



New Fluorescent Alkoxy-Functionalized Perfluoroaryl Self-Assembled Low Molecular Weight Gelators

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ABSTRACT

The molecular design, synthesis and photophysical properties of a new class of thermoreversible and fluorescent low molecular weight organogels from alkoxy-functionalized perfluoroaryls are described. Both of CuI-catalyzed decarboxylative cross-coupling and S_NAr (Nucleophilic Aromatic Substitution) chemistry were employed for the preparation of those highly fluorinated gelators, in high yields and excellent purity via simple filtration, from the corresponding potassium fluorobenzoate salts and aryl iodides. A variety of fluorinated *para* terphenyls were prepared with a variety of *para* terminal alkoxy tails. The UV-Vis absorption and fluorescence emission spectra of those new materials display a solvatochromic and solvatofluorochromic behavior respectively. Self-assembly of these molecules via cooperative π - π stacking and van der Waals interactions induced gelation of a variety of organic solvents are described. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies reveal the formation of fiber-like nanostructures.

Introduction

The low molecular weight organogels have an increased significance due to their thermoreversibility, chemical sensitivity, and the multiplicity of their macroscale architectures [1-7]. Organogels are commonly used in different potential applications such as biomedical, cosmetics, and foodstuffs purposes [8-14]. Liquid crystalline organogels produced via self-assembled non-covalent physical entanglements have attracted significant interests. The design of liquid crystalline organogels can demonstrate unique optoelectronic properties such as improved charge transport, fluorescence, and molecular recognition [15-17]. Additionally, highly fluorinated materials usually introduce increased surface roughness that can be employed in hydrophobic/self-cleaning surfaces [18-19].

In contrast, only limited work has been explored on liquid crystalline organogels. Surprisingly, there is no report of low molecular weight organogel based on fluorinated terphenyl derivatives although fluorinated terphenyl derivatives have played significant roles in the recent advances of optoelectronic applications. Herein we report, to the best of our knowledge, the first fluorescent liquid crystalline physical organogel based

on a rigid *para* terphenyl core and flexible alkoxy side chains (see Figure 1). The design, synthesis and photophysical properties of fluorinated *para* terphenyl derivatives with two alkoxy terminal units are investigated for potential optoelectronic applications. A copper-catalyzed decarboxylative cross-coupling starting from the corresponding potassium perfluorobenzoate salts and aryl iodides leads to the creation of an extended, rigid, and conjugated *para* terphenyl core with a strong fluorescence emission. The synthetic route of alkoxy-functionalized highly fluorinated terphenyls and their liquid crystalline properties have been studied recently by our research group. Those highly fluorinated *para* terphenyls are found to exhibit fluorescence in the blue region of the visible spectrum and are suitable candidates for low energy consuming displays especially in the case of portable electronics [20-22]. They also are able to function as solvatochromic and solvatofluorochromic probes. The supramolecular self-assembly and gelation properties of fluorinated *para* terphenyls in some organic solvents are investigated. Both of SEM and TEM are used to study the novel properties of the nano-scale structures that can be fabricated by the fluorescent organogel self-assembly.

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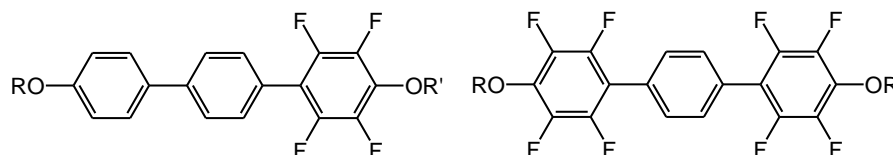


Fig. 1: Fluorinated *para* terphenyls comprising a rigid aromatic core and flexible alkoxy side chains; R and R' are aliphatic chains.

