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

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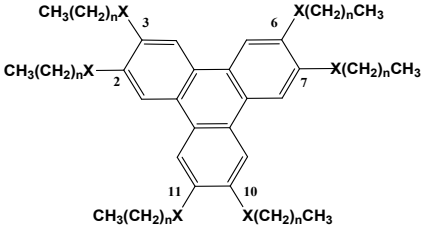
A series of three triphenylene compounds -denoted **2,7-THTP-DiCnOH**- bearing four hexyloxy ancillary chains and two variable-length alkoxy chains terminally functionalized with hydroxyl groups have been synthesized and characterized. The studied compounds exhibited thermotropic mesomorphism; the detailed nature of the mesophases was found to depend on the relative positions of the terminal functional groups relative to the crown formed by the ancillary chains. All the studied compounds were able to act as supramolecular gelators in a variety of alcohols, their organogelating ability has been rationalized in terms of physicochemical parameters like dielectric constant, which allowed to establish very precise predictive "solvent gelation windows" for each compound. Remarkably stable gels have been detected for **2,7-THTP-DiC6OH** in methanol. As a proof of principle, we present the water sensing performance as a rapid method for the assessment of water content in alcohols samples based on the influence that the water content exerts on gels´thermostability.

Introduction

Hexasubstituted triphenylenes (TPs) bearing long aliphatic chains at the 2,3,6,7,10,11- positions (scheme 1) exhibit a remarkable ability to act as structural organizers. Indeed, in the bulk state, such compounds can self-organize into liquid crystalline (LC) phases and, in the presence of organic solvents, some of them have shown to yield supramolecular gels.[1 2] The detailed structural features of their LC phases (type of organization, structural parameters, thermal range, etc) depend on the chain length *n* (e.g.: for X = O, columnar hexagonal mesophases Col_h are observed for *n* = 4 - 13 but not for *n* = 3)[3] and on the nature of the bridging group X (e.g.: OR chains usually give rise to Col_h mesophases, O-C(O)R substituents usually lead to rectangular Col_r mesophases, whereas the compound with SC_6H_{12} chains exhibited a Col_h mesophase with helical superstructure).[4] Moreover, several kindred compounds, in which the core is not rigorously triphenylene, but nitrogenated analogs, like hexaazatriphenylenes[5] also exhibit Col mesophases. Intercalation of acceptor moieties like trinitrofluorenone (TNF) between TP cores promotes the occurrence of columnar nematic (N_c) or Col_h mesophases in otherwise non-mesogenic TP-based polymers[6] as well as switching between Col_r and Col_h mesophases in TP-based oligomers[7].



Scheme 1: General structure of 2,3,6,7,10,11-hexa-substituted triphenylenes

When the hexasubstituted TP bears one or more terminal functional groups, the range of self-organizing possibilities increases remarkably.[8 9] These terminal functional groups can: i) interact through non-covalent or excluded volume interactions, thus modifying the structure of the LC phase in pure compounds,[10 11 12] ii) allow the incorporation of TP

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Electronic Supplementary Information (ESI) available: Temperature variable WAXS and SAXS experiments, calculation of molecular volumes in the Col LC phase, extra SEM images of xerogels, additional images of gels, detailed ^{1}H-NMR spectra of the three compounds. See DOI: 10.1039/x0xx00000x

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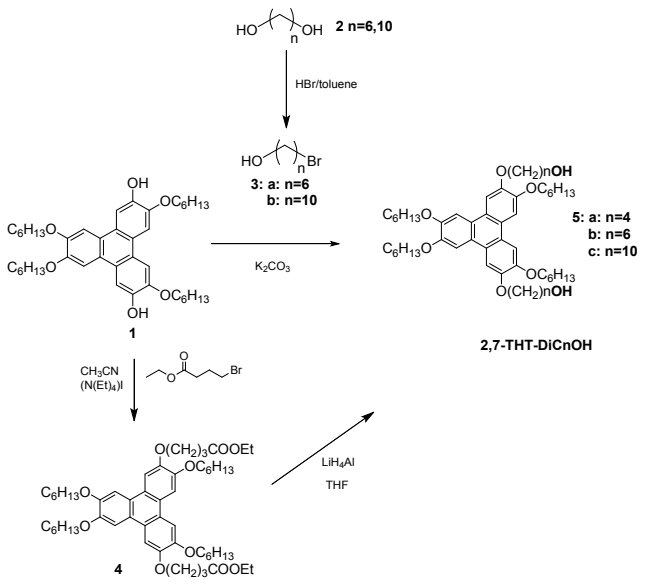


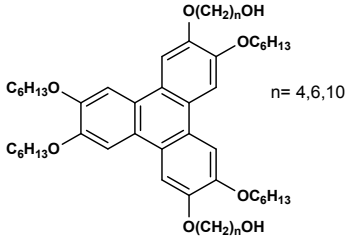
Scheme 2: Synthesis of 2,7 THTP-DiC*n*OH compounds

moieties in multiblock architectures, either as discrete molecules[13 14 15 16 17 18]or extended main-chain[19 20 21]or side-chain[22 23 24 25 26] polymeric liquid crystals. iii) self-assemble in a liquid media by reversible interactions among them or with solvent molecules, yielding different types of supramolecular organogels[27 28 29 30 31 32].

The number, nature and position of the terminal functional groups are key factors defining the supramolecular self-assembly they can build up.

In the present study, we analyze the organizing ability of three different TPs "decorated" with hydroxyl groups in the terminal positions of the alkoxy chains located at the 2 and 7 positions of an hexa(alkoxy)triphenylene bearing four linear hexyloxy chains in the other positions (**2,7-THTP-DiC*n*OH,** scheme 2).

The three compounds differ in the length of the spacer between the OH functional groups and the TP core (*n= 4, 6* and *10)*. The shortest spacer (*n* = 4) places the OH groups inside the "crown" formed by the aliphatic chains, the intermediate one (*n* = 6) locates them exactly at the edge, and the longer



Scheme 3: Structure of triphenylene derivatives studied in the present work. **THTP** stands for tetra(hexyloxy)triphenylene

one (*n* = 10), outside this region. For each one of these compounds we studied the mesomorphic properties as well as the organogelating ability in different solvents. In this paper we focus on the molecular features giving rise to the experimental trends; and additionally we suggest a simple method, based on these compounds, to assess the water content of light alcohol samples.

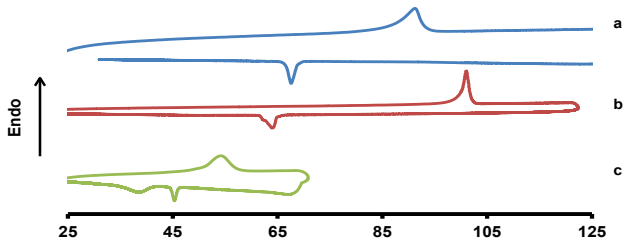


Fig. 1 DSC traces of compound: **5a** (a), **5b** (b) and **5c** (c)

Results and Discussion

Synthesis and Characterization:

Target compounds have been prepared by attaching to the **2,7-THTP-DiOH** precursor (**1**, synthesized after Cecchi *et al* [33]) two aliphatic chains of variable length containing terminal hydroxyl functional groups (Scheme 3). In the *n* = 10 and 6 cases, the precursor has directly been etherified with the corresponding α,ω-bromoalcohol **2**. In the *n* = 4 case, due to some difficulties found in the purification of the synthesized 4-bromo-butanol ascribed to its higher volatility, etherification of **2,7-THTP-DiOH** has been carried out with a commercial bromoester, followed by reduction of the resulting TP-diester **4** to the targeted diol. All synthesized compounds have been characterized by ^{1}H-NMR, ^{13}C-NMR, elemental analysis, and MS-ESI (see Experimental section and supplementary Information).

