Electronic Supplementary Information (ESI)

Atmospheric Water triggers Supramolecular Gel Formation of Novel Low Molecular Weight Maslinic and Oleanolic Triterpenic Derivatives

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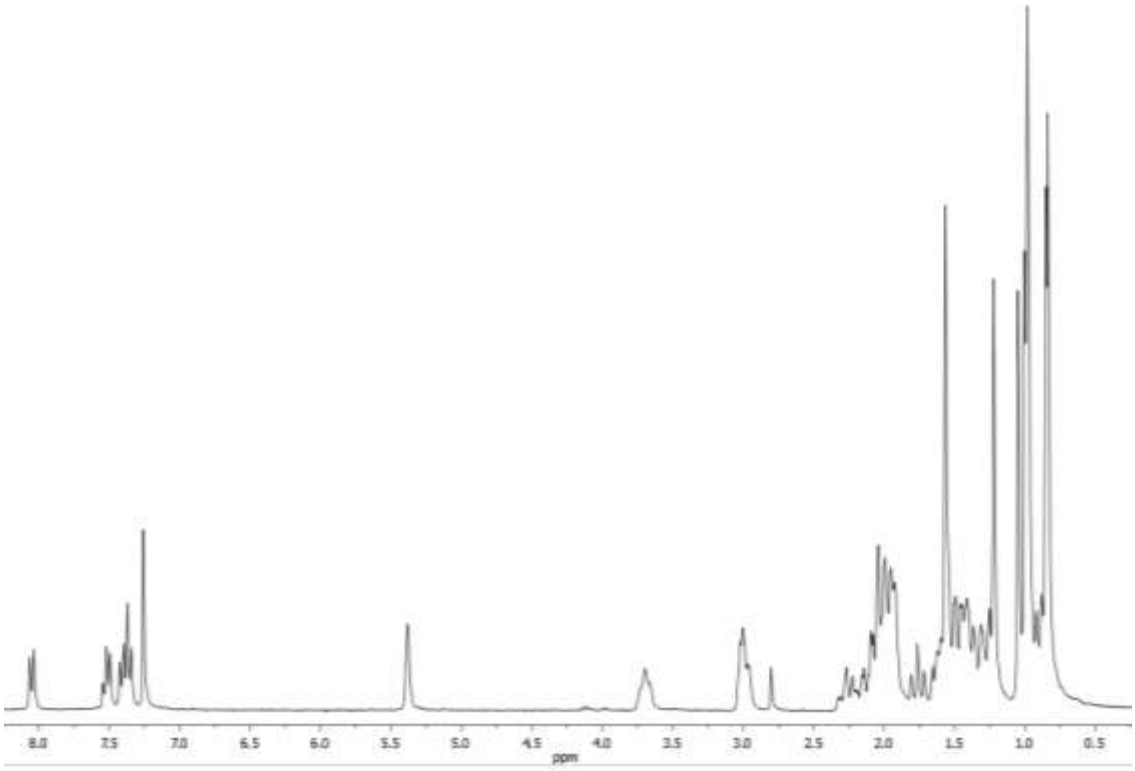
MATBTU ^{1}H-NMR: ($CDCl_3$ 500 MHz): 8.05 (m, 1H, TBTU group), 7.52 (m,1H, TBTU group), 7.38 (m, 2H, TBTU group), 5.38 (dd, 1H, J1 = J2 = 3.6 Hz, H-12), 3.69 (ddd, 1H, J1 =4.4, J2 =10.0, J3 = 14.4 Hz, H-2), 3.01 (d, 1H, J = 10.0 Hz, H-3), 2.98 (dd, 1H, J1 = 4.0, J2 = 13.5 Hz, H-18), 1.22, 1.05, 1.00, 0.98, 0.97, 0.85, 0.84 (s, 3H each, methyl groups); ^{13}C-NMR ($CDCl_3$, 100 MHz): 16.8 (CH_3), 16.9 (CH_3), 17.5 (CH_3), 18.5 (CH_2), 23.3 (CH_2), 23.7 (CH), 23.7 (CH_3), 25.9 (CH_3), 28.2 (CH_2), 28.8 (CH_3), 30.8 (C), 32.6 (CH_2), 32.9 (CH_2), 33.1 (CH_3), 33.8 (CH_2), 38.4 (C), 39.3 (C), 39.7 (C), 41.7 (CH), 42.1 (C), 45.6 (CH_2), 46.6 (CH_2), 47.7 (CH), 47.8 (C), 55.5 (CH), 69 (CH), 84.1 (CH), 108.3 (CH TBTU), 120.7 (CH TBTU), 123.9 (CH), 124.8 (CH TBTU), 128.6 (CH TBTU), 128.9 (C TBTU), 142.3 (C), 143.7 (C TBTU), 173.7 (COOH); ESI-HRMS m/z calcd for $C_{36}H_{52}N_3O_4$ $[M+1]^+$ 590.3958, found 590.3954.