Materials and methods

Melting points were obtained by differential scanning calorimetry (TA instruments 2920). IR spectra were recorded with a Bruker Vectra-33 IR-Spectrometer with ATR probe. UV-Vis absorption spectra were measured on a HP-8453 (HEWLETT PACKARD) spectrophotometer. Fluorescence spectra were measured on a VARIAN CARY ECLIPSE fluorescence spectrophotometer. NMR spectra were recorded using a BRUKER AVANCE 400 spectrometer at 400 MHz; chemical shifts are given in ppm relative to internal standard TMS at 295K. In case of scanning electron microscopy SEM, the gel formed from **4** in *n*-propanol was scooped up and placed on carbon tapes pasted on aluminum stubs and allowed to dry at room temperature in a desiccator connected to vacuum pump. The dried samples were then annealed overnight in an oven at 45°C, followed by application of a 10 nm gold-coating before recording images. SEM images were obtained using Hitachi S-2600N operating at 20 kV. For Transmission electron microscopy TEM, a piece of gel **4** in *n*-propanol was placed on a carbon-coated copper grid (200 mesh) and allowed to dry in vacuum at room temperature for two days. TEM was done on JEM-1200EX at an accelerating voltage of 80 kV. All materials and reagents were obtained from commercial sources and were used without further purification.

Gelation procedure:

The gelation tests were performed by dissolution of compounds **4**, **5** and **6** in the selected solvents by heating to boiling temperature and then cooling to room temperature to form the gel. The gels formed in 25-45 minutes depending on the gelator concentration. Scanning electron microscopy was achieved on Hitachi S-2600N SEM (operating at 20 kV). The samples were prepared by drop-casting the gel in *n*-octanol on a clean glass substrates followed by drying in air to afford the xerogel. The dried xerogel was then annealed overnight in an oven at 45°C, followed by coating with gold. For transmission electron microscopy, a piece of gel **4** in *n*-propanol was placed on a carbon-coated copper grid (200 mesh) and air-dried overnight at room temperature. TEM was done on JEM-1200EX at an accelerating voltage of 80 kV.

X-ray crystal structure information

Single crystals of compound **4** suitable for X-ray diffraction analysis were obtained by crystallization (with slow solvent evaporation) from hexane. X-ray

crystallography was performed by mounting each crystal onto a thin glass fiber from a pool of Fluorolube™ and immediately placing it under a liquid N₂ cooled N₂ stream, on a Bruker AXS diffractometer. The radiation used was graphite monochromatized Mo K α radiation ($\lambda = 0.7107 \text{ \AA}$). The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination, data collection, structure refinement, scaling, and data reduction were carried out using APEX2 version 1.0-27 software package. The structure was solved using direct methods. Subsequent Fourier synthesis yielded the remaining atom positions. The final refinement of each compound included anisotropic thermal parameters on all non-hydrogen atoms.

Synthetic Procedure

General procedure for the synthesis of a 4''-alkyloxy-4-alkyloxy-2,3,5,6-tetrafluoro-1,1':4',1''-terphenyl from a 4''-alkyloxy-2,3,4,5,6-pentafluoro-1,1':4',1''-terphenyl

In a 100 ml round bottom flask fitted with nitrogen bubbler and stirbar was placed 4''-alkyloxy-2,3,4,5,6-pentafluoro-1,1':4',1''-terphenyl and anhydrous solvent. The resulting mixture was heated just until the terphenyl dissolved and the respective alcohol was added. If solid came out of solution, it was heated until dissolution occurred once again. Potassium *t*-butoxide was added and the reaction was followed by TLC. If the reaction stalled, additional alcohol and base were added. Upon consumption of the starting material (TLC analysis) the solvent was then removed and a recrystallization was performed.

