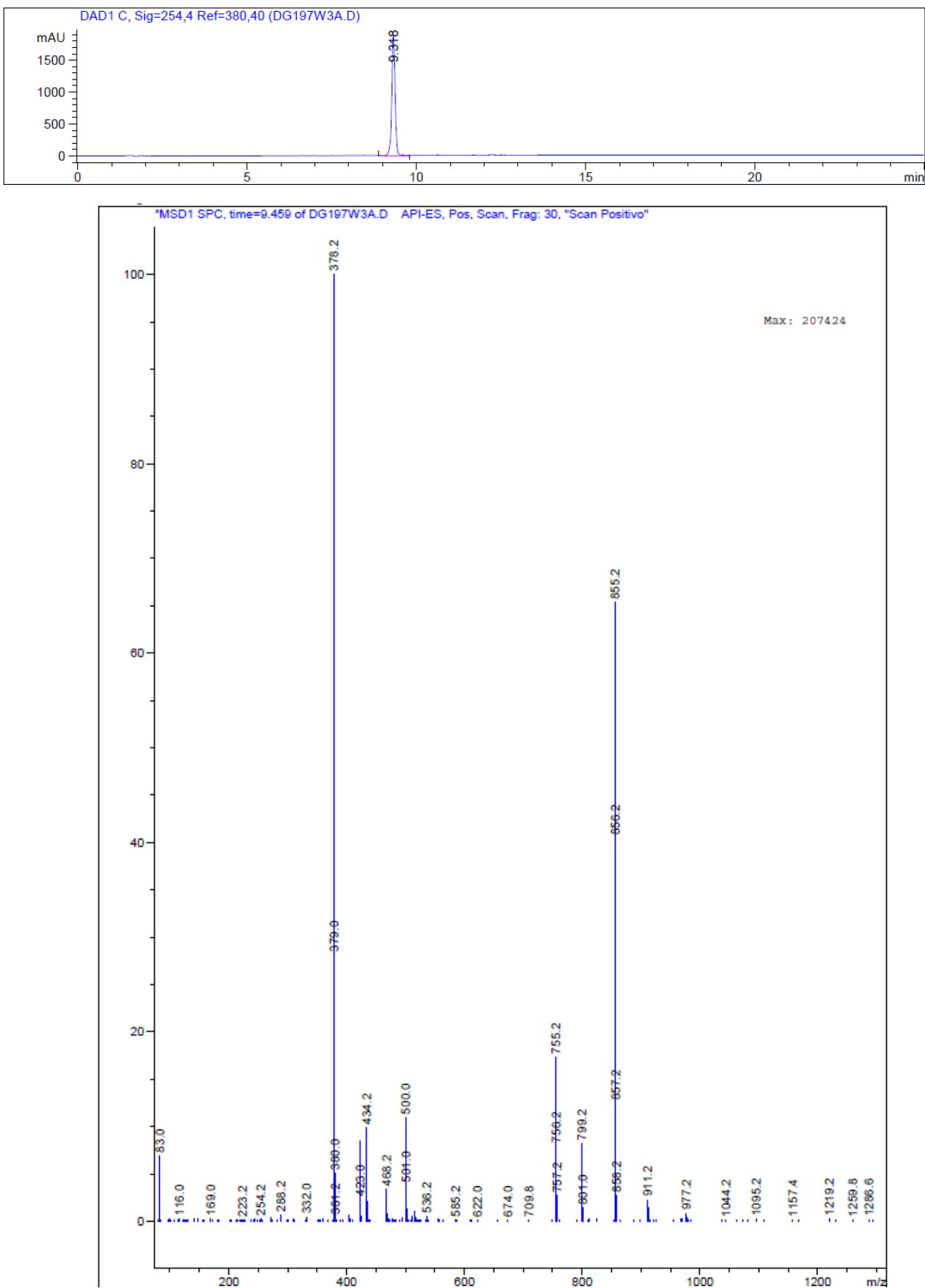


Figure S3. LC chromatogram and MS spectrum of gelator A.