OATBTU ^{1}H-NMR: ($CDCl_3$, 500 MHz): 8.03 (m, 1H, TBTU group), 7.50 (m, 1H, TBTU group), 7.37 (m, 2H, TBTU group), 5.36 (dd, 1H, J1 =J2 = 3.5 Hz, H-12), 3.20 (dd, 1H, J1 = 4.0, J2 = 11.0 Hz, H-3), 2.97 (dd, 1H, J1 = 4.5, J2 = 14.0 Hz, H-18), 1.21, 0.99, 0.98, 0.96, 0.89, 0.84, 0.78 (s, 3H each, methyl groups); ^{13}C-NMR ($CDCl_3$, 125 MHz): 15.5 (CH_3), 15.7 (CH_3), 17.4 (CH_3), 18.4 (CH_2), 23.2 (CH_2), 23.6 (CH), 23.6 (CH_3), 25.8 (CH_3), 27.3 (CH_2), 28.2 (CH_2), 28.2 (CH_3), 30.7 (C), 32.5 (CH_2), 32.9 (CH_2), 33 (CH_3), 33.8 (CH_2), 37.1 (C), 38.7 (CH_2), 38.9 (C), 41.7 (CH), 42 (C), 45.6 (CH_2), 47.7 (CH), 47.7 (C), 55.3 (CH), 79 (CH), 108.3 (CH TBTU), 120.6 (CH TBTU), 124 (CH), 124.7 (CH TBTU), 128.6 (CH TBTU), 128.9 (CH TBTU), 142.2 (C), 143.6 (CH TBTU), 173.7 (COOH); ESI-HRMS m/z calcd for $C_{36}H_{52}N_3O_3$ $[M+1]^+$ 574.4009, found 574.4020.

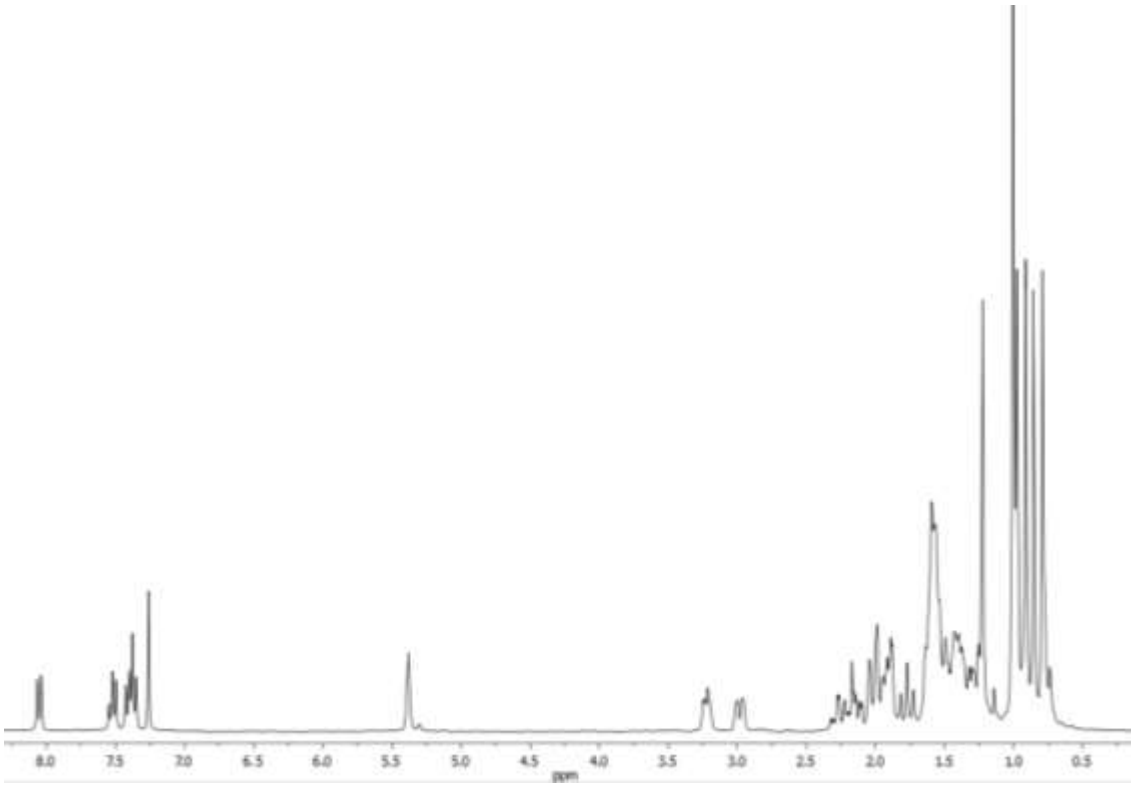


Table S1. Gelification time versus gelator concentration by capturing atmospheric water.

Gelification Time in DMSO

Percent/Percentage (w/v)	Time (h)
1 %	20
2 %	20
3 %	20
4 %	6
6 %	5
8 %	5
10 %	5
15 %	5

Gelification Time in DMF

Percent/Percentage (w/v)	Time (h)
4 %	48
8 %	48
10 %	30

Table S2. Ratios of DMF and H_2O needed to form gels as a function of gelator concentration.

	1, %(v/v)		**2, %(v/v)**	
GELADOR %(w/v)	**DMF**	**H_2O**	**DMF**	**H_2O**
1%	75	25	86	14
4%	82	18	90	10
8%	83	17	94	6

Figure S1. TEM images of xerogels 1 and 2 in DMSO-H2O (A and B, respectively) and DMF-H2O (C and D, respectively). Xerogel of 1 in toluene after air-drying (E).