4''-propyloxy-4-hexyloxy-2,3,5,6-tetrafluoro-1-1':4',1''-terphenyl **4**

Prepared from 4''-propyloxy-2,3,4,5,6-tetrafluoro-1,1':4',1''-terphenyl (0.300 gm, 0.79 mmol), *n*-hexanol (5 ml, excess), DMF (15 ml), potassium *t*-butoxide (0.068 gm, 0.6 mmol), recrystallized from *n*-propanol, white crystals product (0.230 gm, 63% yield); ¹H NMR (400 MHz, CDCl₃) δ : 7.69 (d, 2H), 7.59 (d, 2H), 7.52 (d, 2H), 7.02 (d, 2H), 4.30 (t, 2H), 4.05 (t, 2H), 1.87 (m, 4H), 1.54 (m, 2H), 1.38 (m, 4H), 1.10 (t, 3H), 0.95 (t, 3H); ¹³C NMR (400 MHz, CDCl₃) δ : 158.4, 143.1, 142.2, 136.0, 135.1, 130.6, 129.9, 128.7, 115.6, 113.0, 73.5, 67.3, 31.0, 29.8, 26.9, 25.0, 24.8, 18.7, 14.0, 13.9; IR (neat, cm⁻¹): 3045.1, 2961.8, 2872.2, 1650.4, 1608.5; DSC ($^{\circ}$ C): heating-crystal 123.2 SmA 144.2 iso-cooling-iso 141.6 SmA 97.61 Cr.

4''-propyloxy-4-ethoxy-2,3,5,6-tetrafluoro-1,1':4',1''-terphenyl 5

Prepared from 4''-propyloxy-2,3,4,5,6-tetrafluoro-1,1':4',1''-terphenyl (0.300 gm, 0.79 mmol), ethanol (5 ml, excess), DMF (15 ml), potassium *t*-butoxide (0.270 gm, 2.4 mmol), recrystallized from *n*-propanol, white crystals product (0.120 gm, 37% yield); ¹H NMR (400 MHz, CDCl₃) δ: 7.59 (d, 2H), 7.52 (d, 2H), 7.50 (d, 2H), 7.02 (d, 2H), 4.37 (q, 2H), 4.02 (t, 2H), 1.86 (m, 2H), 1.49 (t, 3H), 1.10 (t, 3H); ¹³C NMR (400 MHz, CDCl₃) δ: 157.9, 144.1, 141.4, 136.6, 134.2, 129.0, 128.8, 128.2, 115.2, 112.9, 72.3, 66.1, 24.8, 14.0, 12.9; IR (neat, cm⁻¹): 3045.1, 2958.2, 2905.2, 2865.4, 1730.4; DSC (°C): heating-crystal 139.3 N 147.8 SmA 163.2 iso-cooling-iso 119.7 SmA 101.7 N 85.86 Cr.

4''-hexyloxy-4-(2-methyl)butyloxy-2,3,5,6-tetrafluoro-1,1':4',1''-terphenyl 6

Prepared from 4''-hexyloxy-2,3,4,5,6-tetrafluoro-1,1':4',1''-terphenyl (0.210 gm, 0.5 mmol), 2-methyl-1-butanol (5 ml, excess), DMF (15 ml), potassium *t*-butoxide (0.068 gm, 0.6 mmol), recrystallized from *n*-propanol, product (0.117 gm, 48.0%); ¹H NMR (400 MHz, CDCl₃) δ: 7.69 (d, 2H, *J* = 8.4 Hz), 7.59 (d, 2H, *J* = 8.8 Hz), 7.52 (d, 2H, *J* = 8.4 Hz), 7.02 (d, 2H, *J* = 8.8 Hz), 4.13 (m, 2H), 4.04 (t, 2H, *J* = 6.8 Hz), 1.88 (m, 3H), 1.63 (m, 1H), 1.51 (m, 2H), 1.39 (m, 5H), 1.09 (d, 3H, *J* = 6.8 Hz), 0.98 (t, 3H, *J* = 7.4 Hz), 0.93 (t, 3H, *J* = 6.8 Hz). ¹³C NMR (400 MHz, CDCl₃) δ (ppm): 159.10, 141.35, 132.60, 130.55, 128.15, 126.75, 125.56, 114.90, 80.11, 68.14, 35.51, 29.27, 31.61, 25.75, 25.68, 22.62, 16.11, 14.04, 11.20; ¹⁹F NMR (400 MHz, CDCl₃) δ (ppm): -145.36 (q, 2F), -157.51 (q, 2F); IR (neat, v/cm⁻¹): 2994.0, 2862.7, 1493.2, 997.3, 801.8; DSC (°C)-heating-crystal 108.7 SmA 125.1 iso-cooling-iso 123.7 SmA 92.2 crystal.

