Journal Name

ARTICLE

Supplementary Information for:

Supramolecular organogels based on mesogenic 2,7-difunctionalized triphenylenes as simple system for water content assessment in light alcohols

Nahir Vadra, Cristián Huck-Iriart, Lisandro Giovanetti, Pablo H. Di Chenna and Fabio D. Cukiernik

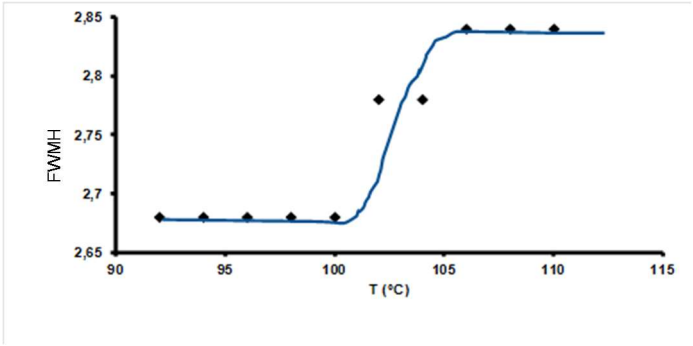


Figure S1 - Evolution of full-width at mid-height (FWMH) for the low-angle reflection detected in the N phase of **2,7-THTP-DiC4OH** as a function of temperature

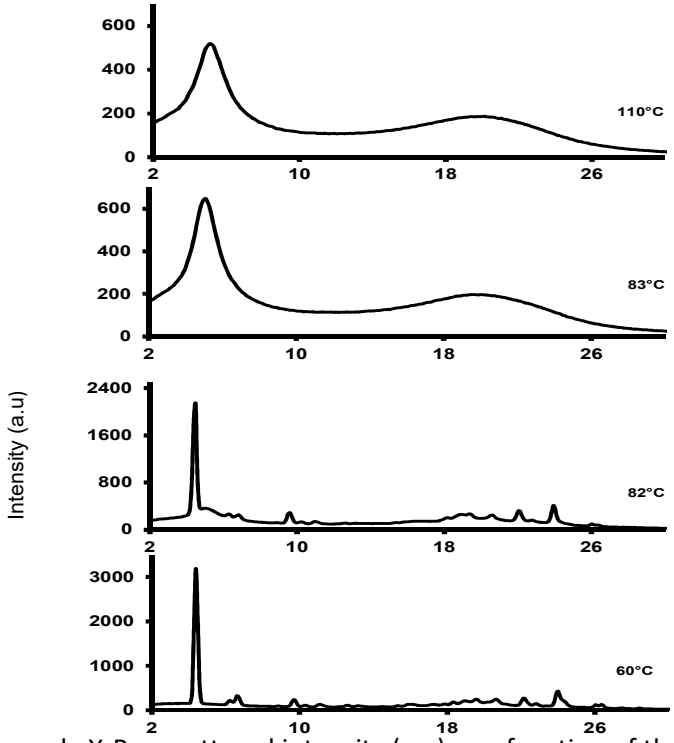


Figure S2 - Wide angle X-Ray scattered intensity (a.u) as a function of the scattering angle for **2,7-THTP-DiC6OH** at various temperatures.