Mesomorphic Properties:

Mesophases characterization:

Mesomorphic properties of all three studied compounds have been studied by Polarized Optical Microscopy (POM), Differential Scanning Calorimetry (DSC) and variable-temperature Wide-Angle X-ray Scattering (T_{var}-WAXS); Small-Angle X-rays Scattering (SAXS) has been used in some cases to assess specific structural aspects of the LC phases of the studied compounds.

The *n* = 4 compound **2,7-THTP-DiC4OH** exhibits, on cooling, two successive LC phases: a nematic one (N) from 100 to 90ºC, and a rectangular columnar one (**Col$_r$**) between 90 and 88ºC. The DSC trace of this compound (Figure 1a) shows only one peak on cooling and one peak on heating. Nevertheless, POM allowed to identify a slightly marbred texture appearing at 98ºC from the non-birrefringent isotropic liquid (Figure 2a), and a distinctive second texture characterized by Malta

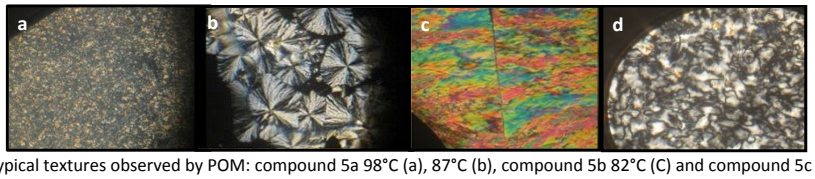


Fig. 2 Typical textures observed by POM: compound 5a 98°C (a), 87°C (b), compound 5b 82°C (C) and compound 5c 44°C (d)

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Crosses (Figure 2b) that was detected in experiments conducted under very careful cooling conditions, below 90ºC. The nature of each of these two mesophases has been firmly established through T_{var}-WAXS experiments (Figure 3). The WAXS diffraction pattern collected at 92ºC shows a low-angle peak narrower than the one found at higher temperatures (the detailed evolution of its full-width at mid-height –FWMH-, showing its abrupt increase at the transition temperature, is shown on supplementary Figure S1) while at wide angles only a broad halo at *ca*. 19º is seen. On these basis, the high temperature mesophase of **2,7-THTP-DiC4OH** is assigned as N_D. Between 90 and 88ºC, the wide angle region exhibits, at *ca*. 25°, a weak peak corresponding to π-stacking, thus confirming the ordered columnar nature of this phase (Figure 3 and Table 1); narrow peaks at low angles, indexed as 11 and 20, complete the picture of a Col_r mesophase.

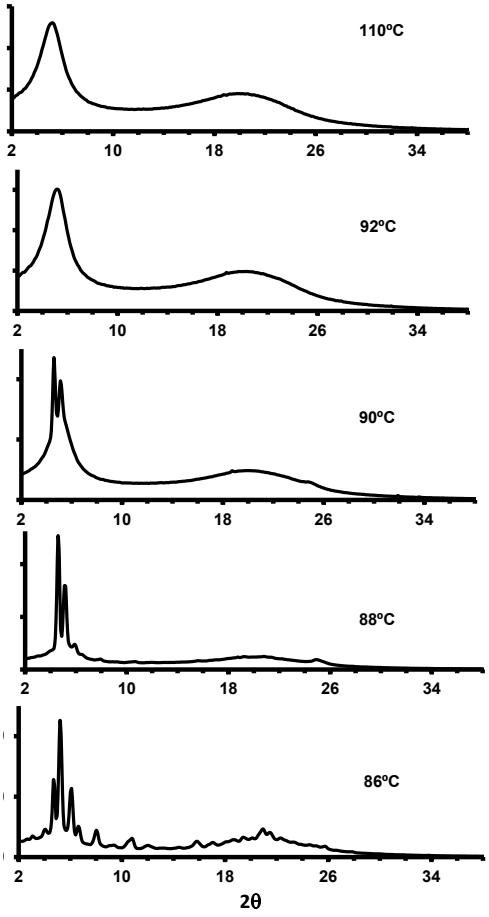

Fig. 3 WAXS patterns for **2,7-THTP-DiC4OH** at various temperatures.

The *n* = 6 homolog **2,7-THTP-DiC6OH** exhibits a monotropic nematic mesophase (N) in a narrow thermal range, which in turn depends on the cooling rate. Indeed, some experiments showed a "mosaic" texture at *ca*. 80ºC, whereas others did not. A WAXS pattern of this compound in the N phase, detected by this technique from 84 to 82ºC, is shown on Figure 4 (top), which also collects the relevant WAXS and SAXS patterns for each of the studied compounds. DSC runs (Figure 2b) only show the endothermic peak corresponding to clearing near 97ºC on heating and its exothermic counterpart on cooling (*ca*. 60ºC), the latter certainly corresponds to crystallization, as revealed by T_{var}-WAXS (Figure S2).

The heaviest *n* = 10 homolog exhibits a monotropic mesophase between 46 and 39ºC. Indeed, its DSC trace (Figure 1c) shows one endothermic peak on heating and two exothermic peaks

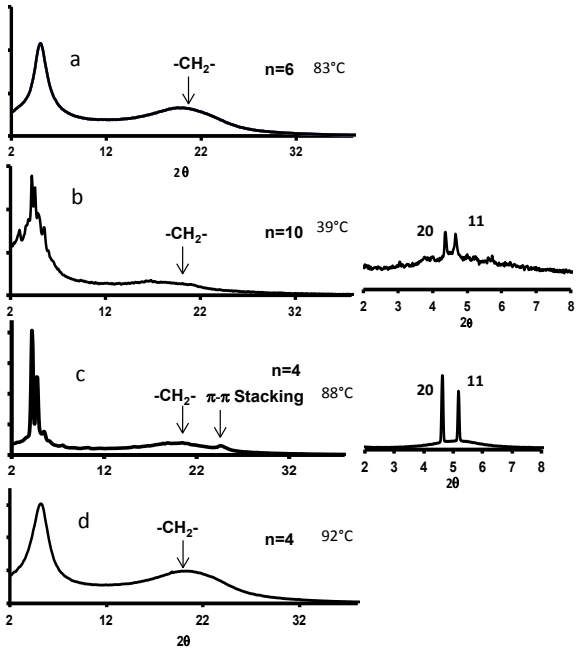

Fig. 4 WAXS patterns of each of the LC phases opf the three **2,7-THTP-DiCnOH** compounds studied in this work. Also shown: SAXS details of the Col_r phases.

on cooling. POM in this intermediate phase (Figure 2d) shows a texture compatible with Col mesophases, with small different regions. WAXS (Figure S3) reveals a low degree of organization both in the high temperature phase (isotropic liquid), and in the phase present at room temperature (amorphous solid). Nevertheless, the WAXS pattern corresponding to the phase present at intermediate temperatures corresponds to an ordered material, with peaks both in the low-angle region and the region corresponding to aliphatic chains (*ca*. 19º i.e. 4.5 Å). A detailed analysis of this intermediate phase, carried out by SAXS (Figure 4b) allows to assign this phase as LC Col_r, with cell parameters a = 40.8 Å and b = 21.7Å. In some patterns (Figure S4), additional peaks, corresponding to a superimposed crystalline phase, are also detected, in agreement with the two coexisting textures observed by POM, a kinetic issue associated to the monotropic character of the LC phase.