Results and Discussion**Photophysical studies**

The UV-Vis absorption and fluorescence emission spectra of these fluorinated compounds were studied in some selected solvents. Values for λ_{max} were determined for compounds as listed in **Table 1**. The UV-Vis absorption and emission spectra for both the asymmetric series and symmetric series were measured in a variety of solvents including THF, DMSO, Pyridine, Ethanol, CH₂Cl₂, CH₃CN and Hexane in diluted solutions to guarantee that the samples are completely soluble (see **Figures 2 and 3**). All derivatives were found to absorb in the UV-Vis region with maxima located below 315 nm. Those absorption bands can be attributed to the π-π* transitions. All derivatives display strong fluorescence in solution in the near UV-blue region of the electromagnetic spectrum. Hence, the *para* terphenyl derivatives display strong charge transfer character and/or a conformational relaxation in the excited state. The high radiative character of the *para* terphenyls can be attributed to the extended planar conjugated structural system of both core and terminal benzene rings^[15-17]. On the other side, the fluorine atoms significantly enhance the intramolecular charge transfer ICT character.

The peripheral (thio)alkoxy tails, being linear or branched, only slightly influence the optical properties of *para* terphenyls. It was found that the increasing the length of the aliphatic chain leads to a slight increase (Bathochromic shift) in the UV-Vis absorption maxima accompanied by slight decrease (hypsochromic shift) in the fluorescence emission maxima. The asymmetric derivatives consist of organic molecular structures in which electron-donating groups (alkoxy terminal groups) are linked through a conjugated system to an electron-accepting fluorinated fragment. This kind of system, where ICT occurs, is susceptible to exhibiting solvatochromic properties. A considerable solvatochromic emission influence, known as solvatofluorochromism, was observed in different solvents with different polarities. Both UV-Vis absorption and fluorescence emission spectra display an increase in the maximal wavelength with increasing solvents polarity (positive solvatochromism). This red-shift reveals that the ground state is less polar than the excited state and the fluorinated *para* terphenyls will be better stabilized by polar solvents.

Gelation Properties

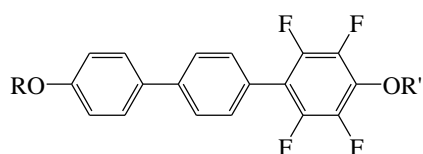
Molecular self-assembly can be represented in different dimensions starting from the molecular level (nanometers), consisting of just a few molecules, to macroscopic level which is visible to the naked eye. Understanding the self-assembled aggregates of the organogels and liquid crystals is the main force to investigate their potential applications^[23]. Organogels can be defined as a viscoelastic three dimensional solid matrix created by the entrapment of a solvent in the elastic self-assembled entanglements by either chemical or physical interactions. The strong chemical interactions affords thermally irreversible organogels whereas the physical interactions affords reversible organogels as a result of the weak non-covalent interactions such as hydrogen bonding, metal coordination, π-π stacking, push-pull interactions, and van der Waals interactions^[24]. The phase transition, molecular alignment and orientation control of liquid crystals are significant properties for photonic applications^[25]. Organogels derived from liquid crystals comprise an entrapped mesogenic phase-segregated in a micro-scale fibrous entanglement of a low molecular weight organogel. They can function for a variety of potential technological applications such as rewritable information recording devices and electro-optical displays^[26].

The liquid crystalline highly fluorinated gelators consist of two terminal alkoxy units separated by the rigid *para* terphenyl core that is responsible for π-π stacking interactions. The liquid crystalline properties of the gelators **4**, **5** and **6** have been described recently by our research group. Regarding the self-assembly of these liquid crystalline gelators, the aggregation of the fluorinated gelator molecules affords a three dimensional network of nano-scale fibrous aggregates that is controlled by the opposite forces rising from their solubility and crystals formation. Compounds **4**, **5** and **6**