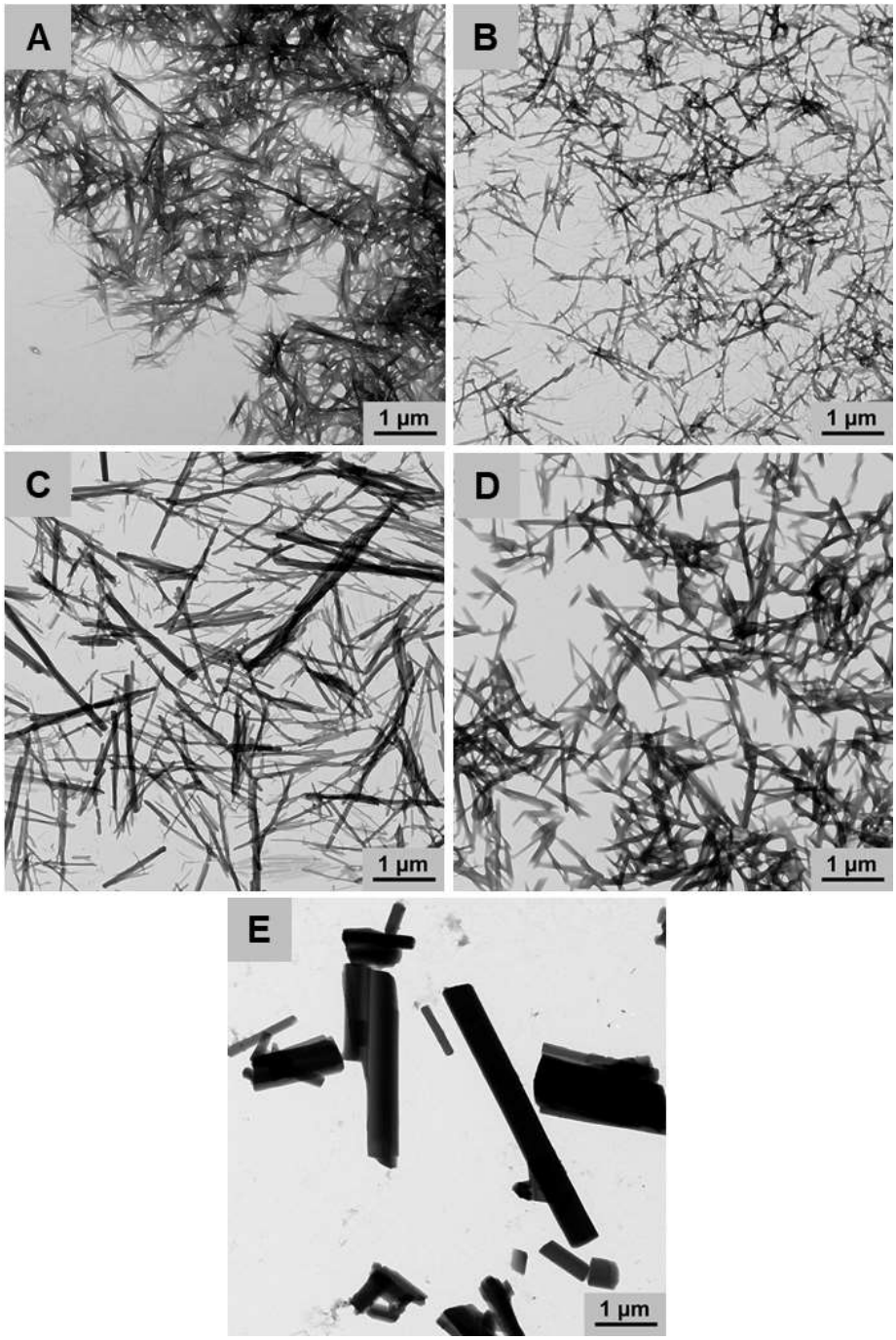


Figure S2. FT-IR spectra of compound 2 (OATBTU) in DMSO-H_2O.

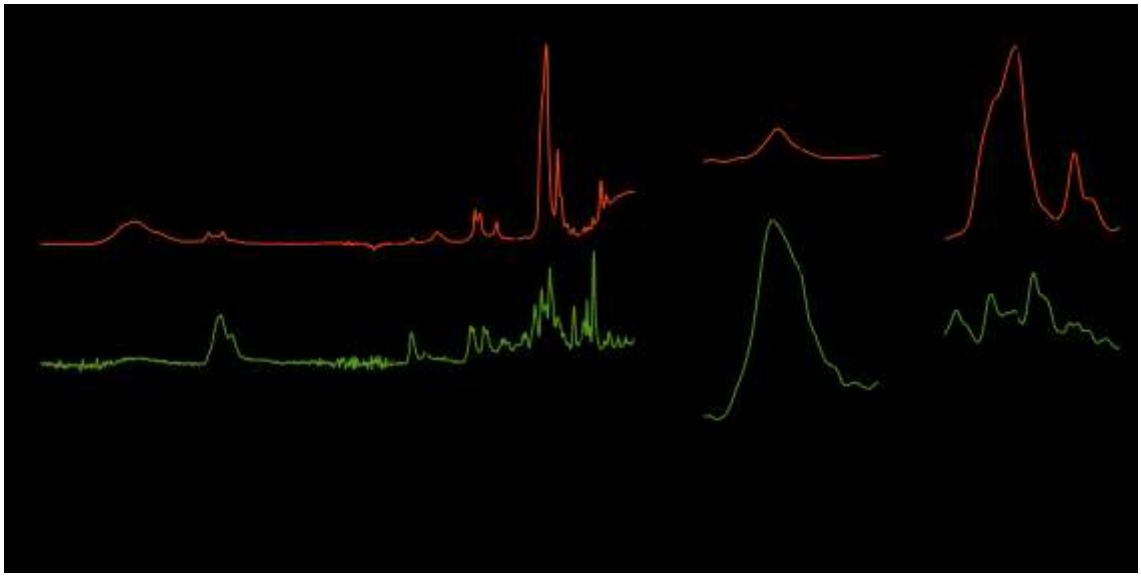


Figure S3. FT-IR spectra of compound 1 (MATBTU) in DMF-H_2O.