Molecular analysis of the mesomorphic trends:

n	Phases	Lattice parameters [Å]	*d* spacing [Å] Obsd (calcd)	Miller indices
4	I · 100°C · N · 90°C · Colr · 88°C · Cr	a=38.5;b=19.4	19.3 (19.3); 17.3 (17.3)	20; 11
6	I · 84°C · N · 82°C · Cr	-	-	-
10	I · 46°C · Colr · 39°C · Cr	a= 40.8; b=21.7	20.4 (20.4); 19.1 (19.1); 14.7 (14.9)	20;11; 21

Table 1. Phase sequence and structure for the three studied compounds

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As described above, Col_r mesophases have been detected for **2,7-THTP-DiC4OH** and **2,7-THTP-DiC10OH** but not for **2,7-THTP-DiC6OH**. It suggests that the relative length of the ancillary *vs*. functionalized chains plays a significant role in the occurrence of such rectangular mesophases, which seem to appear when the functionalized chains in the 2 and 7 positions are either longer or shorter than the ancillary ones. This fact can be interpreted on the basis of a simple geometrical model, schematically depicted in Figure 5: in the case of the *n*=6 derivative, the six aliphatic chains (which are likely conformationally disordered, as in the models nowadays accepted for columnar mesophases)[34 35 36 37] are of the same length and can thus give rise to a discotic molecular geometry. In the case of the *n*=10 homolog, the two functionalized chains (also "molten") are longer than the four ancillary ones, thus yielding an overall elliptical molecular geometry. A similar situation can be suggested for the *n* = 4 derivative, where the ancillary chains might be forced to further coil/fold in order to fill the void space created by the shorter bridging chains, yielding again an elliptical molecular geometry. It should be pointed out that the molecular volumes calculated for the two compounds exhibiting Colr mesophases (see ESI for details) agree with those measured for closely related compounds in columnar mesophases, yield plausible bulk densities, and suggest a volume contribution per added methylene consistent with the one found in other homologous series[38].

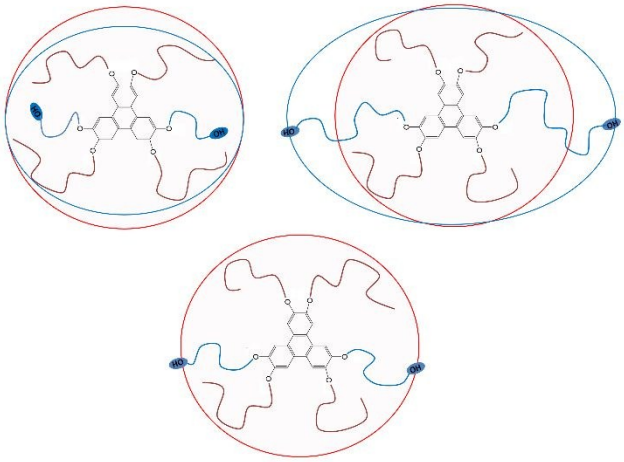

Fig. 5 Schematic sketch of the molecular geometries of 2,7-THTP-DiCnOH compounds. Red: rather discoid form of the compound bearing six aliphatic chains of approximately the same length (n = 6). Blue: elliptic form suggested for the other derivatives, arising from longer bridging (blue) than ancillary (brown) chains (n = 10) or further folding/coiling of the ancillary chains filling the void space around the short functionalized chains (n = 4).

The lack of intracolumnar diffraction peaks at *ca* 3.5 Å in the case of the *n* = 10 derivative suggests that the interactions between terminal hydroxyl groups prevail over π-stacking, thus avoiding intracolumnar order. It seems it can only manifest when hydroxyl groups are hindered by the ancillary aliphatic chains, (as in the case of the *n* = 4 derivative). The absence of an organized Col mesophase for the *n* = 6 derivative seems in line with this reasoning: although the overall shape is discoid, lateral interactions between hydroxyl groups can be dominant thus yielding a N_D rather than a Col_h mesophase.

Previous reported studies on tetra(pentyloxy)triphenylenes bearing two alkoxy chains terminally functionalized with hydroxyl groups at different positions (2,3-; 3,6- and 2,7-) seem to agree with this behavior.[9,39,40] Detailed comparisons of those results with the ones we report here are precluded due to the lack of detailed information about the precise nature of some of the reported phases (unidentified discotics, non-reported POM textures or XRD patterns) and even some inconsistencies among different sources in the reported phase sequences (phases´ nature and/or transition temperatures). Nevertheless, it seems clear from those reports that compounds in which the bridging chains are as long as the ancillary ones give rise to less ordered mesophases (or even lack of mesomorphism at all), as we find for the compounds studied here. Indeed, the mesomorphic behavior arises from a delicate balance between geometrical features, core-core, interchain and lateral interactions, in turn depending on the terminal functional groups.

A second pertinent comparison can thus be made with other di-decorated TP, particularly with those containing two carboxylic moieties –strong H-bond donor and acceptor- as terminal functional groups. The thermotropic mesomorphism of some derivatives terminally decorated at the 2,3- or 2,7-positions have been studied.[11,41,42] In most cases, they exhibited monotropic Col mesophases, also dependent on the cooling rate. A lack of mesomorphism has been pointed out for derivatives in which the length of the bridging chain largely exceeds that of the ancillary chains. It has been pointed out that the strong intermolecular interactions mediated by the carboxylic groups, able to fully develop when the functional groups are not hindered by the "crown", preclude columnar mesomorphism by avoiding free rotation around the molecular axis. Within the framework of this analysis, in our **2,7-THTP-DiCnOH** series, terminal OH groups behave as intermediate H-bonding moieties, in agreement with their mesomorphic properties.

Organogelating ability:

Supramolecular gels formation, structure and stability:

Organogelating properties of the three compounds were studied using the inverted tube method; [43] the results are summarized on Table 2. The three compounds were able to form supramolecular gels on small alcohols such as methanol, ethanol and 2-propanol after a heating-cooling process rendering translucid or turbid gels depending on concentration (Figure S5). To accelerate the gelling process it was necessary to cool down to 0ºC but, once formed, the gels were stable at room temperature. Gels of compounds **2,7-THTP-DiC4OH and 2,7-THTP-DiC10OH** were stable for a few hours at room temperature and then slowly started to exudate solvent, evidenced by tube inversion. However, gels of compound **2,7-THTP-DiC6OH** from alcohol and alcohol/water 85/15 mixture were stable for at least three months not observing fluidity or liquid exudation during that period of time. As can be also seen in table 2, compounds **2,7-THTP-DiC6OH** and **2,7-THTP-**

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DiC4OH are better gelators than **2,7-THTP-DiC10OH** reflected in their lower critical concentration for gelation (CCG) and also have a wider gelling scope since they are also able to form gels in *n*-butanol and acetonitrile. Only when temperature was raised and reached the transition temperature (T_{gel}) the material material fell down. The Tg vs concentration dependence was also explored, they all exhibited the expected behavior for supramolecular gels, i.e. T_{gel} (Gel-to-sol transition temperature) increasing with concentration up to a *plateau* zone where a maximum Tg (T_{gel}^{max}) is reached (Figure 6). It is worthy to note that in some cases this saturation behavior yielded a well-defined maximum value in T_{gel}. The gel-sol transitions of the gels were also studied by POM and birefringence was not observed supporting the absence of crystallites or liquid crystal transitions. These first results suggest that the two smaller homologs of this series are better supramolecular organogelators than the bigger one that has the hydroxyl groups outside the alkyl crown. This statement seems in line with the lower gelling ability of **2,7-THTP-DiC10OH**: gels formed by this compound require higher concentrations and exhibit T_{gel}^{max} lower than 30°C, instead of *ca*. 50ºC found for **2,7-THTP-DiC6OH** and **2,7-THTP-DiC4OH**.