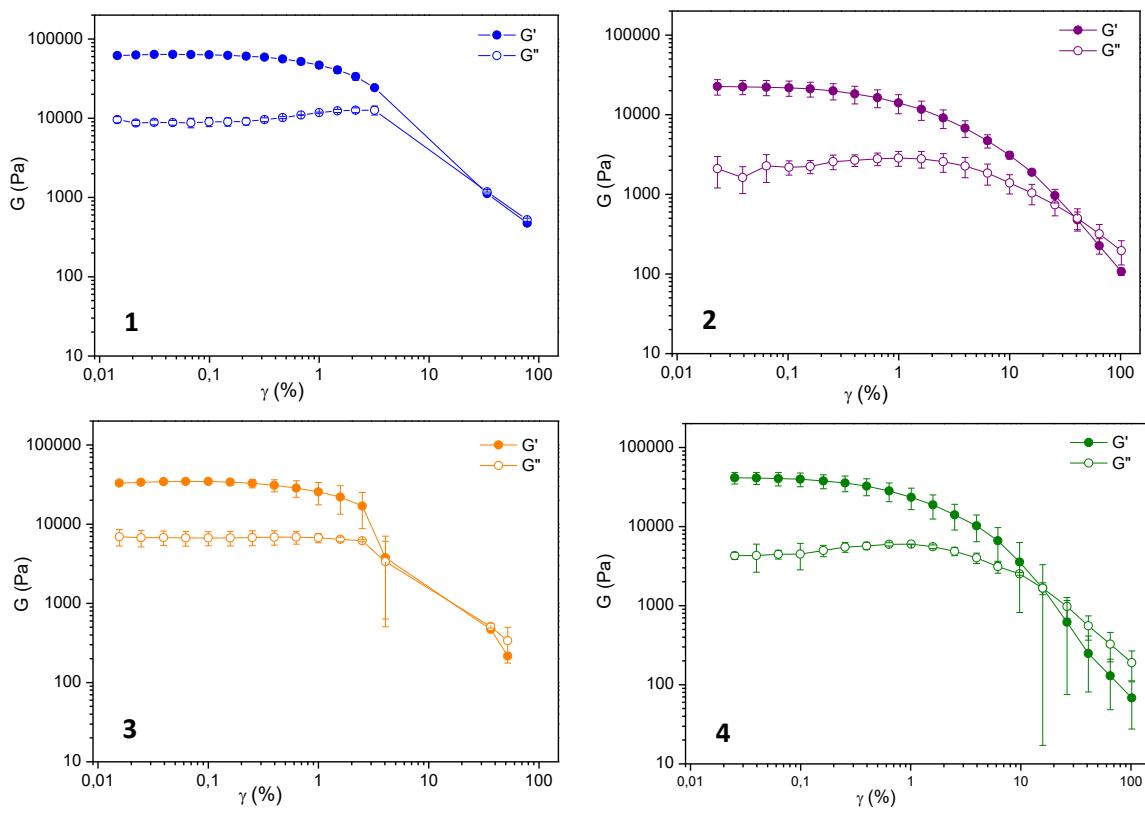


Figure S4. Amplitude sweep experiments of the hydrogels **1**, **2**, **3** and **4**, made with 1% w/w gelator concentration of gelator **A**. The analyses were performed on the gels about 20 hours after the gelation begun. (Storage modulus (solid circles) and loss modulus (empty circles)).