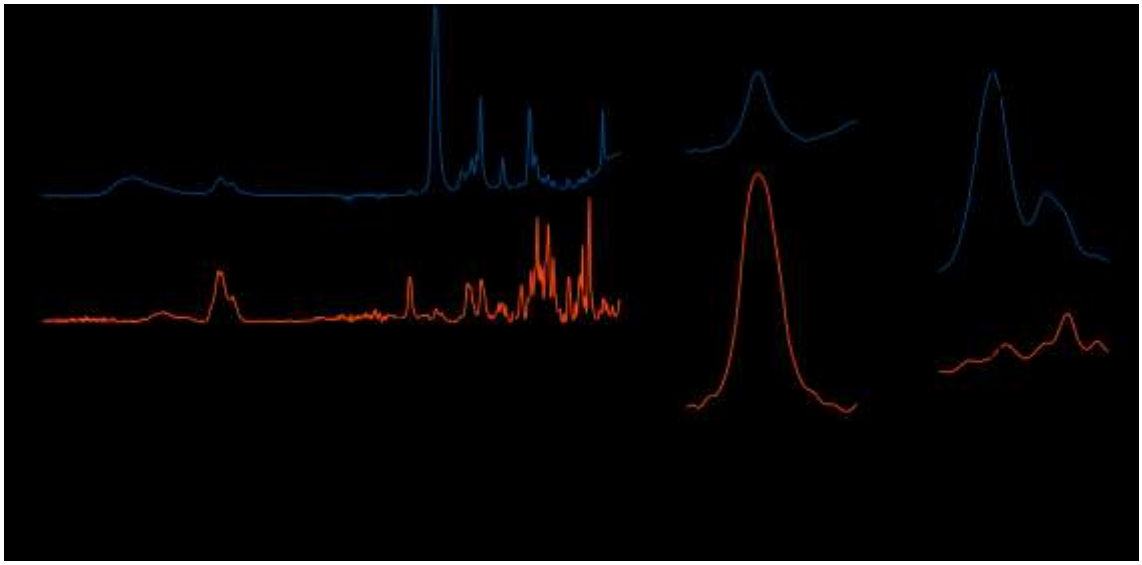
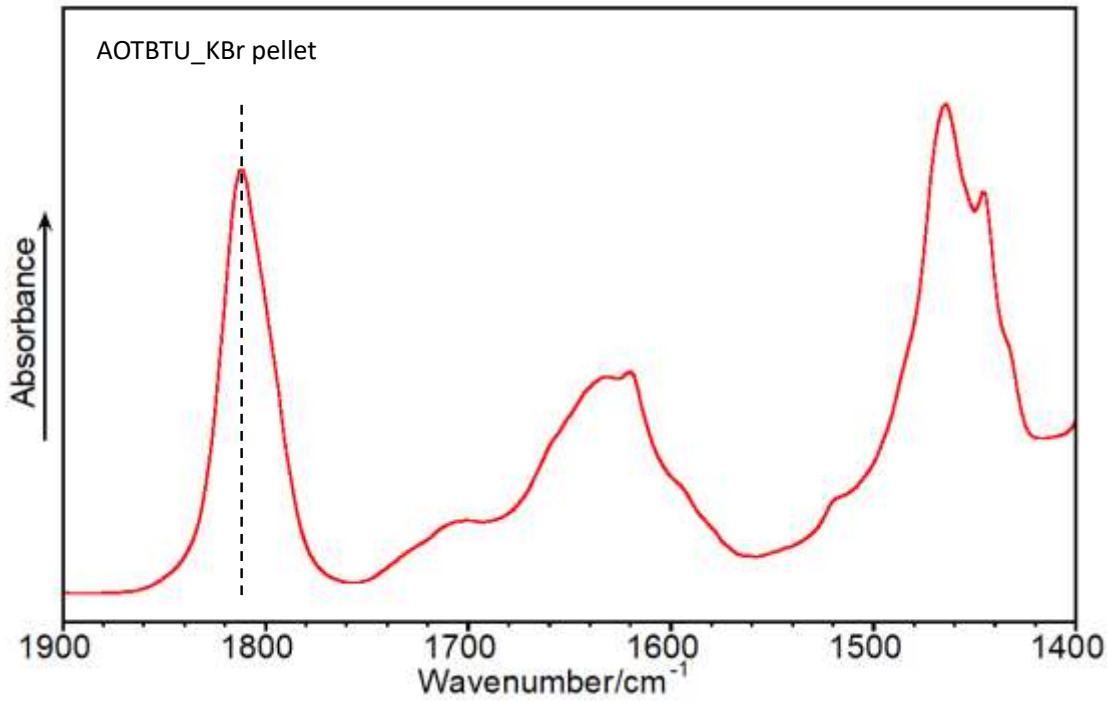
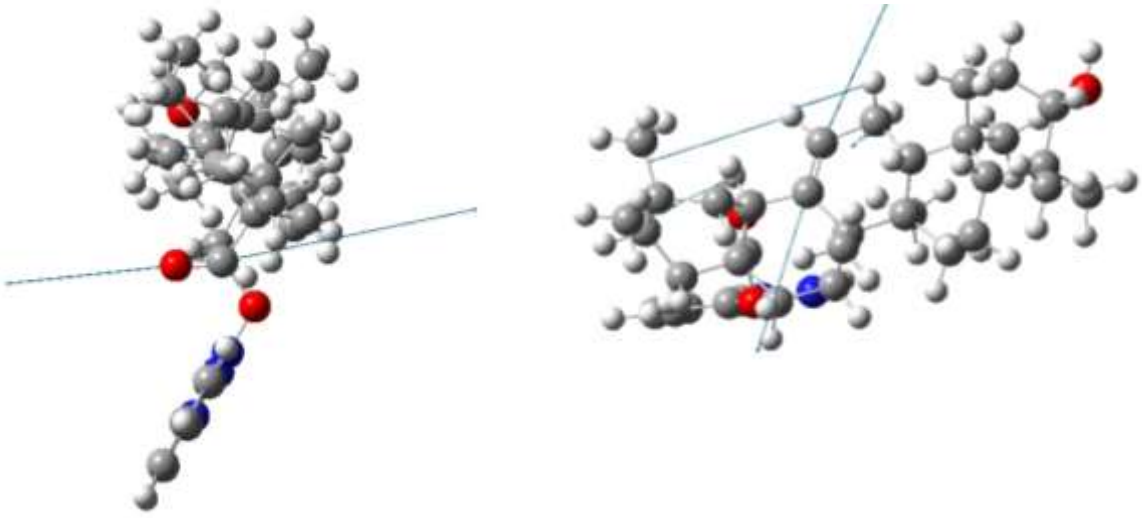


Figure S4.

a. FT-IR spectrum of OATBTU (2) in BrK pellet.



b. Vibrational eigenvectors and eigenvalues (scaled by 0.98) for C=O and C=C stretching vibrations of OATBTU (2) obtained by DFT (b3lyp/cc-pvdz) calculations.



