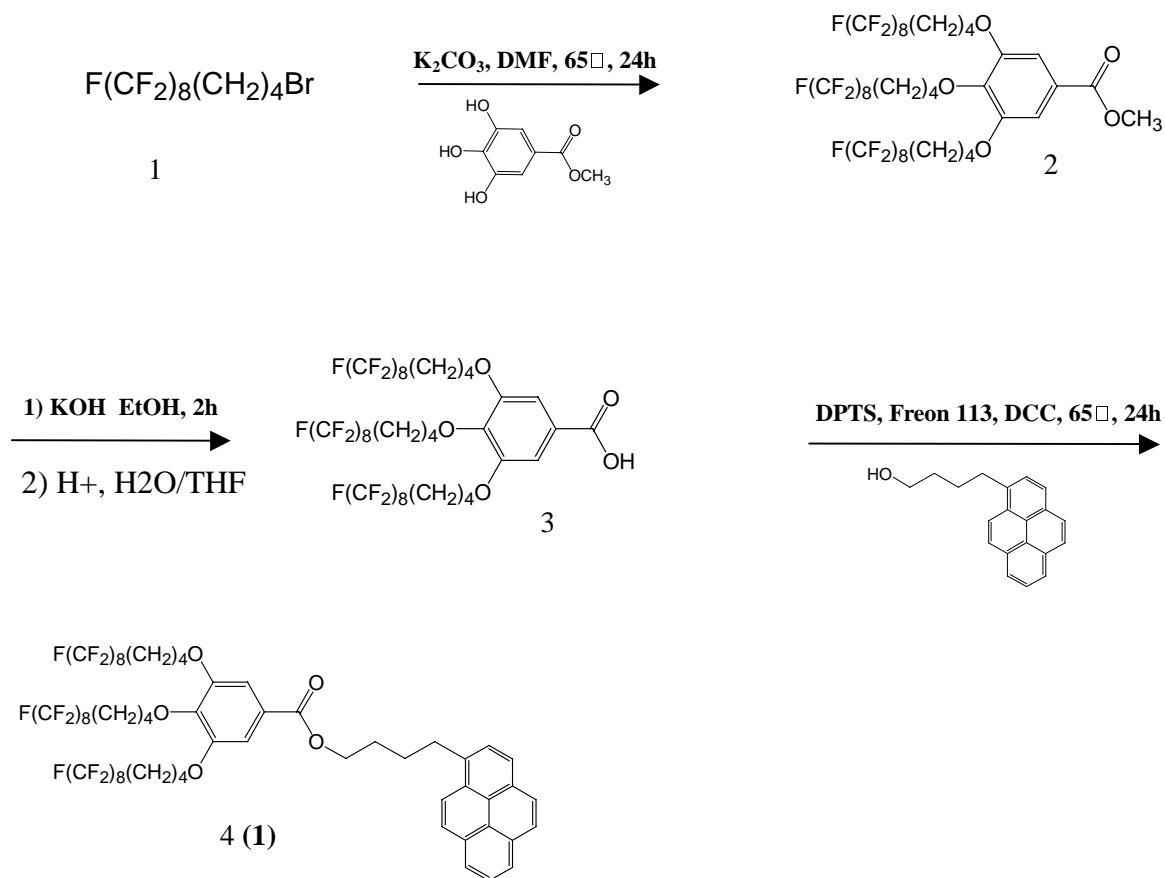


Supporting information

Photoluminescence Properties of a Perfluorinated Supramolecular Columnar Liquid Crystal with a Pyrene Core: Effects of the Ordering and Orientation of the Columns**

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1. Synthesis



Scheme 1. Synthetic procedure for **1**.

The synthetic route to the supramolecular material [4-(1-pyrenyl)-butyl] 3,4,5-tris-(12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptafluoro-1-dodecan-1-yloxy)-benzoate (**1**) is shown in Scheme 1.