n			solvent
10	6	4	
TG (2%)	TG (0.2%)	TG (0.8%)	Methanol
TG (4%)	TG (1.6%)	TG (1%)	Ethanol
TG (6%)	TG (1.5%)	TG (1.7%)	2-Propanol
S	TG (2%)	TG (2.8%)	n-Butanol
I	TG (0.5%)	TG (4%)	Acetonitrile
I	I	I	1,4-butanediol
S	S	S	Pentanol
I	I	I	n-heptane
S	I	S	cyclohexane
S	S	S	Pentane
S	S	S	Dichloromethane
S	S	S	Acetone
S	S	S	Toluene
S	S	S	Ethyl acetate
I	I	I	Ethyleneglycol

Table 2. Gelation test results: after a heating-cooling to 0ºC process the system was classified as: TG: Turbid gel, S: soluble; I: insoluble. Critical Concentration for Gelation (CCG) is shown between brackets (% wt./V). Initial concentration was 10% wt./V except for 2,7-THTP-DiC4OH in methanol were it was 5% wt./V.

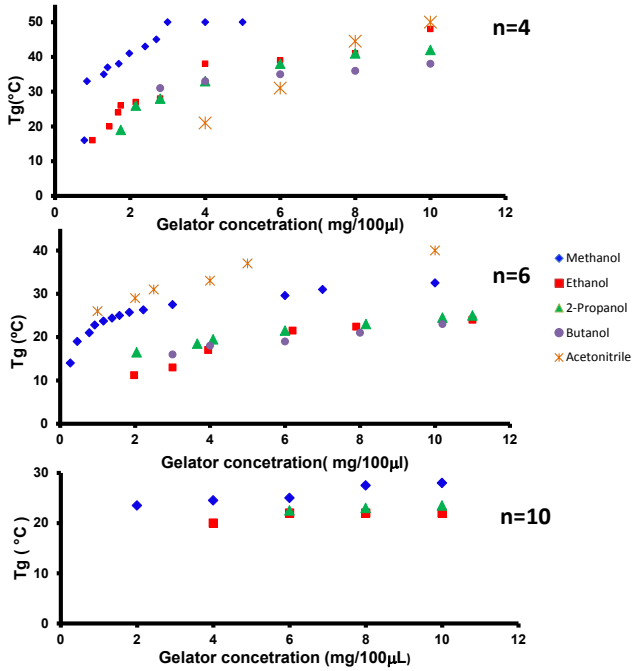

Fig. 6 T_{gel} vs concentration plot for **2,7-THTP-DiC4OH** (top), **2,7-THTP-DiC6OH** (mid) and **2,7-THTP-DiC10OH** (bottom).

The gels formed with **2,7-THTP-DiC4OH** in methanol have a higher thermostability than those formed by this gelator in other monoalcohols like ethanol, 2-propanol or 1-butanol. Indeed, T_{gel} in methanol is systematically 10-15 °C higher than that for the other solvents at similar concentrations below the CCG. Although T_{gel}^{max} is approximately the same (≈ 50ºC) in the studied solvents, this value is reached in methanol at a lower concentration (3.5% wt./v), roughly one third of the concentration needed to reach saturation in the other solvents.

The most stable gels obtained from **2,7-THTP-DiC6OH** were those of methanol and acetonitrile. Gels produced by this compound in 2-propanol, *n*-butanol and ethanol exhibited lower T_{gel} (T_{gel}^{max} *ca*. 25ºC). SAXS experiments on ethanol, methanol and acetonitrile gels of this derivative were determined (Figure 7). They show two peaks in a 1: $\sqrt{2}$ positional ratio in all cases, thus suggesting a tetragonal array of triphenylenes. Although the structural parameter a = 20.5 Å is the same in the three cases, showing the same kind of structural organization independent on solvent nature, the detected peaks are significantly narrower in acetonitrile than in methanol or ethanol, showing the structural organization is longer range in ACN. This result is in line with the thermal stability of the respective gels; indeed, Tgel shows a marked correlation with the degree of structural organization of the gels (Figure S6).

To get an insight into the morphology of the self-assembled supramolecular structures of the organogels we also performed SEM microscopy to the xerogels. High vacuum drying provoked the collapse of the microstructure of the systems so we slowly evaporated the solvent at room temperature and atmospheric pressure and the solids so obtained were metalized with a film of platinum before analysis. The images obtained can be seen in Figure 8. All the

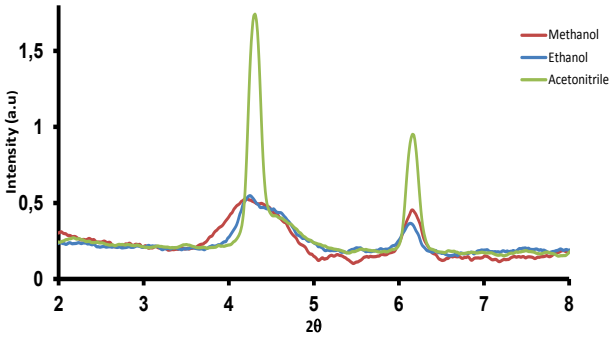

Figure 7 – SAXS pattern of the gels formed by **2,7-THTP-DiC6OH**, with three different solvents; peaks are indexed as the 10 and 11 reflexions of a tetragonal array.

xerogels showed the characteristic morphology of the cross-linked fibrillar network usually observed in supramolecular gels. As can be seen the xerogels of **2,7-THTP-DiC6OH** show a less defined microstructure probably due to the collapse of the crossed-linked system. Even though, the fibrillar network is clearly visible in all xerogels with fibers several tens of microns in length and widths between 60-80 nm (extra SEM images can be found at figure S7). This suggests the presence of a self-assembled fibrillar network on the gel phase.

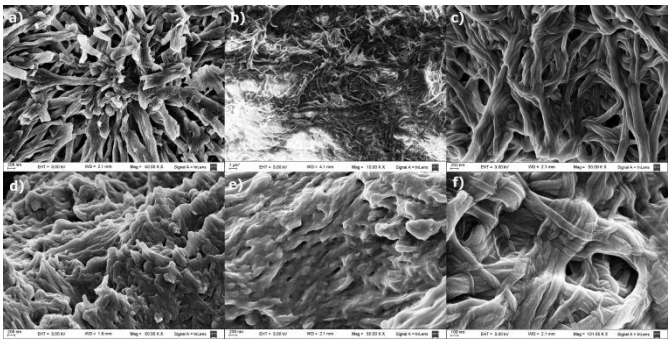

Fig. 8 SEM images of **2,7-THTP-DiCnOH** xerogels obtained from methanol (a) n= 4 (b) n= 6 and (c) n= 10 and from 2-propanol (d) n= 4 (e) n= 6 and (f) n= 10

Solvent parameters "windows" for gelation: gelation solvents prediction:

As a general trend, solvents able to be gelled by the studied compounds seem to be small alcohols with dielectric constants in the range *ca*. 14 to 37 for **2,7-THTP-DiC4OH** and **2,7-THTP-DiC6OH** and 18 to 37 for **2,7-THTP-DiC10OH**. Solvents not fulfilling both conditions cannot be gelled with any of the studied compounds. As representative examples alcohols with lower and higher dielectric constant i.g pentanol (ε 13.9) and 1,4-butanediol (ε 32.9) respectively, do not form gels in the presence of the studied compounds. A remarkable case is *n*-butanol: it can be gelled by **2,7-THTP-DiC4OH** and **2,7-THTP-DiC6OH**, but not by **2,7-THTP-DiC10OH** which is highly soluble in that solvent. The difference in the gelating ability of this compound for *n*-butanol (ε = 17.8) and 2-propanol (ε = 18.3) allows for a precise determination of the lower limit of its gelation window, and reflects the delicate balance of factors governing supramolecular gels formation. An exception to these general trend is acetonitrile (ACN) which, despite not fulfilling either of the two conditions, do form stable gels with both **2,7-THTP-DiC4OH** and **2,7-THTP-DiC6OH** . Perhaps the H-bond acceptor character of ACN accounts for this behavior.

The "gelation windows" built up with these simultaneous conditions (Figure 9), allowed us to predict the gelation of *n*-propanol for the three TP-based gelators, a prediction confirmed by experiments performed with the inverted tube method. Moreover, the "gelation windows" predict gelation of cyclohexanol for the *n* = 4 and 6 but not for the *n* = 10 derivatives, in perfect agreement with our experimental findings.

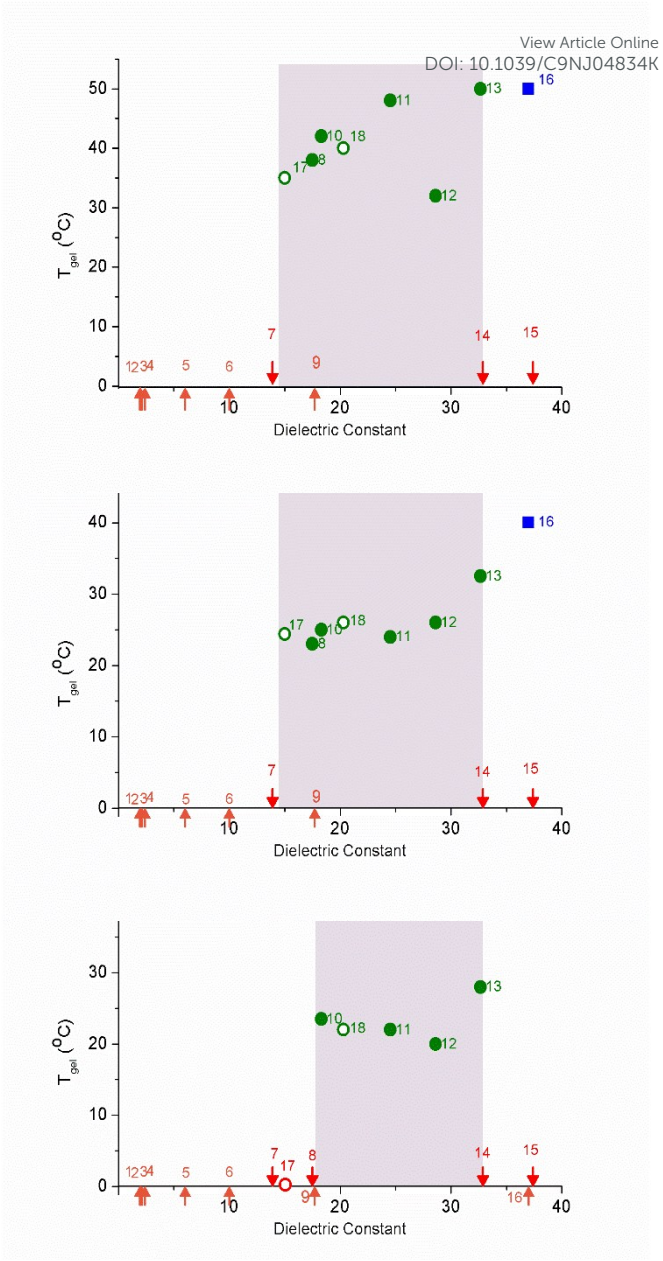

Fig. 9 Solvent gelation scope or "gelation windows" based on solvent´s dielectric constants (ε). Top: **2,7-THTP-DiC4OH**, middle: **2,7-THTP—DiC6OH**, bottom: **2,7-THTP-DiC10OH**. Full green circles: measured Tgel in alcohols (10% wt./v concentration was used in all cases except for n=4 in methanol were a 5% concentration was used); full blue square: measured T_{gel} in ACN; down red arrows: ε of the alcohols not forming gels; up orange arrows: ε of other solvents not forming gels, grey area: gelation window established for each gelator on the basis of the preceding points; open green circles: experimental T_{gel} in alcohols where gelation is predicted (see text); open red circles: prediction of no gel formation. Code: 1: n-heptane, 2: cyclohexane, 3: n-pentane, 4: toluene, 5: ethyl acetate, 6: dichloromethane, 7: 1-pentanol, 8: 1-butanol, 9: acetone, 10: 2-propanol, 11: ethanol, 12: 1:1 ethanol:methanol mixture, 13: methanol, 14: 2,4 butanediol, 15: ethylenglycol, 16: acetonitrile, 17: cyclohexanol, 18: 1-propano Plotted temperatures arise from duplicate uns; their uncertainties are less than ± 1ºC.

Another useful tool used with success to predict the solvent supramolecular gelation scope of low molecular weight organogelators involves the determination of a gelling zone in a three-dimensional diagram known as the Hansen space[44]

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where the three Hansen solubility parameters: dispersive interactions (δd), dipolar interactions (δp) and hydrogen-bond interactions (δH) are plotted. The corresponding diagram for the three compounds studied here is shown in Figure 10.
A "gelation region" is clearly seen; it involves intermediate δH values, in agreement with the gelation ability found for light alcohols and for ACN with the lighter gelator homologs. In agreement with the previous method, both ACN and cyclohexanol, being gelated by the *n* = 4 and 6 but not *n* = 10 derivative, lie near the frontier of this general "gelation region".

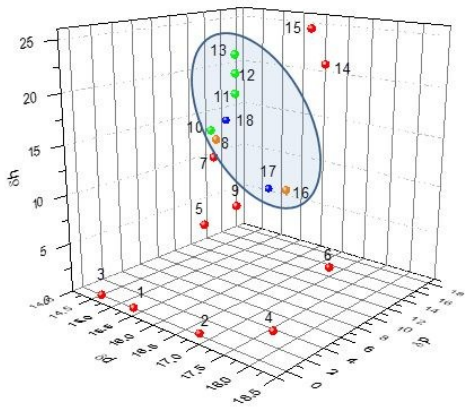


Figure 10: 3-D representation of the Hansen Space and gelation ability of **2,7-THT-DiC*n*OH** (*n* = 4, 6, 10) for different solvents. Green symbols correspond to solvents gelled by all gelators; red symbols to solvents that cannot be gelled; orange symbols correspond to n-butanol and ACN that cannot be gelled by **2,7-THT-DiC10OH**. Blue symbols correspond to the solvents for which a prediction about gelation has been made following the gelation window criterion based on the dielectric constant. Axis corresponds to the Hansen´s parameters. Solvents´code as in Figure 9.