1830 cm^{-1} 1667 cm^{-1}

Figure S5. Optimized structures, relative energies and calculated infrared and VCD spectra (b3lyp-pvdz) of the two conformations studied for MATBTU (1) and OATBTU (2). Red lines: conformations 1A and 2A. Blue lines: conformations 1B and 2B.

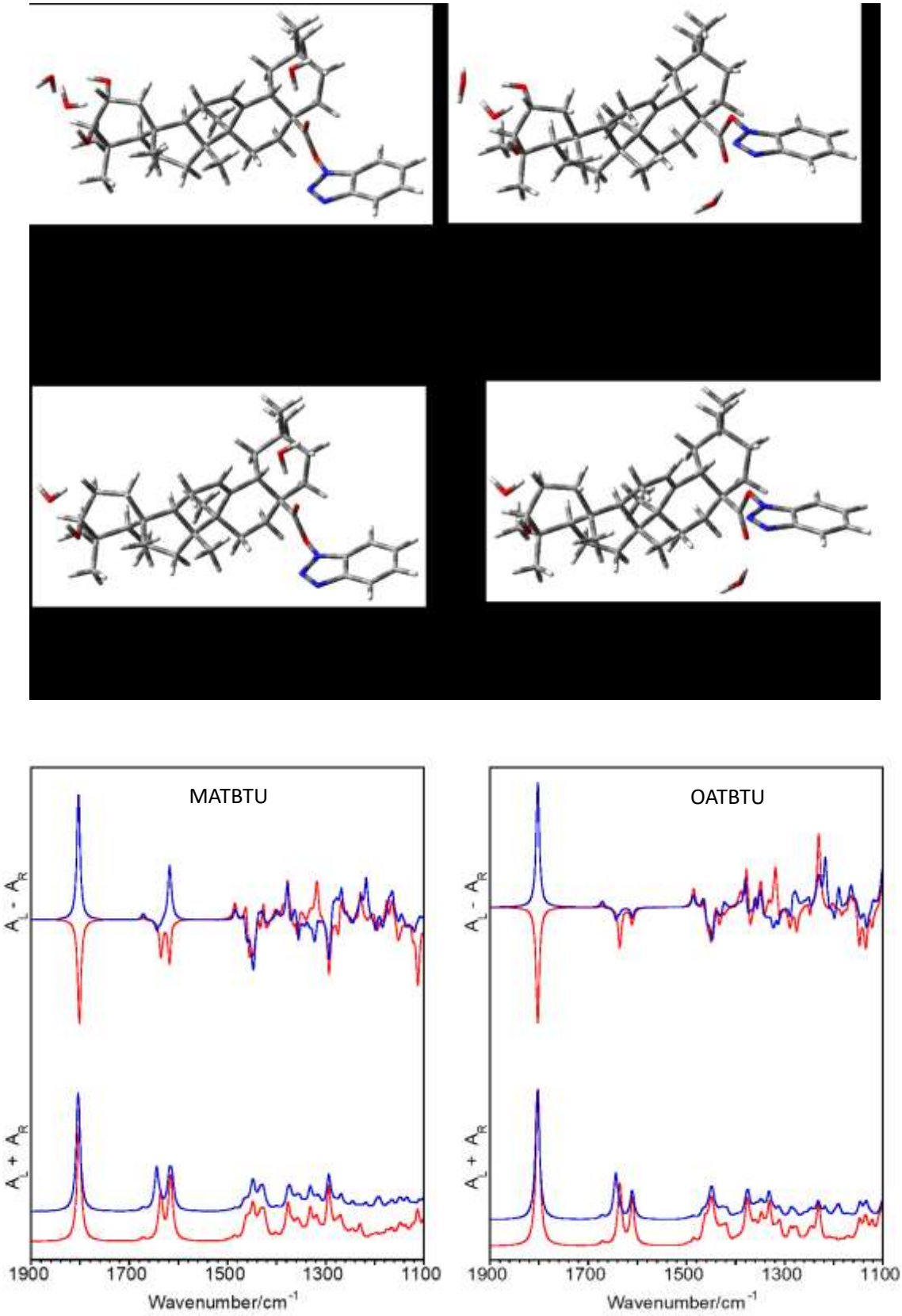


Figure S6. X ray diffraction (XRD) of xerogels of 1 (MATBTU) from toluene, DMF and DMSO. Xerogel of 2 (OATBTU) from DMSO.