1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyl bromide (**1**) was synthesized as reported previously. Briefly, compound **1** was prepared via alkylation from (1) and 3,4,5-trihydroxybenzoate to produce (**2**), the basic hydrolysis of the methyl ester group with KOH in a mixture of EtOH and THF to produce (**3**),

and then the reaction of (3) with 1-pyrenebutanol. Methyl 3,4,5-trihydroxybenzoate was reacted with 1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyl bromide (1) in DMF at 70°C under reflux with K₂CO₃ as the base to afford (2) in 78.95% yield after 24 h. Basic hydrolysis was then carried out with KOH in a mixture of EtOH and THF under reflux for 6 h, followed by acidification with 35% HCl; the mixture was then once again concentrated and precipitated into 1500 mL of cool water. After filtration, a yield of 100% of a white powder was obtained. The target product (**1**) was synthesized as shown in Scheme 3.2. Product (4) was obtained by reacting (3) with 1-pyrenebutanol in the presence of DCC and DPTS at 45°C under reflux for 24 h. In this process, it was necessary to use Freon 113 as a co-solvent with CH₂Cl₂ due to the poor solubility of compound (3). The reaction mixture was cooled to room temperature and the product was precipitated in MeOH, then precipitated in MeOH three times from CH₂Cl₂ solution. The crude product was purified by using column chromatography (SiO₂, CH₂Cl₂) and after precipitation in EtOH from CH₂Cl₂ solution yielded 60.29% of compound (4) as a white solid. TLC: R_f = 0.52 (CH₂Cl₂/hexanes: 2/1). ¹H NMR (CDCl₃, 300 MHz, 20 °C): δ 8.26 (d, 1H, *J* = 7.6 Hz), 8.18-7.98 (m, 7H), 7.89 (d, 1H, *J* = 7.8 Hz), 7.24 (s, 2H), 4.4 (t, 2H, *J* = 6.0 Hz), 3.98 (m, 6H), 3.44 (t, 2H, *J* = 7.3 Hz), 2.13 (m, 8H), 1.81 (m, 14H). [The numbering system in this description of the synthesis needs to be changed to remove confusion between **1** and (1) and (4).

2. Differential scanning calorimetry (DSC)

Figure 1 shows the DSC cooling and subsequent heating thermal diagrams for compound **1**. Cooling at a rate of 5°C/min results in a major exothermic transition at 80.7°C, indicating the occurrence of a high-ordered mesophase transition. The subsequent heating scan resulted in an endothermic transition at 83.2°C.

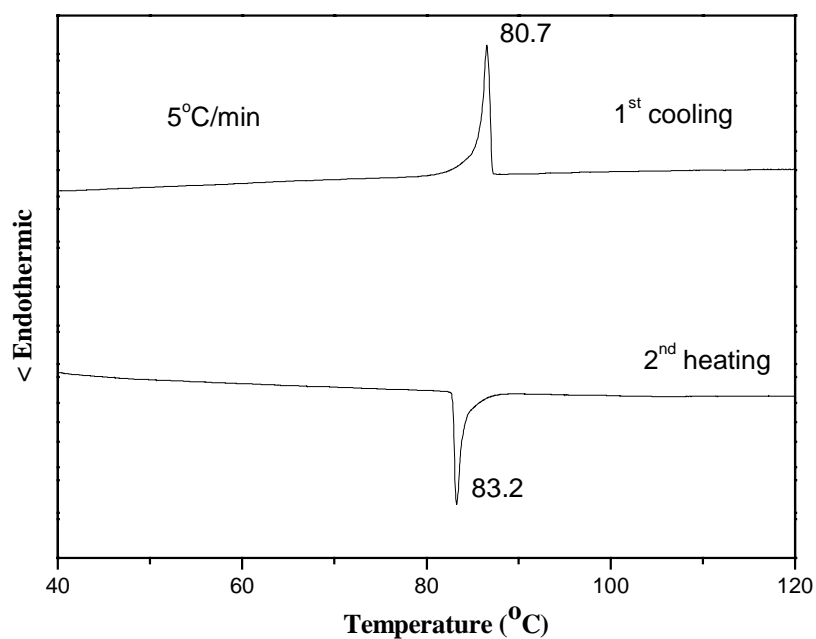


Figure 1. DSC thermograms of **1**.