A closer look to the gel-sol transition and the gels stabilities

DSC studies of the supramolecular gels showed a strong dependence on concentration of both T_{gel} and ΔH_{gel} (see Figure 11 as an example). This trend can be ascribed to the fact that an increase in gelator concentration should yield an increase in the number of formed fibers, thus increasing its crosslinking; a higher crosslinking degree is expected to increase both T_{gel} and ΔH_{gel}. Taking this into account, enthalpies associated to gel breaking have been measured at the highest possible concentration in each case, in order to be able to perform meaningful comparisons. The obtained results are collected on Table 3.

	T_{gel} , in °C (ΔH_{gel}, in kJ/mol)		
Solvent	**n=4**	**n=6**	**n=10**
Methanol	56 (61)	50 (165)	30 (38)
Ethanol	53 (63)	28 (32)	x
2-Propanol	46 (50)	31 (30)	x
Butanol	X	X	NO GEL
Acetonitrile	57 (85)	53 (44)	NO GEL

Table 3 - Temperatures (± 1ºC) and enthalpies (± 5 %) for the gel-sol transition measured by DSC for gel breaking. X: non-measured due to mechanical breaking of the corresponding gel during handling. 10%wt./v concentration was used in all cases except for n=4 in methanol were a 5% concentration was used.

Inspection of Table 3 shows that as the chain length increases, both T_{gel} and ΔH_{gel} decrease. Indeed, for **2,7-THTP-DiC10OH**, the only solvent in which measurement was possible was methanol: in ethanol and 2-propanol the gels broke during manipulation, exuding solvent. The gel formed by **2,7-THTP-DiC6OH** in methanol exhibits ΔH_{gel} = 165 kJ/mol, significantly higher than the enthalpies measured for all the other solvents. DSC results for **2,7-THTP-DiC4OH** in Methanol are in agreement with the peculiar thermic behavior observed with the inverted tube method: although ΔH_{gel} is similar to the values found for the other solvents, the maximum thermal stability is reached at half the concentration (5%). It is worthy to note the outstanding stability of the gels formed by **2,7-THTP-DiC6OH** in methanol compared to the others, with ΔH_{gel} more than twice the value found for any other system, thus showing a high selectivity for this solvent. The cooling curves were also measured but the transitions were wider and hysteresis was observed. Opening the sealed pan it was evident that some solvent evaporated after the sol phase was reached and, though, the cooling curves were not representative of the same system due to a change in concentration. For the same reason, subsequent heating curves were not measured.

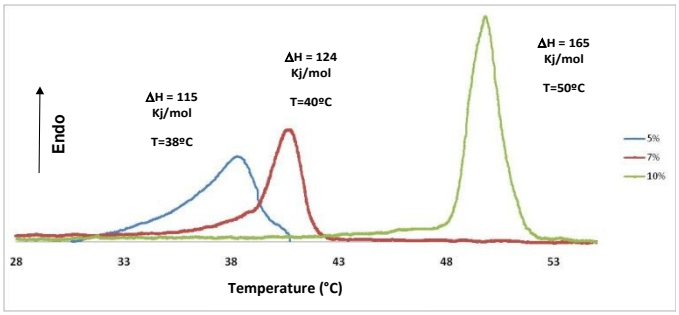


Fig. 11 DSC traces for gels of **2 7-THT-DiC6OH** in methanol at different concentrations

Water influence on gel formation: a simple method for the assessment of water content in alcohols:

Addition of a small amount of water, up to 20 %, increases the stability of the gels formed by **2,7-THT-DiC6OH** and **2,7-THT-DiC10OH** in ethanol, as can be inferred from the increase in both T_{gel} and ΔH_{gel} (Table 4). These ethanol/water gels were stable for at least three months at room temperature. Addition of water to 2-propanol has the same effect for the n=10 gelator while it does not affect the stability of the gels formed by the n=6 derivative. On the other hand, the addition of

	T_{gel} ,in °C (ΔH_{gel}, in kJ/mol)	
Solvent	**n=6**	**n=10**
Methanol	50 (165)	30 (38)
Methanol-Water 9:1	NO GEL	NO GEL
Ethanol	28 (32)	X
Ethanol-Water 9:1	41 (88)	44 (31)
2-popanol	31 (30)	X
2-Propanol-Water 9:1	33 (26)	34 (15)

Table 4 – Thermal properties of the gels formed by **2,7-THTP-DiC*n*OH** in light alcohol:water mixtures compared to those in pure alcohols (uncertainties as in Table 3).

water to methanol has a strongly destabilizing effect: **2,7-THT-DiC*n*OH** no longer form gels under these conditions but rending dissolved.

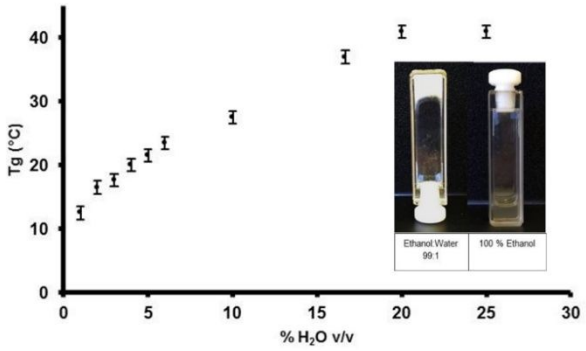
The sensitivity of some gels´ thermostability to the presence of small amounts of water suggested that the measurement of the Tg of a gel at a known concentration of gelator would be a useful semiquantitative method to assess for the water content in some light alcohols. Following this idea, we first tried to establish the detection limit of this method: ethanol or 2-propanol solutions of either **2,7-THT-DiC6OH** or **2,7-THT-DiC10OH**, in concentrations below the critical concentration for gel formation at 0ºC were prepared, then increasing amounts of water were added to each solution until a stable gel was obtained. The so obtained water detection limits are collected in Table 5.

n	Solvent (%wt/V)	Water Detection Limit
6	Ethanol (1,4)	1%
	2-Propanol (1)	3%
10	Ethanol (2)	2%
	2-propanol (4)	6%

Table 5. Detection limit of water in light alcohols

It is worthy to note that, using this visual method, **2,7-THT-DiC6OH** allows for the detection of water even when its content is as low as 1 % in ethanol or 3% in 2-propanol. **2,7-THT-DiC6OH** exhibits some advantages when compared to **2,7-THT-DiC10OH** for the purpose of water detection: not only its detection limit is lower, but also a lower concentration is required (Table 5).

As a proof of principle for the quantitative determination of water content in ethanol, a calibration curve T_{gel} *vs* water content has been constructed using a 1.4% wt./v concentration of **2,7-THT-DiC6OH** (Figure 12), varying the water content in the range for which gelation was observed (1 to 20 %). It allows for a quantitative assessment of water content in a given sample of ethanol, just by preparing a 1.4% solution of **2,7-THT-DiC6OH** (heating previously for dissolution and cooling to 0°C) and measuring its T_{gel} by the inverted tube method. No need for sophisticated equipment is required but a calibrated thermometer. The curve also shows that if the water content exceeds 10%, a stable gel is obtained at room temperature without cooling, which provides a visual method



(dissolve, stir and look) to qualitatively decide whether a sample of Ethanol contains or not (more than 10%) water.

Figure 12 – Water content dependence of T_{gel} for **2,7-THTP-DiC6OH**/Ethanol gels. Uncertainties in individual Tgel easurements are less than 1ºC; curves (not shown) linking the "upper" and "lower" confidence limits of individual measurements allow to estimate the uncertainty of this mehod as 1-2 % for low water content and 2-3 % for water content higher than 10 %.