are soluble in some selected organic solvents only at high temperature. When dissolving the powder of the fluorinated gelators **4**, **5** and **6** in the organic solvents by gentle heating followed by cooling the solution to room temperature, a non-flowing solid-like gel was indicated by means of the “stable to inversion” technique as shown in **Figure 4**. The gelation properties of compounds **4**, **5** and **6** were investigated in different organic solvents under the same experimental condition. The critical gelation concentration values for liquid crystalline gelator **6** were solvent dependent and in the range of 2.34 and 7.3 mM. Gelator **6** reveals a significant ability to gelate a variety of organic solvents

such as toluene (4.2 mM), *n*-propanol (2.34 mM), 1,2-dichloroethane (7.3 mM), and 1-octanol (3.80 mM). However, **6** was partially gelled in tetrahydrofuran, dimethylsulfoxide and acetonitrile and showed no gelation in chloroform, ethylacetate and dichloromethane. The results of the gelation studies of compounds **4**, **5** and **6** are summarized in **Table 2**. All gels produced from the organic solvents listed above are either white or transparent solid-like gels. The sol-gel switching process is completely thermoreversible. All investigated gelators reveal comparable photophysical properties in dilute solutions as shown in the photophysical properties.

Table 1: UV-Vis absorption and fluorescence emission parameters in some selected solvents at room temperature.



Comp. # (R, R')	$(\lambda_{\max} \text{ nm})$													
	Hexane		DMSO		Ethanol		THF		CH ₂ Cl ₂		CH ₃ CN		Pyridine	
	<i>abs.</i>	<i>em.</i>	<i>abs.</i>	<i>em.</i>	<i>abs.</i>	<i>em.</i>	<i>abs.</i>	<i>em.</i>	<i>abs.</i>	<i>em.</i>	<i>abs.</i>	<i>em.</i>	<i>abs.</i>	<i>em.</i>
1 (dodecyl, hexyl)	288	367	275	402	289	388	288	410	293	393	285	385	297	378
2 (hexyl, hexyl)	289	361	293	392	279	376	230	399	292	392	284	384	288	399
3 (hexyl, ethyl)	280	356	290	390	299	399	265	390	273	373	300	400	309	376
4 (propyl, hexyl)	285	355	297	396	289	409	265	386	269	362	306	409	302	396
5 (propyl, ethyl)	282	367	303	401	294	372	271	404	299	392	298	398	311	379
6 (hexyl, 2-methylbutyl)	290	356	292	392	286	375	298	392	289	388	288	401	304	408
7 (hexyl, methyl)	288	356	293	398	286	376	292	399	289	375	294	387	305	385

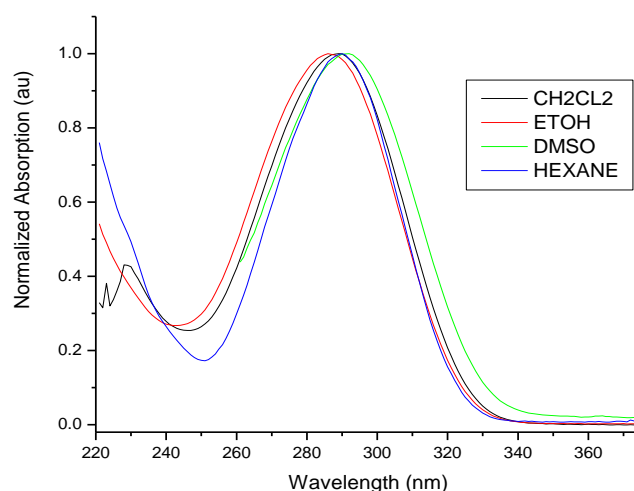


Fig. 2: Normalized UV-Vis absorption spectra of **6** in some chosen solvents.