3. X-ray diffraction (XRD)

The XRD pattern in Figure 2 was obtained at room temperature and reveals the bulk structure of **1** when it is thermally annealed at a rate of $-2^{\circ}\text{C}/\text{min}$. The sharp peaks indicate the presence of a highly ordered structure that can be indexed as the (10), (11), and (20) planes of a hexagonal cylindrical mesophase with lattice parameter $a=4.18\text{ nm}$. The relative positions of the peaks, 1, $\sqrt{3}$, and 2, are attributed to hexagonal packing, with a d spacing of the (10) space of 3.6 nm.

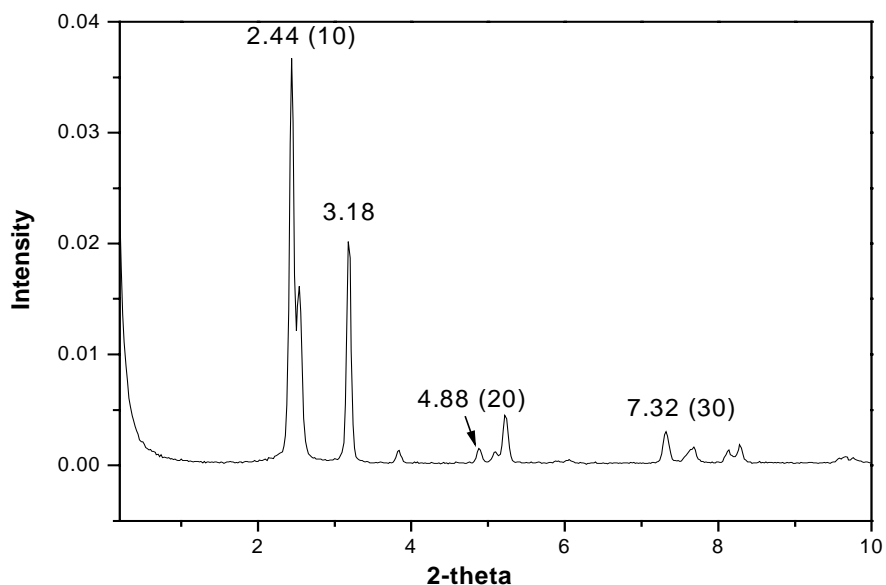


Figure 2. X-ray diffraction pattern of the material at 25°C.

4. Variation of the PL spectra with concentration

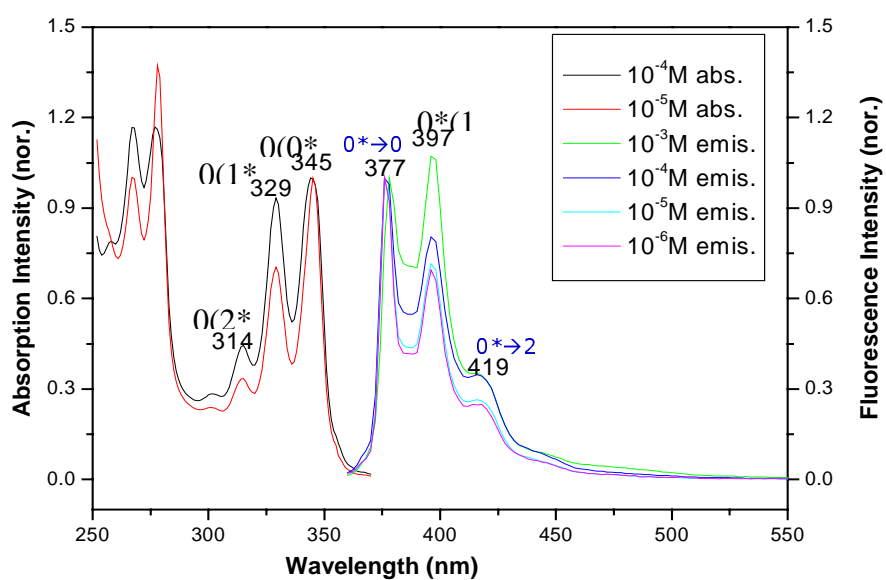


Figure 3. Concentration dependent absorption and PL spectra of **1** in chloroform; the PL spectra were measured by carrying out excitation at 345 nm and then normalized to maximum intensity. As the concentration increases, the PL spectrum becomes increasingly red-shifted.