Experimental

Physicochemical measurements:

Elemental analyses were carried out at Servicio a Terceros of INQUIMAE, on a Carlo Erba CHNS-O EA1108 analyzer. ^{1}H and ^{13}C NMR spectra were measured at UMYMFOR on a Bruker AM500 spectrometer, using $CDCl_3$ as solvent and its residual peaks as internal references (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C). Mass spectra were recorded in a Xevo G2S QTof (CIBION) with ESI ion source.

Mesomorphic properties have been studied by means of variable temperature polarizing optical microscopy (POM), Differential Scanning Calorimetry (DSC) and variable temperature wide and small angle X-ray scattering (WAXS and SAXS). POM was carried out between crossed polarizers using a Leitz DMRX microscope equipped with a Leitz 1350 hot-stage. DSC experiments were performed on a Shimadzu DSC-50 calorimeter. SAXS/WAXS experiments were performed at INIFTA facilities using a XEUSS 1.0 (XENOCS) with a Cu K_α radiation parallel x-ray beam microsource. A Plilatus 100K was employed with 533 cm sample detector distance for SAXS geometry and 10 cm for WAXS experiments. Samples were placed in borosilicate capillars and inside a temperature controlled sample-holder from Linkam®. Each sample was kept at a temperature above the isotropic phase transition for at least 30 minutes before cooling down with a 1ºC/min cooling rate.

Gelation studies:

The gelation ability was investigated by a typical inverted tube experiment. A mixture of a defined amount of gelator and a volume of the solvent (10% wt./v) in a closed flask was heated and shaken until the solid was dissolved and then cooled down to 0°C. If a stable gel was observed after inversion of the flask, it was considered a gel (G). The critical concentration for gelation (CCG) was determined by subsequent dilution of the original organogel followed by heating-cooling process until gel formation was not observed. The xerogels were prepared by slow evaporation of solvent at room temperature.

SEM pictures of xerogels were taken on a Carl Zeiss NTS SUPRA 40FEG scattering electron microscope and xerogels were. Prior to examination the xerogels were coated with a thin layer of platinum.

Synthesis:

2,7-Dihydroxy-tetrakis(hexyloxy)triphenylene (1):

This compound was synthetized following a reported methodology.[33]

6-Bromohexan-1-ol (3a):

Compound **2a** was prepared according to the method described by Chong *et al*[45]. An HBr 47% aqueous solution (0.58 ml, 3.73 mmol) was added to a solution of 1,2-hexanediol (0.44 g; 3.73 mmol) in toluene (6ml). The resulting mixture was stirred and heated at reflux for 3 hs. Water (5ml) was added and the solution was extracted with ether. The organic phase was washed with 1 M aqueous NaOH. The organic phase was dried with anhydrous Na_2SO_4, then filtered and the solvent

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evaporated under reduced pressure to dryness. The crude product was purified by column chromatography (silicagel, cyclohexane/ethyl acetate 85:15) to yield a yellow oil (0.45 g, 74%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.66 (t, *J* = 6.6Hz, 2H); 3.43 (t, *J* = 6.8 Hz, 2H); 1.89 (m, 2H); 1.61 (m, 2H); 1.52 (m, 2H); 1.41(m, 2H).

10-Bromodecan-1-ol (3b):

Compound 2b was prepared following a similar procedure, using 0.44 ml (2.57 mmol) of 47% HBr (ac) and 0.45 g (2.57 mmol) of 1,2-decanediol of in toluene (10 ml), and refluxing for 6 h. The crude product was purified by column chromatography (silica, cyclohexane/ethyl acetate 90:10) to yield a yellow oil (0.45 g, 77%). ^{1}H-NMR (500 MHz, CDCl3) δ 3.66 (t, J=6.6 Hz, 2H); 3.43 (t, 6.9 Hz, 2H); 1.87 (m, 2H); 1.59 (m, 2H); 1.44 (m, 2H), 1.31 (m, 10H).

Diethyl 4,4'-((3,6,10,11-tetrakis(hexyloxy)triphenylene-2,7-diyl)bis(oxy))dibutanoate (4)

A solution of ethyl 4-bromobutanoate (0.25 ml, 1.8 mmol) dissolved in CH_3CN (6 ml) was added to a mixture of 2,7-dihydroxy-tetrakis(hexyloxy)triphenylene (**1**) (0.3 g, 0.45 mmol), tetraethylammonium iodide (0.03 g), and anhydrous potassium carbonate (0.64 g) in 15 ml of CH_3CN. The resulting mixture was refluxed for 27 hs, then cooled down to room temperature and poured into $CHCl_3$ (20 ml). The solids were filtered off, the organic layer was dried with Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica, cyclohexane/dichloromethane 20:80) to yield a beige solid (0.35 g, 87%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.90 (S, 2H); 7.88 (S, 2H); 7.85 (S, 2H, 4.32 (t, J=6.2 Hz, 4H); 4.26 (m, 8H); 4.19 (m, 4H); 2.67 (t, J=7.2 Hz, 4H), 2.28 (m, 4H); 1.95 (m, 8H); 1.6 (m, 8H), 1.43 (m, 16H); 0.96 (t, H=7 Hz, 12H); 0.91 (t, J=7.1Hz, 6H)

4,4'-((3,6,10,11-Tetrakis(hexyloxy)triphenylene-2,7-diyl)bis(oxy))bis(butan-1-ol) (5a)

A solution of compound **4** (0.35 g, 0.39 mmol) in dried THF (10 ml) was added dropwise to a mixture of $LiAlH_4$ (0.1 g, 2.63 mmol) and THF (10 ml) keeping the temperature controlled by an ice bath. After the addition, the ice bath was removed and the solution stirred for 4 hs. Methanol (5 ml) and water (5 ml) were added. The mixture was extracted with CH_2Cl_2 (2x10ml) and the organic phase was dried with Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (silica, cyclohexane/ethyl acetate 80:10) and recrystallized from *n*-heptane, to yield a beige solid (0.31 g, 79%). m.p.: 95ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.86 (S, 2H), 7.85 (S, 2H), 7.84(S, 2H), 4.32 (t, *J* = 5.9 Hz, 4H), 4.26 (t, *J* = 6.6 Hz, 8H), 3.83 (q, *J* = 5.7 Hz, 4H), 2.10 (m, 4H), 1.99 (m, 12H), 1.35-1.66 (m, 24H), 0.96 (t, 12H) (Figure S8). ^{13}C-NMR: 149.08; 148.72 ; 148.45; 123.65 123.60, 123.45 ; 107.34; 106.65; 106.45, 69.76, 69.40; 69.31; 62.36; 31.71; 31.68; 30.08; 29.45; 29.30; 25.93; 25.88; 25.83; 22.68; 14.08. HRMS (ESI) m/Z: M+ measured (calculated) 804.5551 (804.5540). Elemental analysis: measured (calculated) for $C_{50}H_{76}O_8$ % C 74.0 (74.6); % H 9.7 (9.5).