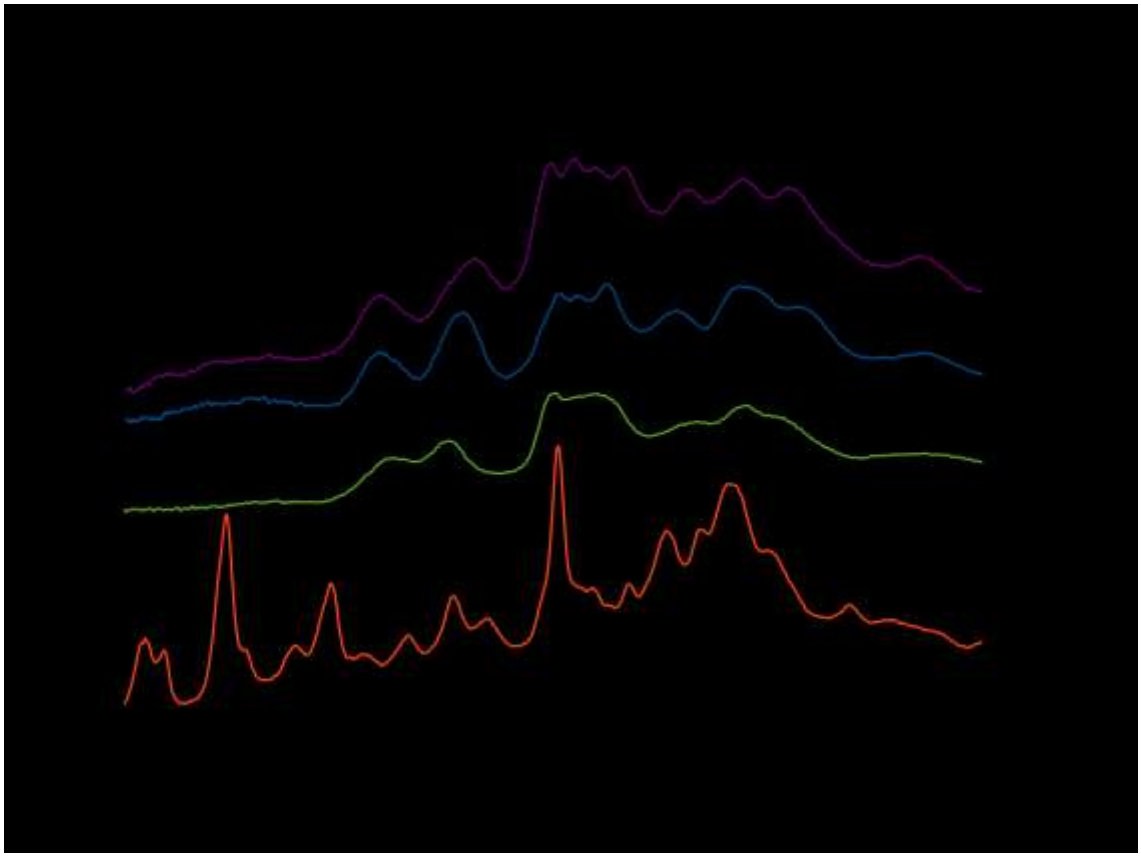
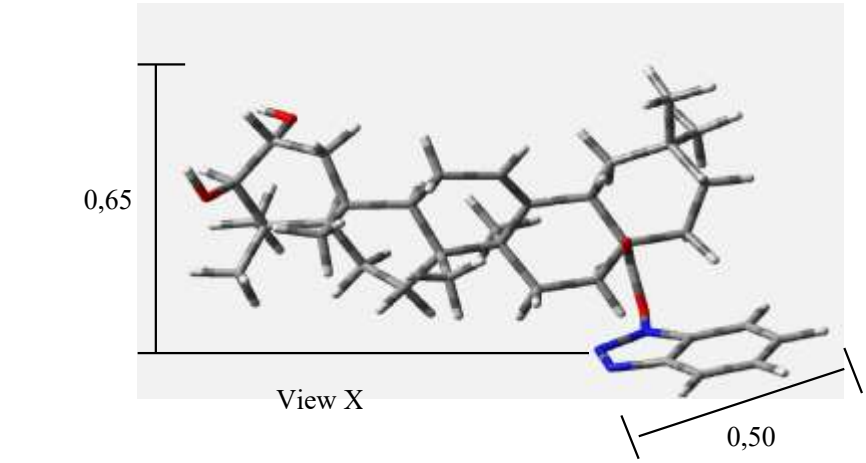
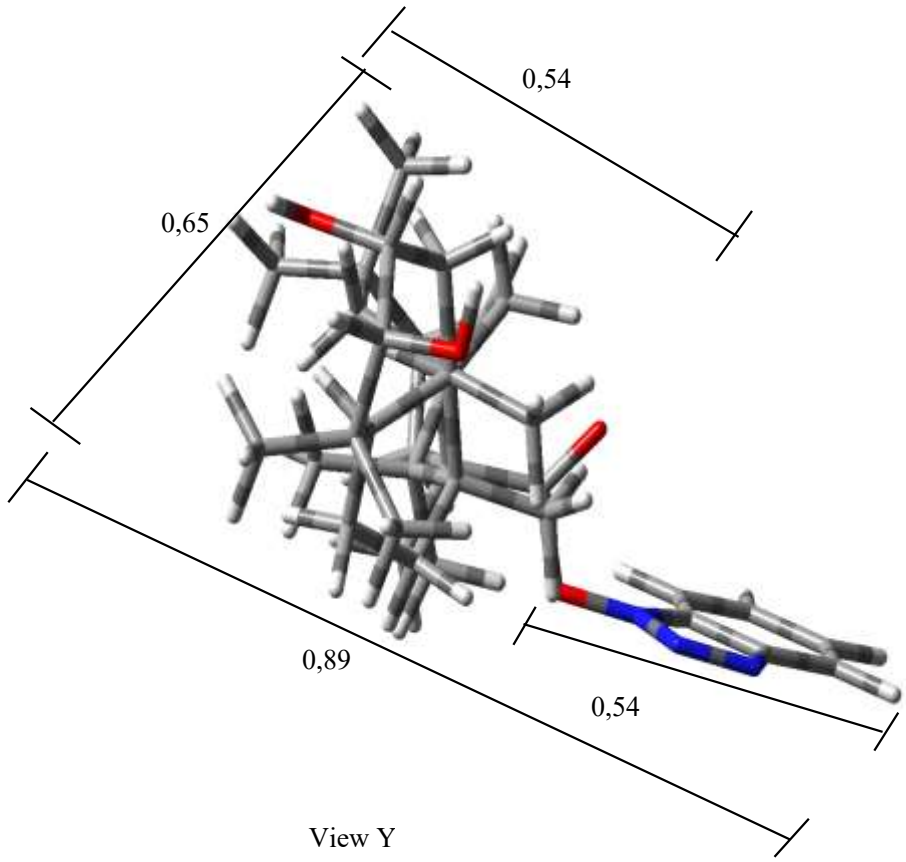