5. Molecular structure and optical properties of other dendrimer containing pyrene chromophore

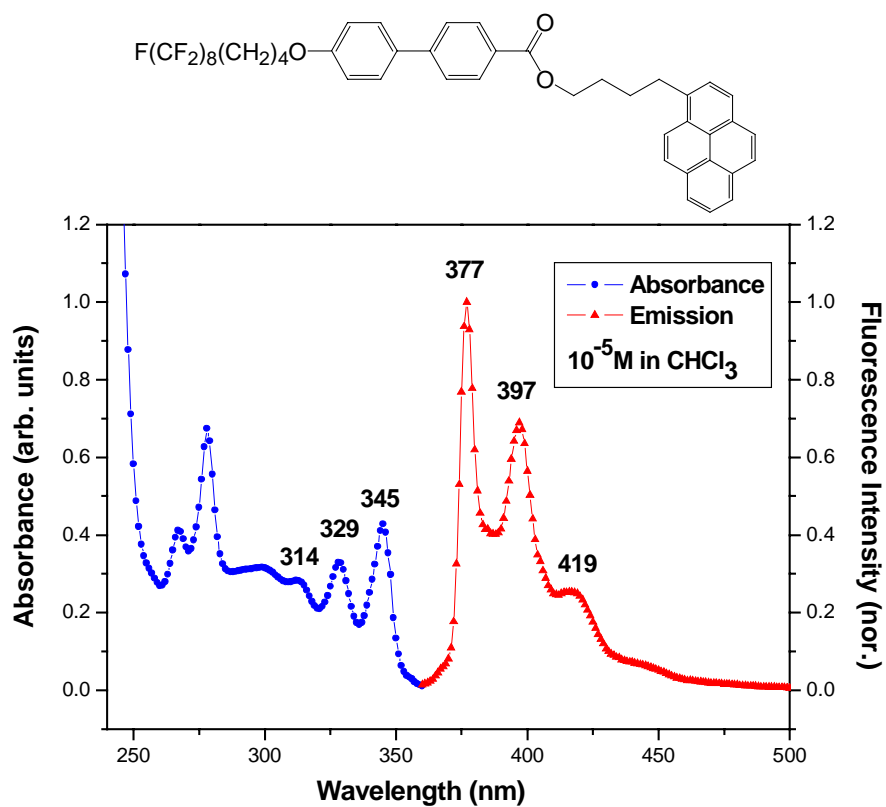


Figure 4. The PL spectra of small molecule containing pyrene chromophore; the spectra show a typical vibronic features of pyrene.

