

Supplementary Information for:

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

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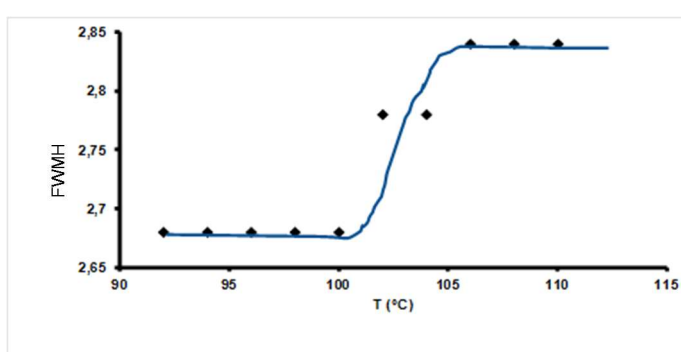


Figure S1 - Evolution of full-width at mid-height (FWMH) for the low-angle reflection detected in the N phase of 2,7-THTP-DiC4OH as a function of temperature

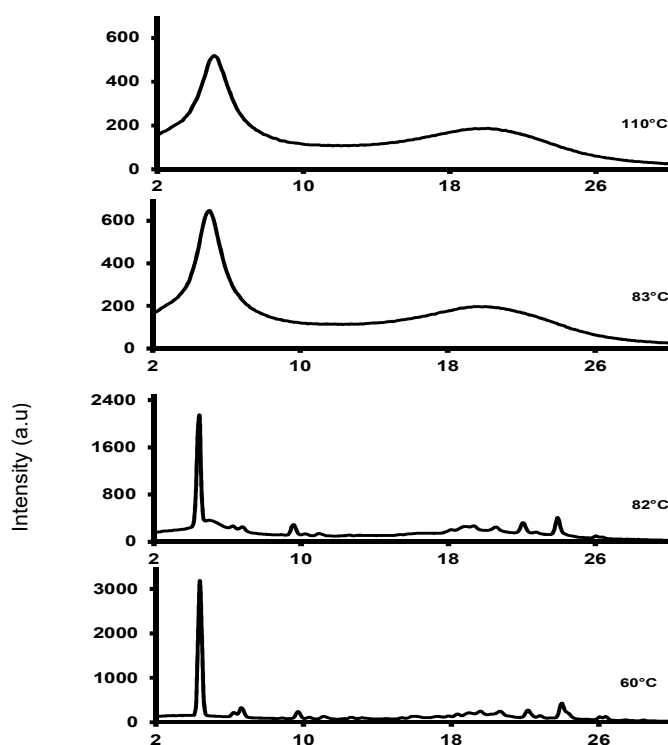
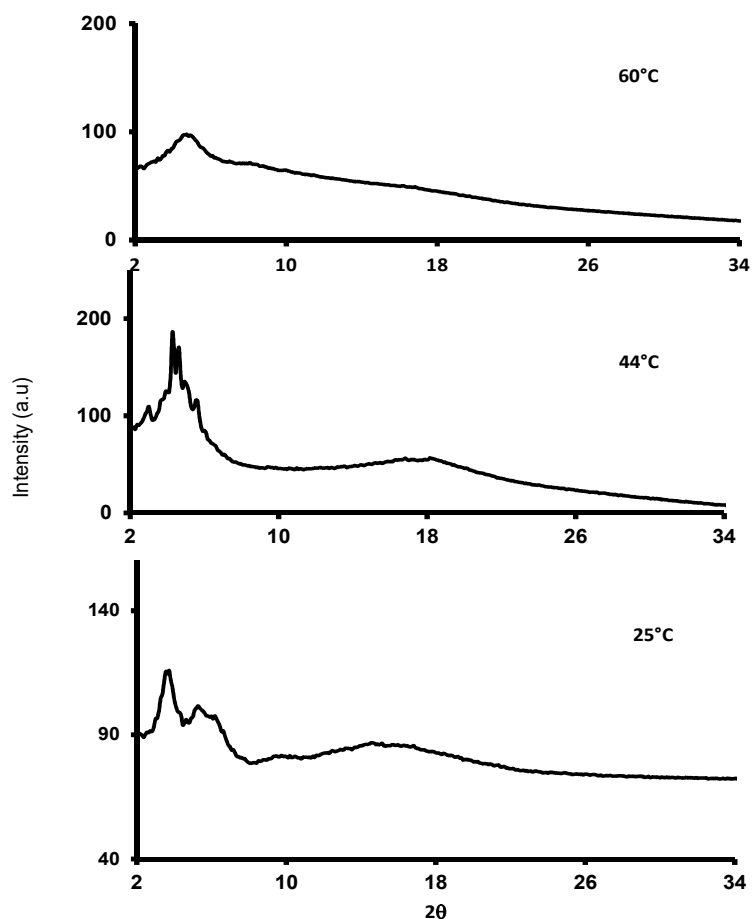
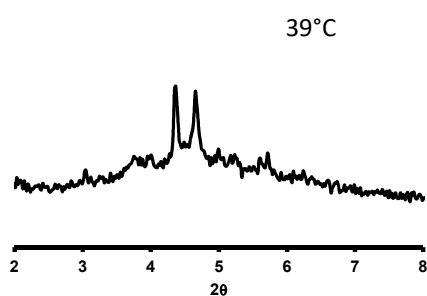