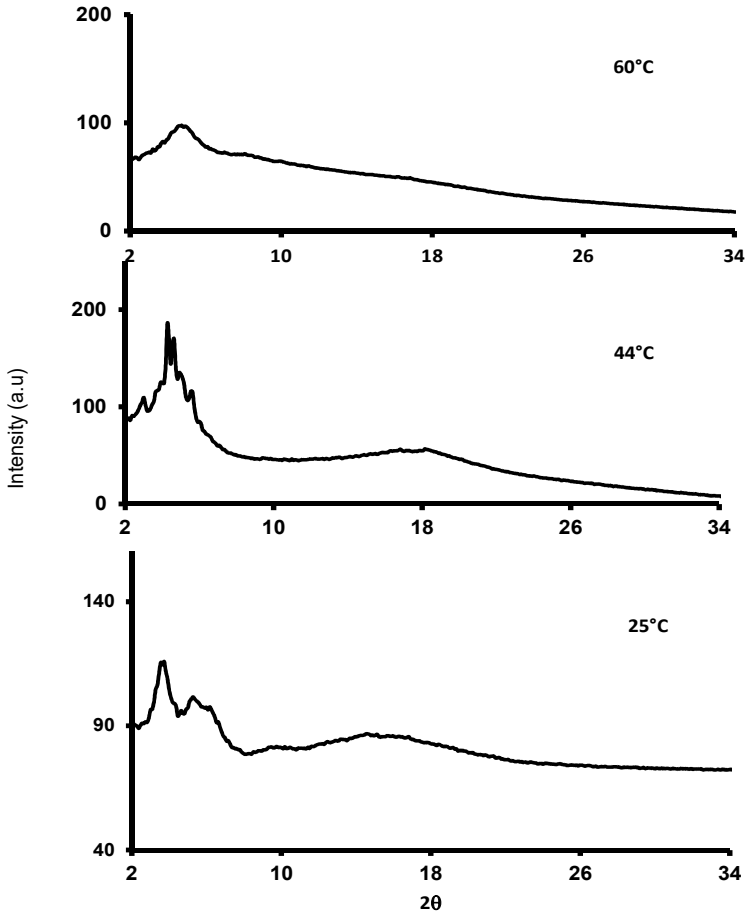


Figure S3- Wide angle X-Ray scattered intensity (a.u) as a function of the scattering angle for **2,7-THTP- DiC10OH** in the liquid (top), LC Col (mid) and amorphous solid (bottom) phases.

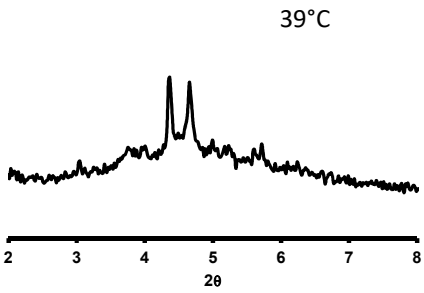


Figure S4 – Small angle X-Ray scattered intensity (a.u) as a function of the scattering angle for **2,7-THTP-DiC10OH** at 39°C

Structural analysis of the Columnar Mesophases

Columnar rectangular mesophases (Colr) have been found for both **2,7-THTP-DiC4OH** and **2,7-THTP-DiC10OH**. In addition to the expected difference in the values of the rectangular unit cell parameters *a* and *b*, the main difference between both cases is that the *n* = 4 derivative exhibits an ordered Colr mesophase, as evidenced by the peak at 3.6 Å, while in the case of the *n* = 10 homologue no such peak has been found.

In the case of the *n* = 4 derivative, the unit cell volume can thus be calculated as:

$V_{u.c.} = a * b * h = 38.5$ Å * 19.4 Å * 3.6 Å = 2688 Å^3

Irrespectively of the specific symmetry group (*C2mm* or *P2gg*), a slice of a rectangular mesophase contains two molecules per unit cell. The molecular volume in the Colr mesophase can thus be calculated for **2,7-THTP-DiC4OH** as half $V_{u.c.}$, i. e. 1344 Å^3 . This molecular volume corresponds to a very plausible 0.99 g/cm^3 bulk density, and is in excellent agreement with the one previously reported for a closely related compound in a Col_h mesophase[1]: **2,7-THTP-DiC5**$^{//}$ (where C5$^{//}$ = pentyloxy chain containing a terminal double bond): 1316 Å^3 .

Assuming the same bulk density for the longer n = 10 homologue (for which an experimental *h* value is not available), a molecular volume of 1593 Å^3 can be calculated. Using the experimental *a* and *b* values of the unit cell of its rectangular mesophase (40.8 Å and 21.7 Å respectively) a mean value for *h* can be calculated as 3.5 Å, in excellent agreement with expectation for polyaromatic systems.