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

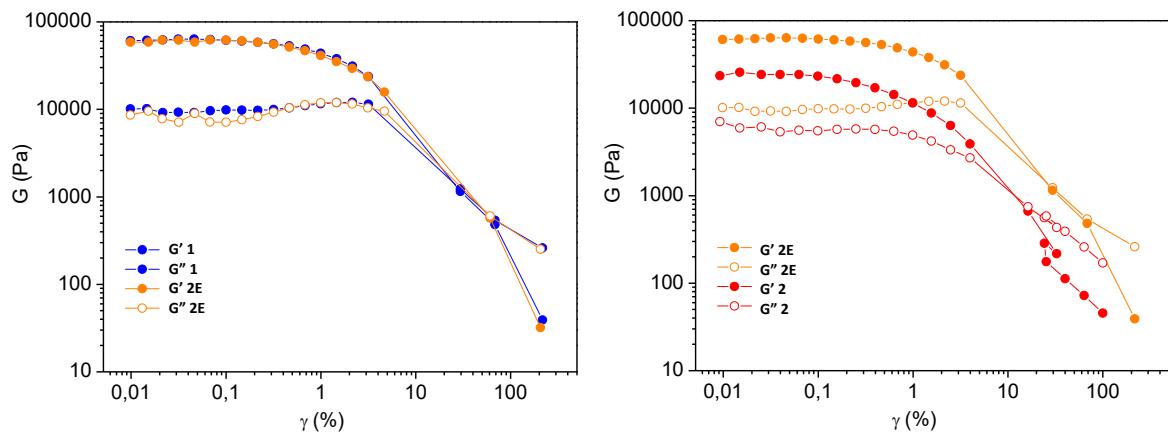


Figure S6. Amplitude sweep experiments performed on the 1 wt.% hydrogels. The results obtained for **2E** were compared with **1** (left) and **2** (right).

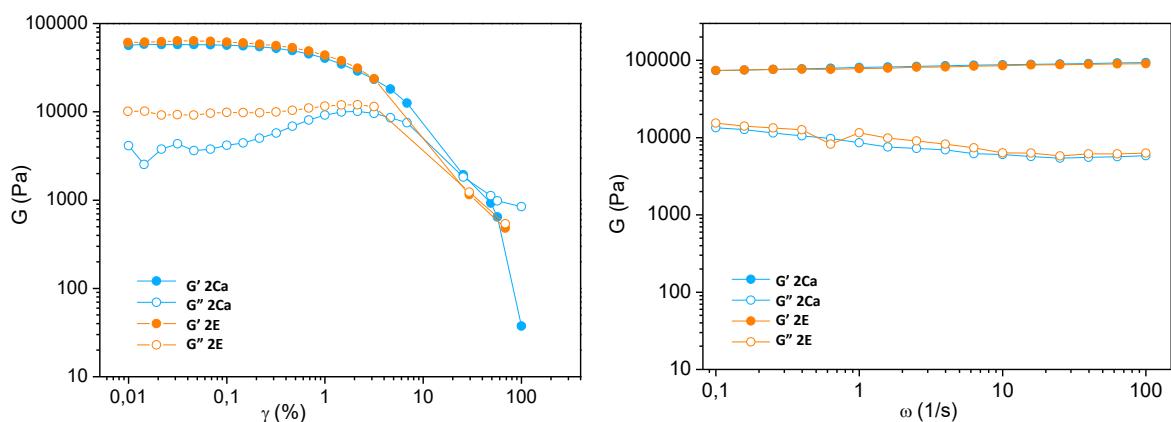


Figure S7. Amplitude sweep experiments (left) and frequency sweep experiments (constant γ = 0.04%, right) performed on the 1 wt.% hydrogels. The results obtained for **2Ca** were compared with **2E**.