6,6'-((3,6,10,11-Tetrakis(hexyloxy)triphenylene-2,7-diyl)bis(oxy))bis(hexan-1-ol) (5b)

6-bromohexan-1-ol (**3a**) (0.45 g, 2.48 mmol) was added to a mixture of 2,7-dihydroxy-tetrakis(hexyloxy)triphenylene (**1**) (0.45 g, 0.76 mmol) and anhydrous potassium carbonate (1 g) in butanone (15 ml). The mixture was refluxed for 26 hs under argon atmosphere, then water (5 ml) was added and the solution was extracted with dichlorometane (2x10 ml). The organic phase was washed with 1 M HCl, dried with Na_2SO_4 and the solvent evaporated under reduced pressure. The crude product was purified by column chromatography (silica, cyclohexane/ethyl acetate 70:30) and recrystallized from *n*-heptane, to yield a beige solid (0.40 g, 68%). m.p.: 101ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.87 (S, 6H), 4.25 (m, 12H), 3.76 (t, J = 6.5, 4H), 2.9-1.9 (m, 12H), 1.72-1.51 (m, 20H), 1.48-1.24 (m, 16H), 0.98 (t, J = 7 Hz, 12H) (Figure S8). ^{13}C-NMR: 149; 148,94, 123,70; 123,62; 107,37; 69,78; 69,55; 62,95; 32,74; 31,69; 29,45; 29,43; 26,02; 25,87; 25,87; 25,86; 25,65; 22,68; 14,07. HRMS (ESI) m/Z: M+ measured (calculated) 860.6190 (860.6166). Elemental analysis: Measured (calculated) for $C_{54}H_{84}O_8$ %C: 74.9 (75.3); %H: 9.8 (9.8)

10,10'-((3,6,10,11-Tetrakis(hexyloxy)triphenylene-2,7-diyl)bis(oxy))bis(decan-1-ol) (5c):

10-bromodecan-1-ol (3b) (0.45 g, 1.9 mmol) was added to a mixture of 2,7-dihydroxy-tetrakis(hexyloxy)triphenylene (1) (0.38 g, 0.57 mmol)) and anhydrous potassium carbonate (1 g) in butanone (15 ml). The resulting mixture was refluxed for 26 hs under argon atmosphere. Water (5ml) was added and the solution was extracted with dichlorometane (2x10 ml). The organic phase was washed with 1 M HCl, dried (Na_2SO_4) and evaporated under reduced pressure. The crude product was purified by column chromatography (silica, cyclohexane/ acetone 85:15) and recrystallized from *n*-heptane, to yield a beige solid (0.36 g, 65%). m.p.: 51ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.86 (S, 6H), 4.25 (m, 12H), 3.66 (t, *J* = 6.5, 4H), 2.08-1.86 (m, 12H), 1.59 (m, 20H), 1.36 (m, 32H), 0.98 (t, *J* = 6.6Hz, 12H). (Figure S8) ^{13}C-NMR: 148.47; 123.62; 107.38; 69.71; 63.09; 31.70; 29.59; 29.50; 25.87; 22.68; 14.08. HRMS (ESI) m/Z: M+ measured (calculated) 972.7426 (972.7418) Elemental analysis: measured (calculated) for $C_{62}H_{100}O_8$ (973.45) %C: 76.2 (76.5); %H: 10.3 (10.3)

Conclusions

This work confirmed previous suggestions stating that the position of the terminal functional group with respect to the crown defined by the ancillary aliphatic chains is a key parameter defining the LC properties (kind of mesophase, thermal stabilty) of difunctionalized triphenylenes. Moreover, both the number of terminal functional groups and its nature play a crucial role on these properties. Thus, mesophase formation, thermal stability and structure clearly rely on a subtle balance of molecular parameters, allowing for the interpretation of the experimental trends, but making difficult confident predictions. The mesomorphic trends of the series studied here seem to suggest H-bonding interactions can

prevale over π-π stacking giving rise to N_D or Col_r mesophases instead of the Col_r found in the case the hydroxyl groups are hindered by the crown.

The ability of the terminal hydroxyl groups to be involved in intermolecular H-bonds, together with π-π stacking interactions between the TP cores, seems also to be directing the hierarchical self-assemble that forms a 3D fibrillar network that lead to the organogelating nature of the three studied compounds. Indeed, they form stable gels both with aliphatic alcohols (provided the dielectric constant fit specific ranges) and ACN, an H-bond acceptor. This fact suggests solvent molecules are directly involved in the supramolecular organization, as confirmed by the fact that the structure of the gels is different from that of the bulk compounds, and by the thermal data. The high selectivity of **2,7-THTP-DiC6OH** to methanol, giving rise to very stable gels exhibiting ΔH_{gel} as high as 165 kJ/mol, support this hypothesis.

Except for methanol, it has been observed that an increase in the length *n* of the bridging chains decrease the stability of the organogels formed by **2,7-THTP-DiC*n*OH** compounds, as seen both in the thermal stability and the gelling critical concentration.

This behavior differs from the one found for the monohydroxylated analogues[30], where an increase in the length of the bridging chain has been found to increase the organogelating ability of the corresponding 2-**PHTP-C*n*OH** (PHTP= Pentakis hexyloxy triphenylene) compounds. In that homologous series, weak gels have been found for *n* = 4 and 6 derivatives while the gels formed by the *n* = 10 derivative are stronger, a fact interpreted in terms of the ability of the hydroxyl group to easier interact when it is located beyond the limit of the "crown" described above. The presence of a second hydroxyl groups certainly modifies the properties of the organogels, as seen from both structural aspects (the tetragonal structure of the gels obtained here for MeOH, EtOH and ACN differ form that obtained for the monohydroxy derivatives) and thermal properties: taking the *n*=10 derivatives as an example, the corresponding T_{gel} for **2,7-THTP-DiC10OH** is 18ºC higher than that for **2-PHTP-C10OH**., very likely through a different 3-D self-assembly pattern. Indeed, the tetragonal array found here seem to be possible thanks to the presence of two hydroxyl groups per gelator molecule.

Beyond the molecular aspects of the soft phases (LC and gels) yielded by **2,7-THTP-DiC*n*OH** compounds, and the potential applications they can be found in the future as soft materials, the increase in thermal stability observed with the increase in water content prompted us to investigate the use of this effect as an easy and practical method to establish the presence of water in light alcohols, and even to estimate its amount. This interesting preliminary result, together with the remarkable water compatibility (reflected in the increased stability observed in its presence) also makes this organogel material a promising versatile matrix for applications that may require contact with an aqueous environment.

Conflicts of interest

There are no conflicts to declare.

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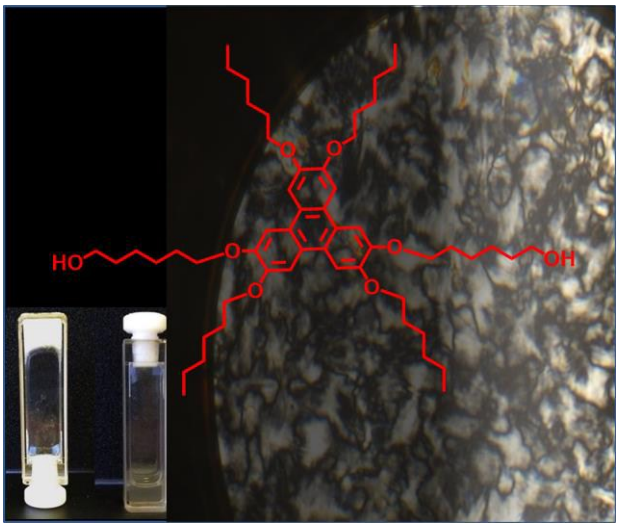
Illustrated Synopsis for TOC:



Self-assembly of di-hydroxylated triphenylenes in columnar mesophases and organogels depends on the spacer length and allows water quantification in alcohols