Moreover, the difference in the molecular volumes calculated for both compounds, 249 Å^3, corresponds to a contribution of 21 Å^3 per added methylene, a value slightly lower than the one found in smectics (28 Å^3)[2], but in perfect agreement with the one found for a homologous series of triphenylene-based discotics.[3]

[1] F. Cecchi, A. Zelcer, P. Alborés, D. Guillon, B. Heinrich, B. Donnio, F. D. Cukiernik, "A convenient synthesis of a 2,7-difunctional tetra(alkoxy)triphenylene involving 4,4´-diacetoxy-3,3´-dialkoxybiphenyl as a key precursor and its conversion to extended hybrid mesogenic compounds", *Liq. Cryst*., 2013, **40**, 1121 - 1134.

[2] D. Guillon, A. Skoulios, J. J. Benattar "Volume and X-ray diffraction study of terephthal-bis-4,n-decylaniline (TBDA)" *J. Phys*., 1986, **47**, 133-138.

[3] [3] I. Paraschiv, P. Delfoterie, M. Giesbers, M. A. Posthumus, A. T. M. Marcelis, H. Zuilhof, E. J. R. Sudho "Asymmetry in liquid crystalline hexaalkoxytriphenylene discotics", *Liq. Cryst.* 2005, **32**, 977–983.

Figure S5. Pictures taken at 25°C of a sol and a gel (inverted flask) of gelator 2,7-THTP-DiC6OH (**5b**) in ethanol/water 95/5.

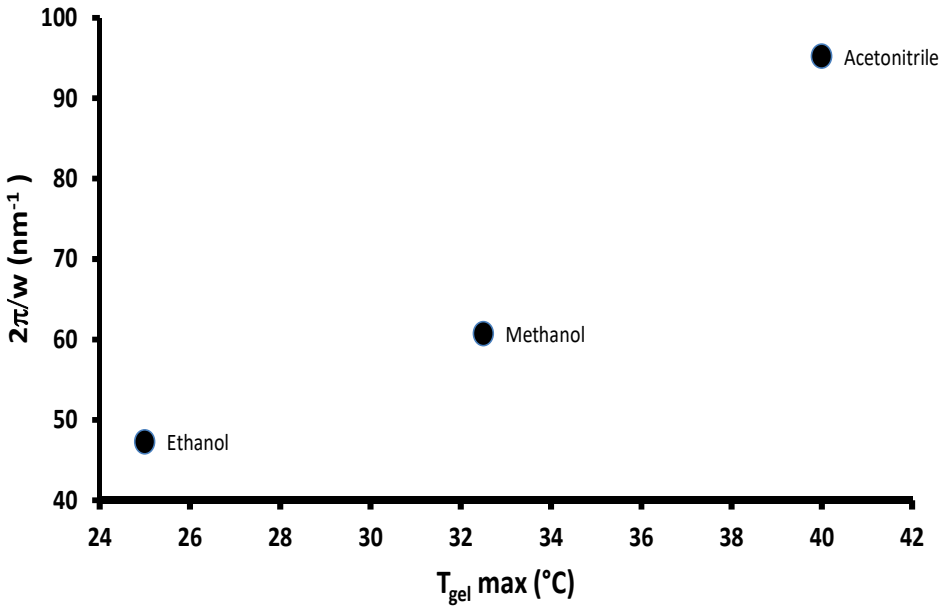
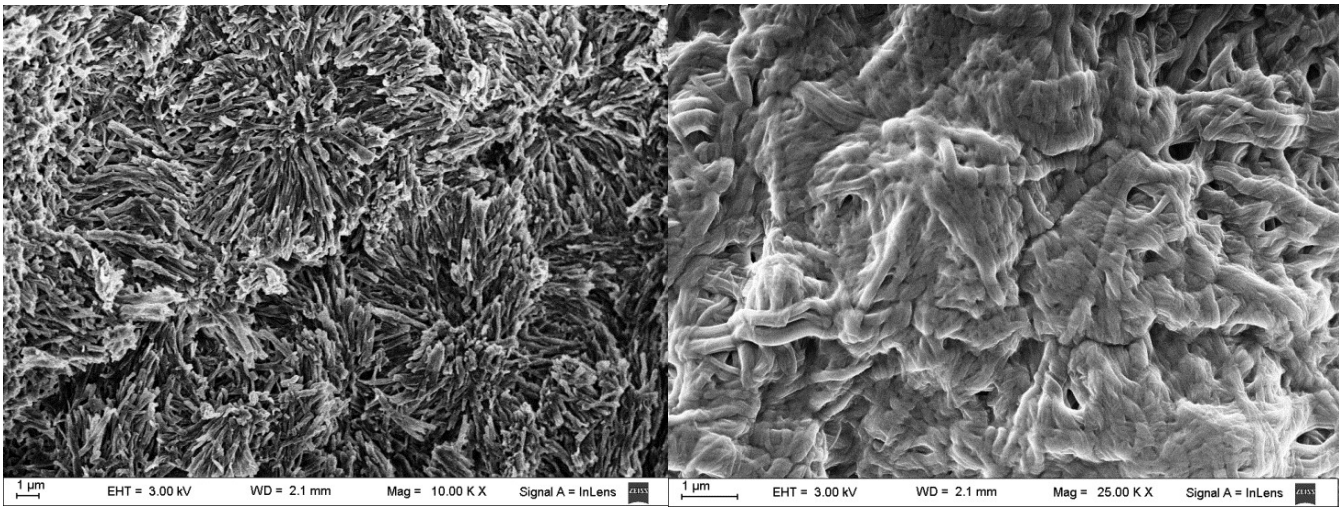