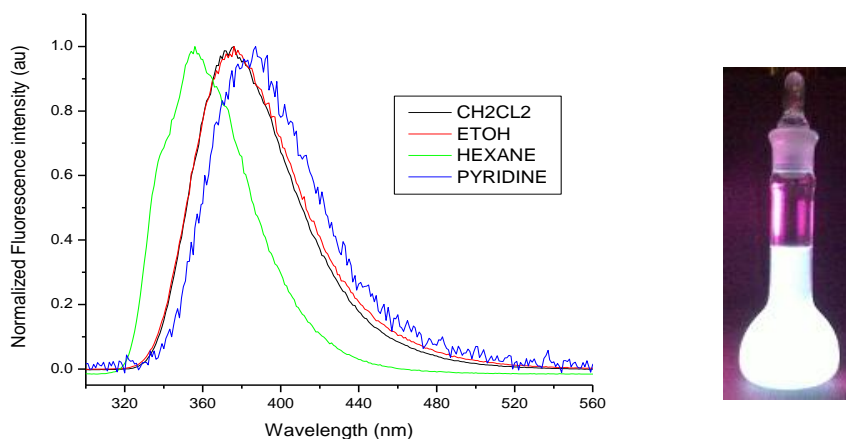


Fig. 3: Normalized fluorescence emission spectra of **6** in some chosen solvents

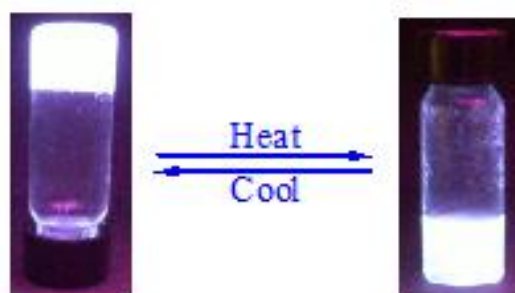


Fig. 4: Thermoreversible fluorescent organogel (using gelator **6**) by means of the “stable to inversion” technique

Table 2: Gelation properties of the fluorinated gelators **4**, **5** and **6** in some selected solvents.

Solvent	gelator 4	gelator 5	gelator 6
<i>n</i> -Propanol	G (6.92 mM)	P	G (3.80 mM)
<i>n</i> -Octanol	G (6.55 mM)	P	G (2.34 mM)
Toluene	G (9.82 mM)	P	G (4.2 mM)
1,2-Dichloroethane	PG	P	G (7.3 mM)
Dichloromethane	S	S	S
Chloroform	S	S	S
Ethylacetate	S	S	S
Acetonitrile	PG	P	PG
Tetrahydrofuran	PG	S	PG
Dimethylsulfoxide	PG	PG	PG

G: gel; S: solution; PG: partial gel. The critical gelation concentration (mM) is shown in a parenthesis.

The aggregation morphology of dried xerogel of gelator **4** was investigated by both of scanning electron microscope (SEM) and transmission electron microscope (TEM). The dried xerogel sample of liquid crystalline gelator **4** was transferred onto a glass slide and studied under SEM. Both of scanning electron microscope and transmission electron microscope images of **4** from *n*-octanol demonstrate three dimensional fibrous entanglements in the range of 320-560 nm in diameter and few micrometers in length (see

Figure 5). The self-assembly of **4** affords fibrous bundles leading to the immobilization of those organic solvents. The inclusion of long alkoxy units in the molecular structure of the gelators has been considered as a critical part toward better stability of the gelators assemblies. In addition to the alkoxy units included in our molecular structure gelators, the existence of fluorine atoms on the rigid core of the *para* terphenyls might stimulate and increase the stability of the molecular assembled architectures. To illustrate the molecular and crystal

packing, we obtained a single crystal of compound **4** from hexane and studied under X-ray crystallography as illustrated in **Figure 6**. In the crystal unit, each molecule interacts with the adjacent molecules in face-to-face intermolecular π - π stacking interactions of the aromatic core in cooperation with tail-to-tail van der Waals interactions between the alkoxy chains. The investigation of the crystal structure of **4** suggests that molecules should have the tendency to aggregate into ladder nanostructures.

Conclusions

We have synthesized the first example of fluorescent low molecular weight organogel from fluoroterphenyl

derivatives as rod-like aromatic segments that is able to immobilize a variety of organic solvents. The fluorinated *para* terphenyl main skeleton are prepared via practical Cu(I)-assisted decarboxylative cross-coupling from their corresponding potassium perfluorobenzoate salts and aryl iodides. A convenient synthesis of fluorinated *para* terphenyls bearing ethers in high yields were performed by S_NAr chemistry. The absorption and fluorescence electronic properties of these new materials display a solvatochromic and solvatofluorochromic behavior. Both of terminal alkoxy units and π - π stacking cooperates to form stable assembled fiber-like architectures.