Figure S2 - Wide angle X-Ray scattered intensity (a.u.) as a function of the scattering angle for 2,7-THTP-DiC6OH at various temperatures.



**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:

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

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.  $1344 \text{ \AA}^3$ . This molecular volume corresponds to a very plausible  $0.99 \text{ g/cm}^3$  bulk density, and is in excellent agreement with the one previously reported for a closely related compound in a  $Col_h$  mesophase<sup>1</sup>: **2,7-THTP-DiC5<sup>//</sup>** (where  $C5^{//}$  = pentyloxy chain containing a terminal double bond):  $1316 \text{ \AA}^3$ .

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

Moreover, the difference in the molecular volumes calculated for both compounds,  $249 \text{ \AA}^3$ , corresponds to a contribution of  $21 \text{ \AA}^3$  per added methylene, a value slightly lower than the one found in smectics ( $28 \text{ \AA}^3$ )<sup>2</sup>, but in perfect agreement with the one found for a homologous series of triphenylene-based discotics.<sup>3</sup>

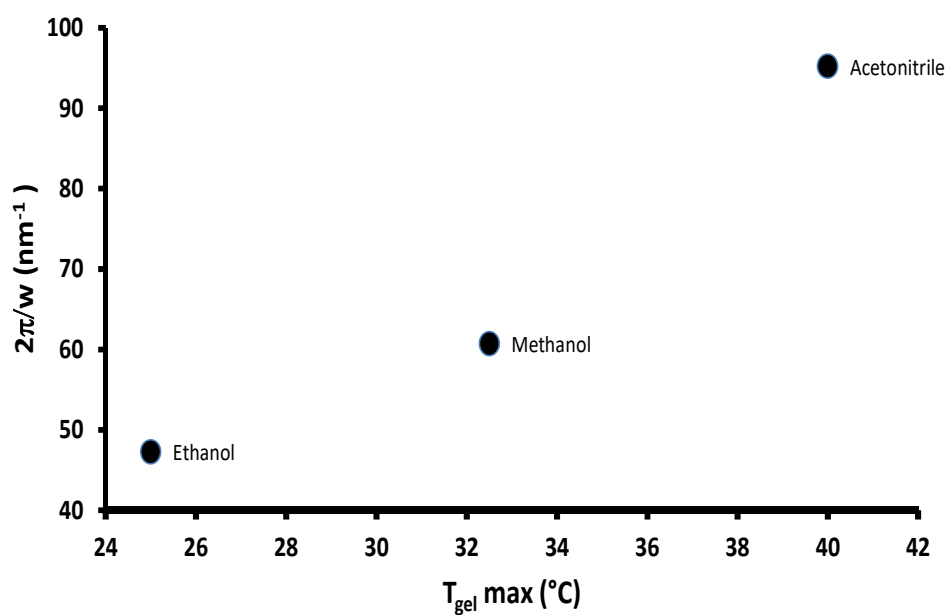
<sup>1</sup> F. Cecchi, A. Zelcer, P. Alborés, D. Guillon, B. Heinrich, B. Donnio, F. D. Cukiernik, "A convenient synthesis of a 2,7-difunctional tetra(alkoxy)triphenylene involving 4,4'-diacetoxy-3,3'-dialkoxybiphenyl as a key precursor and its conversion to extended hybrid mesogenic compounds", *Liq.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

<sup>2</sup> 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.