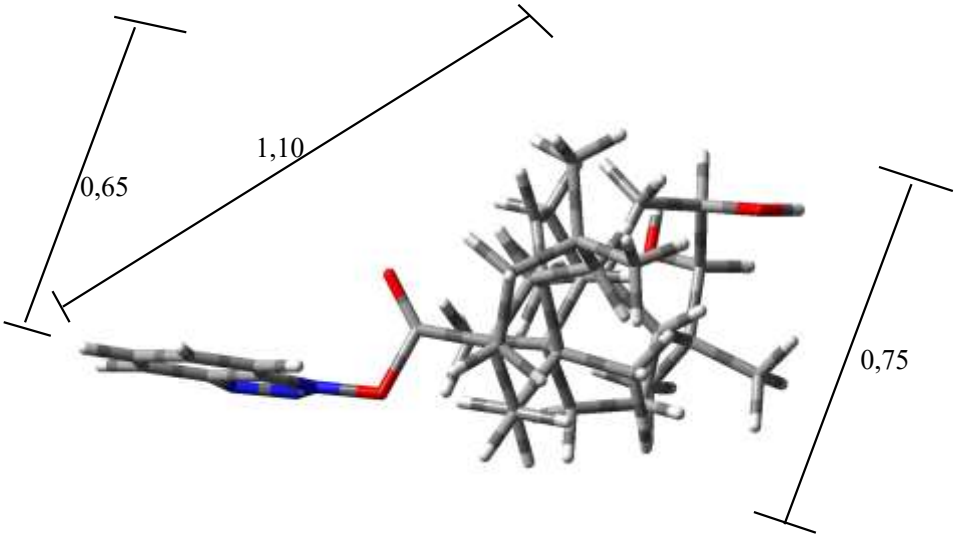
Table S3. Proposed assignations for the d-spacings measured by XRD (nm), on fibers formed in toluene, and molecular dimensions measured in the optimized structure (b3lyp / cc-pvdz) in MATBTU.

XRD spacings	Dimensions (isolated molecule)
0.50	
0.54	0.54
0.65	0.65
0.75	0.75
0.80	
0.89	0.89
1.10	1.10
1.48	1.48
1.61	
2.22	

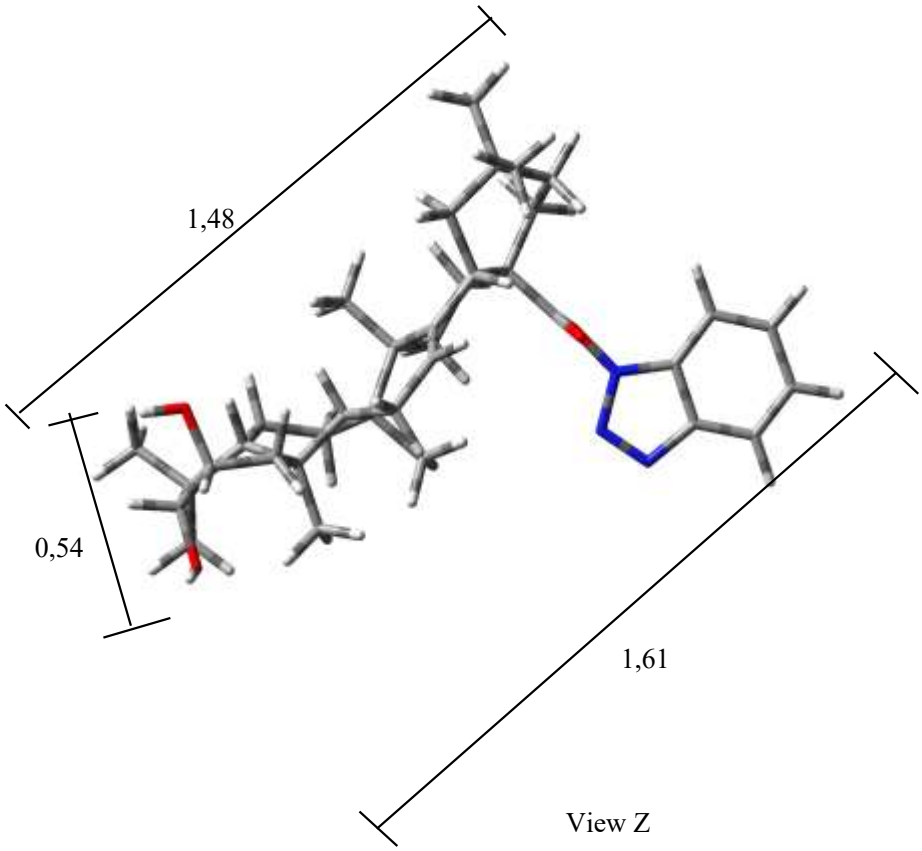
Figure S7. Molecular dimensions measured in the optimized structure (b3lyp / cc-pvdz) in MATBTU.







View -Y



View Z

Figure S8. Simulated packing mode of a dimer of 1 in toluene.