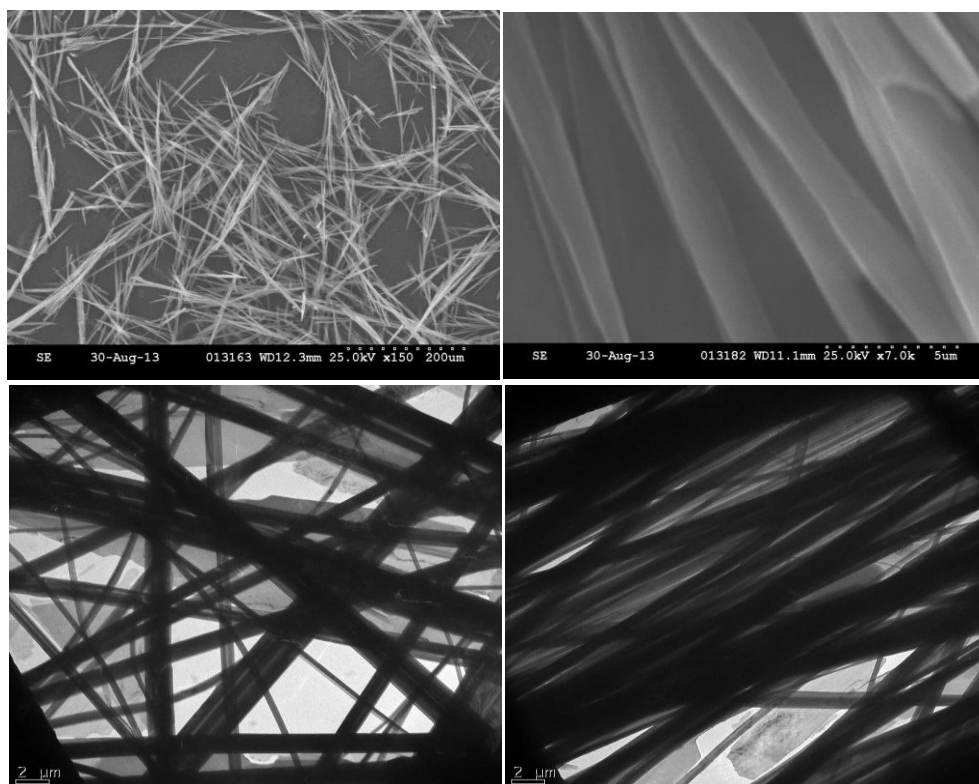


Fig. 5: (top) SEM images, and (bottom) TEM images for the dried xerogel of liquid crystalline gelator **4** obtained from *n*-octanol (6.55 mM)

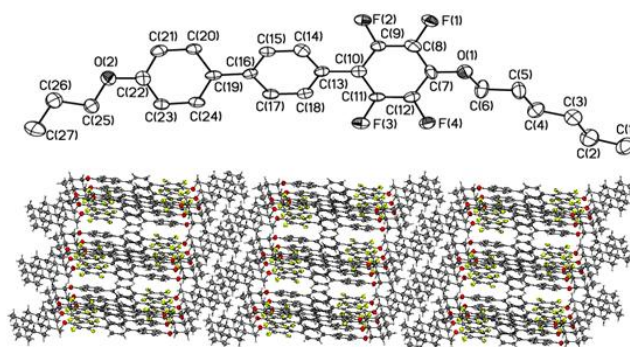


Fig. 6: (top) Crystal structure (ORTEP view) of **4** as derives from the X-ray analysis (thermal ellipsoid plots are drawn at the 30% probability level); (bottom) Face-to-face intermolecular π - π stacking interactions of the rigid aromatic core; and tail-to-tail van der Waals interactions between the terminal alkoxy chains

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