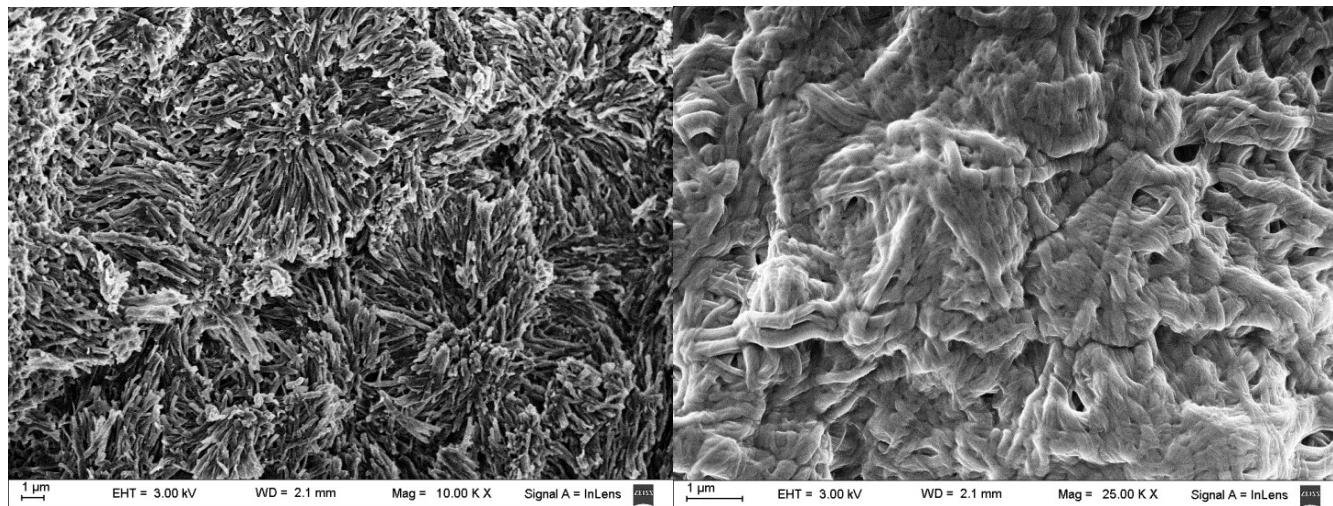
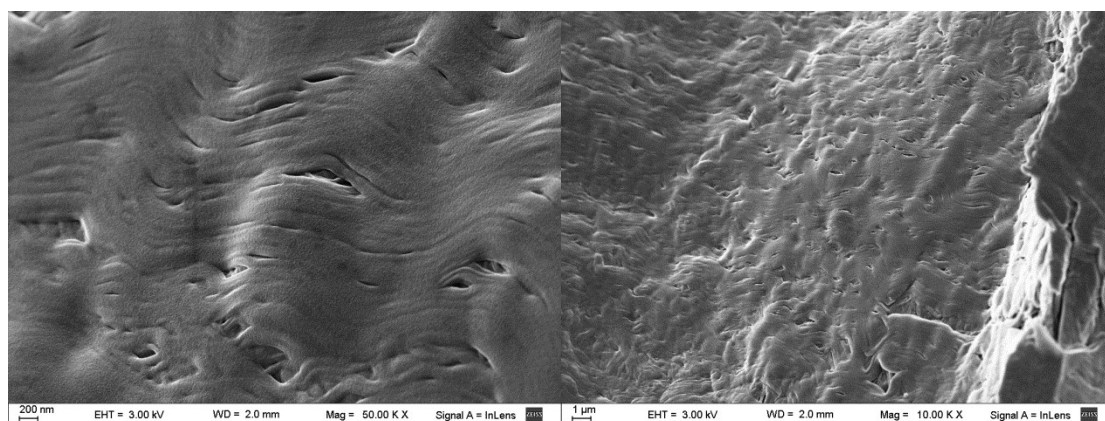
<sup>3</sup> I. Paraschiv, P. Delfoterie, M. Giesbers, M. A. Posthumus, A. T. M. Marcelis, H. Zuilhof, E. J. R. Sudho "Asymmetry in liquid crystalline hexaalkoxytriphenylene discotics", *Liq. Cryst.* 2005, **32**, 977–983.



**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