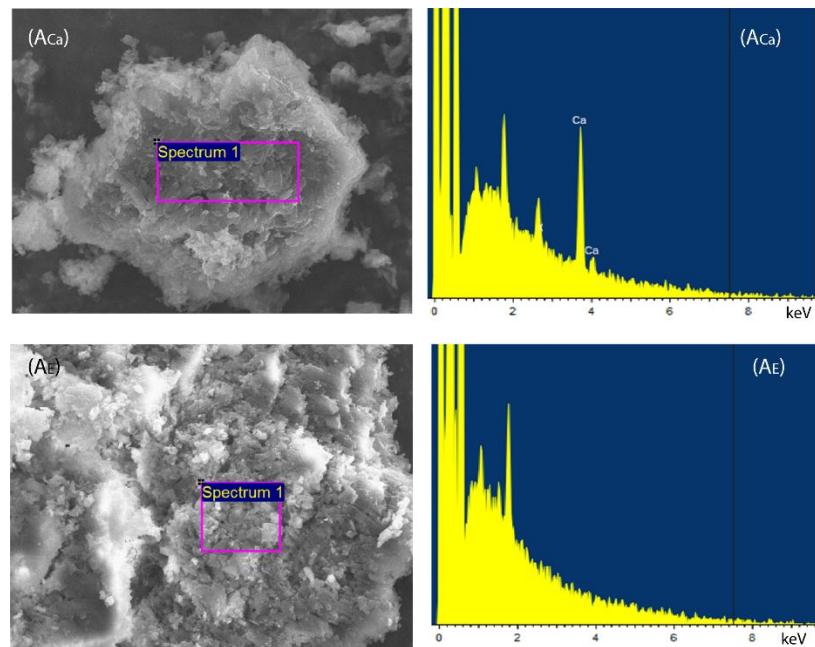


Figure S8. EDX spectrum of the **xero-2Ca** (A_{Ca}) and **xero-2E** (A_E) samples. The area of collection of the EDX spectrum is the one inside the purple colored quadrilateral. Only the sample **xero-2Ca** show the peaks due to the presence of Ca.

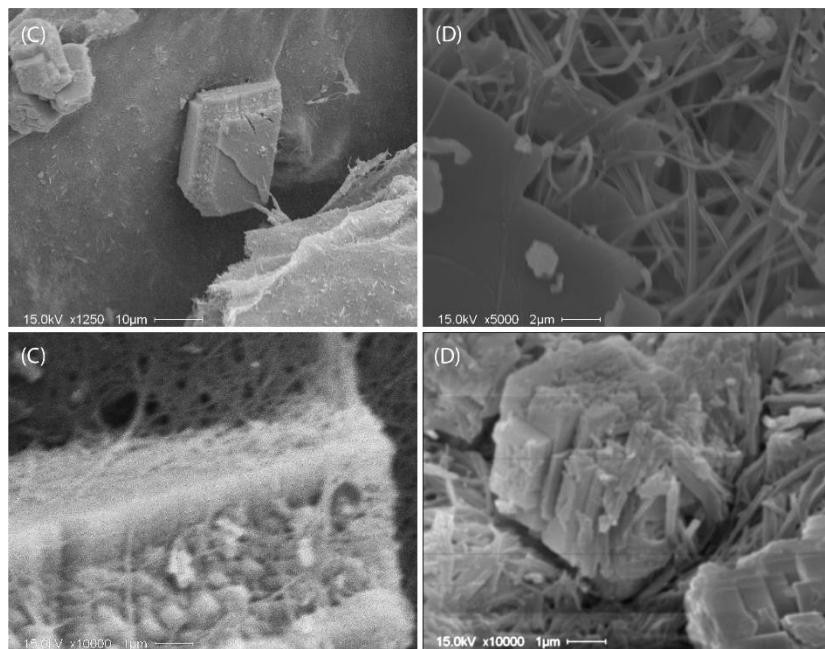


Figure S9. SEM images of the xerogel samples **xero-3** (C) and **xero-4** (D).

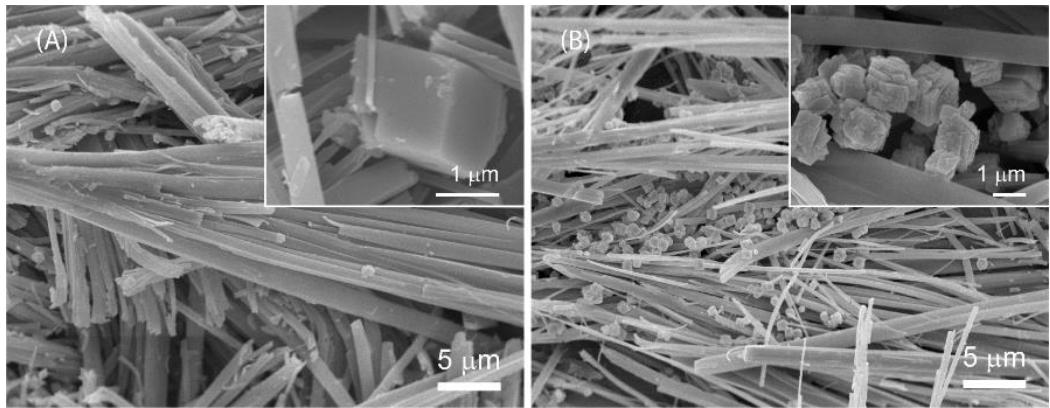


Figure S10. SEM images of the xerogel samples **xero-3#** (A) and **xero-4#** (B).