6. AFM image with height profile

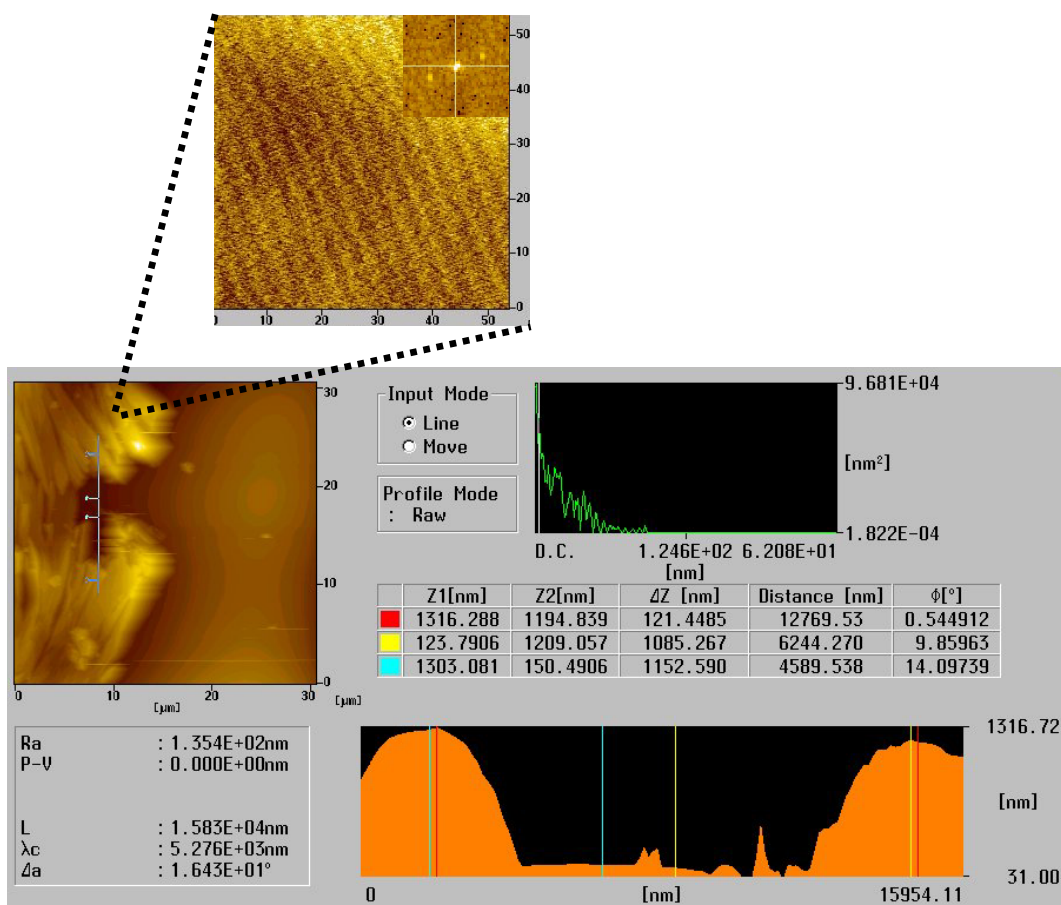


Figure 5. The molecules have planar alignment on the Teflon AF[®] substrate. The height profile shows that the film has $\sim 1 \mu\text{m}$ -height which the planar alignment of columns is preserved over $1 \mu\text{m}$.

7. Variation of the PL spectra with concentration

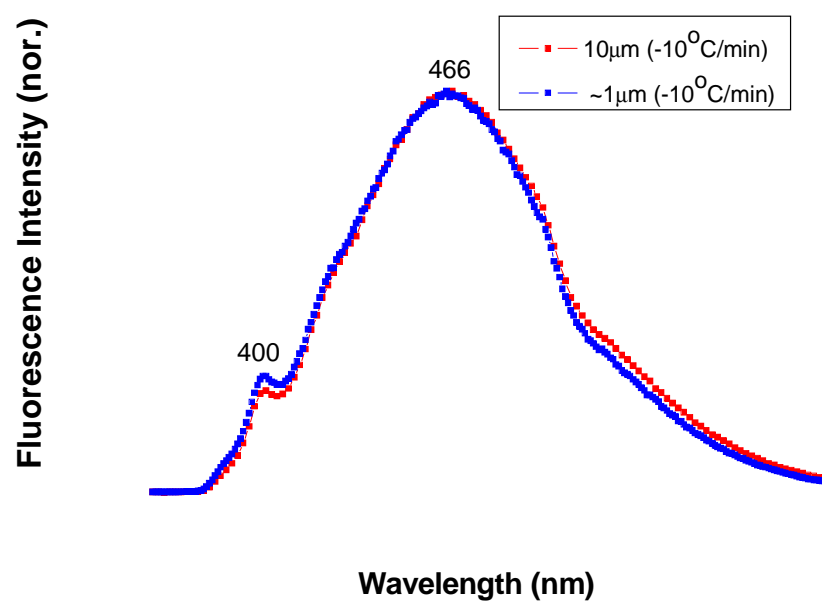


Figure 6. The PL spectra of films with different thickness ($\sim 1\mu\text{m}$ and $10\mu\text{m}$); the PL spectra were similar to each other. The PL spectra were measured with excitation at 345 nm and normalized to maximum intensity.