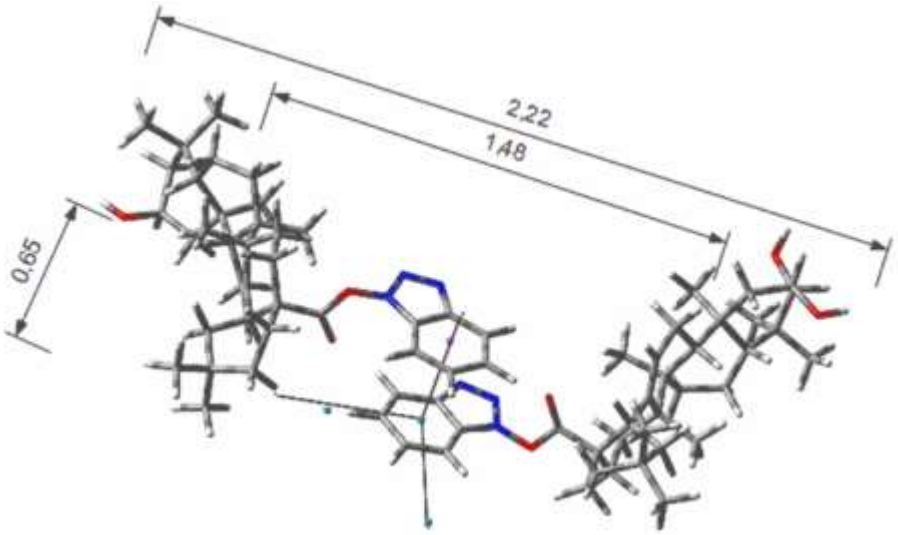


Figure S9. Frequency sweeps: viscoelastic moduli as a function of shear strain frequency, for oscillatory experiments of constant amplitude within the linear viscoelastic region and increasing frequency. A and B: gel 1 (MATBTU) in DMSO; C: gel 1 (MATBTU) in toluene; D and E: gel 2 (OATBTU) in DMSO; Full symbols represent values of the storage modulus; open symbols values of the loss modulus. Gelator concentration (only gels formed by capturing atmospheric water): ■□: 1%; ◆◇: 1.6%; ●○: 2%; ▲△: 3%; ▼▽: 4%; ★☆: 8%. Gelator concentration (only gels formed by direct addition of water): ▶▷: 1%.

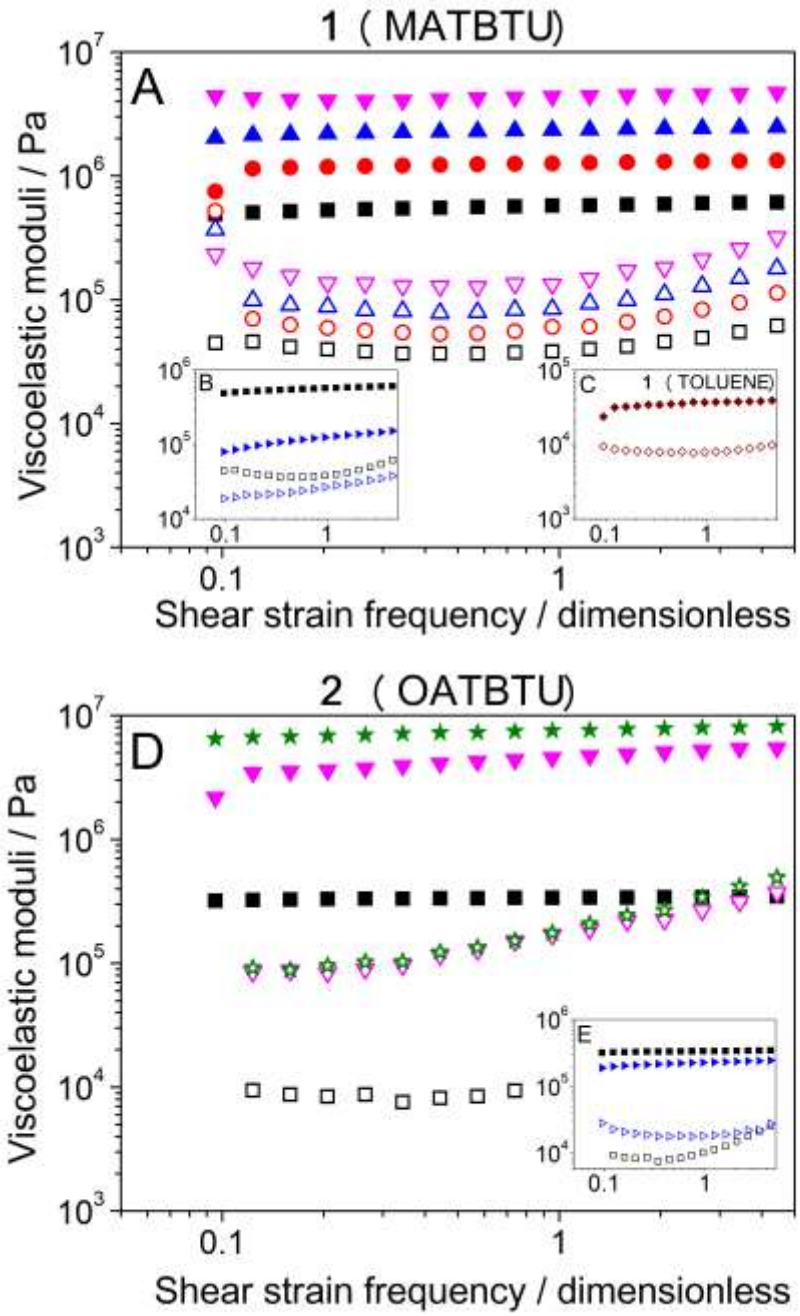


Figure S10. Viscoelastic moduli as a function of temperature for gel 2 (OATBTU) at a gelator concentration of 1% (w/v) in DMSO-H_2O. G': storage modulus; G'': loss modulus.