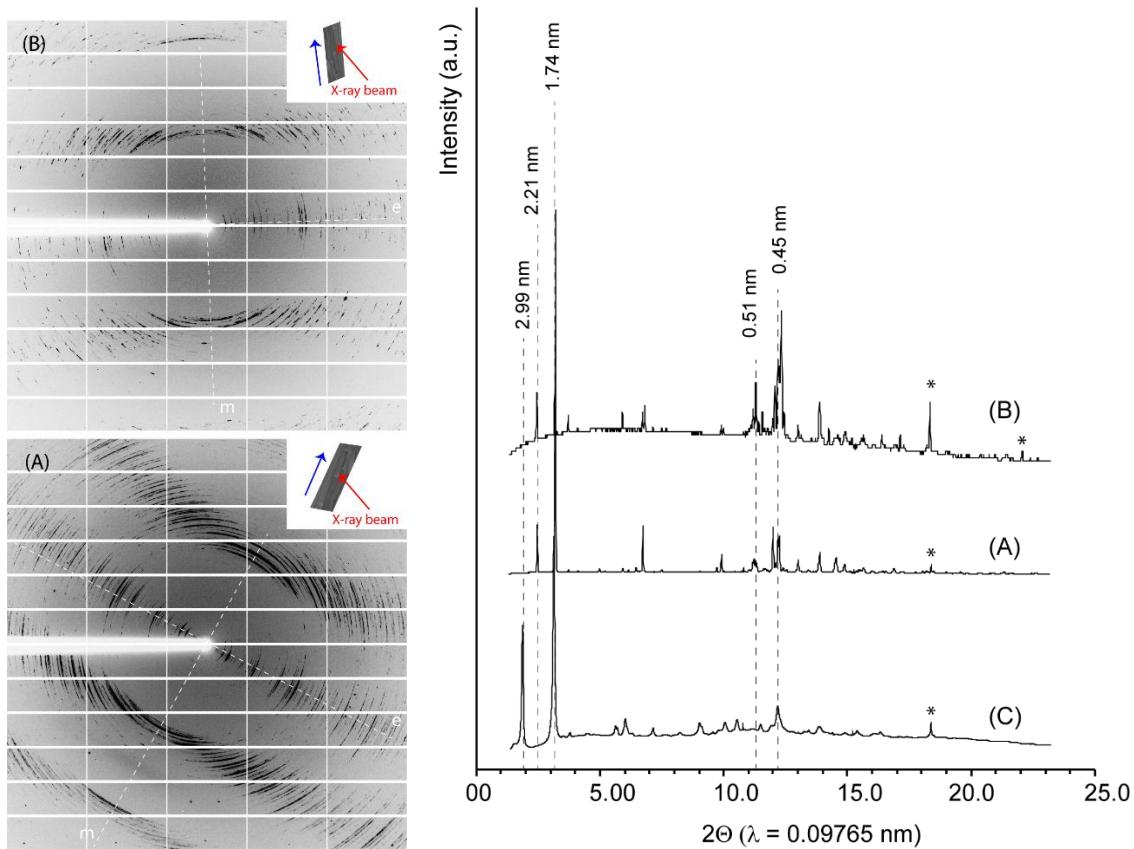


Figure S11. (left) Synchrotron X-ray fiber diffraction image from a bundle of fibers from the samples **xero-3#** (A) and **xero-4#** (B). The fiber orientation is indicated by the blue arrow in the image insets, where also the direction of the X-ray beam is illustrated by the red arrow. In the X-ray 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.