Figure S6. Correlation of the structural organization of the gels with their thermal stability: plot for **2,7-THT-DiOC6OH** of the reciprocal full-width at mid-height of the second diffraction peak 11 (from figure 7) vs. T_{gel}^{max} parameter.

n=4 methanol **n= 10 methanol**



n= 10 ethanol (50 x and 10x)

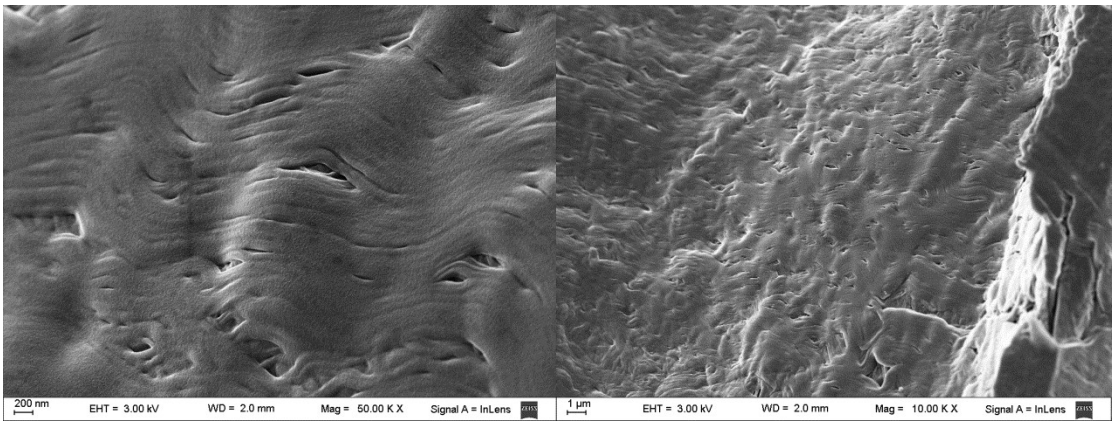


Figure S7 Extra SEM images of xerogels obtained from methanol and ethanol

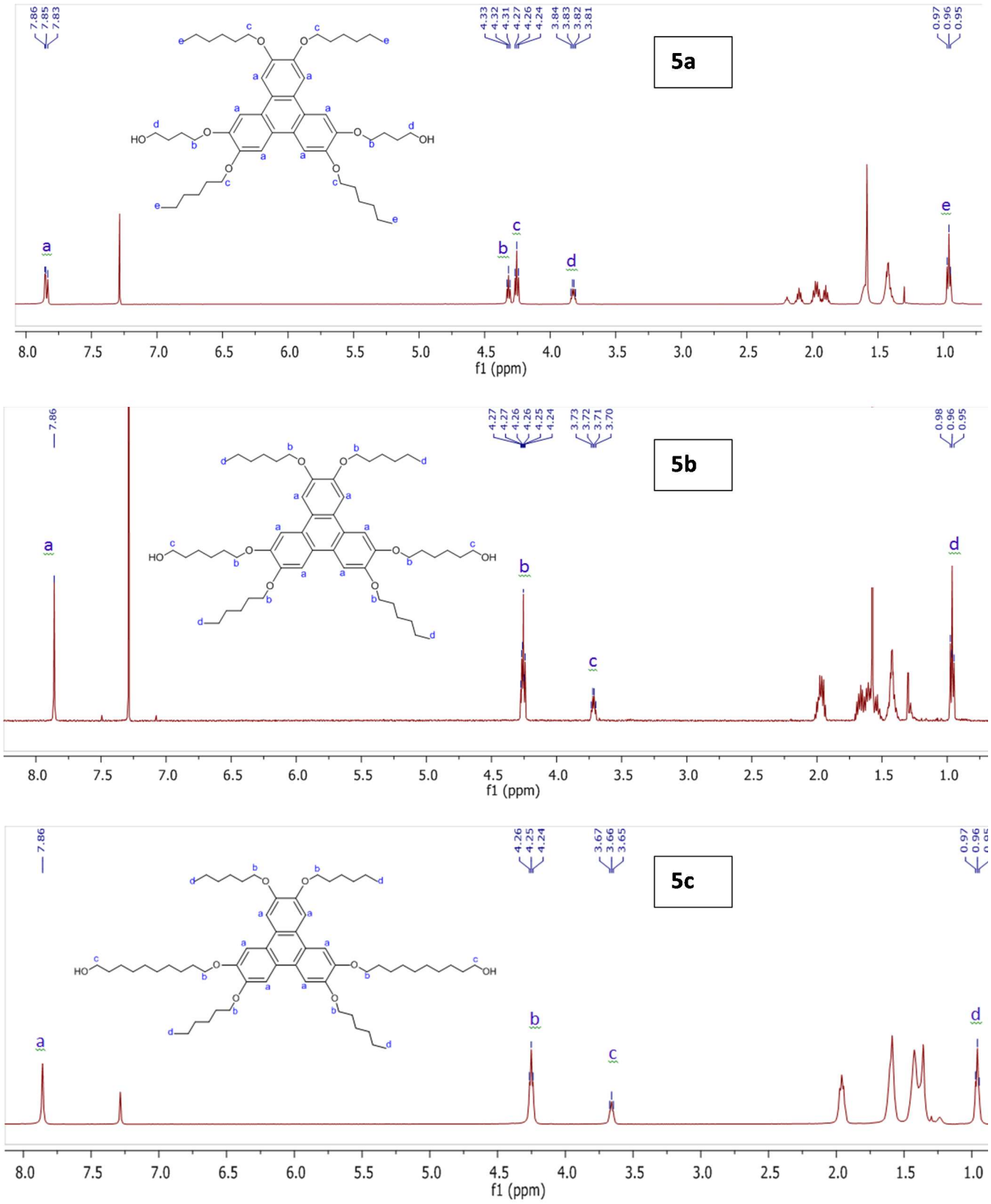


Figure S8. ^{1}H-NMR (500 MHz, $CDCl_3$) of compounds 5a, 5b, and 5C