Supporting Information

Oana M. Martin, Lian Yu and Sandro Mecozzi*
University of Wisconsin – Madison, School of Pharmacy, 777 Highland Ave., Madison, WI 53705

Fluorescence Study
Vesicles of (1) were prepared in a solution of Rhodamine B (5.0 mM Rhodamine B in 10 mM Hepes, 140 mM NaCl, pH 7.4). A thin film of amphiphile, obtained by rotaevaporation of a chloroform solution, was sonicated in 2 mL of the above RhB solution to obtain a 200 µM concentration of (1). Encapsulated RhB was separated from the free dye by gel filtration on a column of cationic DEAE Sephadex A25, using 10 mM Hepes/140 mM NaCl as eluent. The cationic vesicles eluted at 4-5 mL, whereas the free dye started to elute beyond 10 mL. Coincidence of entrapped RhB with the elution of the cationic vesicles confirms the existence of an aqueous interior (Figure 1). Addition of F8P6 (perfluorooctyl – poly(ethylene glycol) (M_n=6000 a.m.u.)) followed by sonication and heating to 95 °C for 1 hour, leads to a significant increase in fluorescence for the samples containing the cationic vesicles. This increase is correlated with the disappearance of self-quenching upon dilution of the dye from the encapsulated volume into the bulk solution.

Fluorescence spectra were obtained with a Hitachi F3010 fluorimeter, with an excitation wavelength of 550 nm. Emission was measured at 576 nm.

Figure 1. Fluorescence intensity of Rhodamine B in vesicles of (1).
Powder X-Ray Diffraction

The samples were placed on glass slides attached to the sample holder. X-Ray diffraction patterns were recorded for the \( p \)-perfluorooctyl-calix[4]arene tetraphenol (2) at 25 °C using a 0.1° step and a step time of 3.0 s. Three samples were analyzed: a powder, a melt and a frozen liquid crystal. The melt was prepared by heating at 10 °C/min to 140 °C followed by quenching to room temperature. The frozen liquid crystalline sample was obtained by heating the melt at 60 °C overnight, followed by quenching to room temperature. The three X-ray diffraction patterns shown in Figure 2 confirm the liquid crystalline like structure of compound (2). The number of sharp peaks at low angles increased for the liquid crystalline sample, confirming the more ordered structure characteristic for liquid crystals.

\[ d \text{ values (Å)}: \]

- powder: 30, 22, 11, 5, 2
- melt: 26, 5, 2
- liquid crystal: 28, 14, 10, 5, 2

![Figure 2. X-ray diffraction pattern of compound (2). Black – powder, red – melt, blue – liquid crystal.](image-url)
Differential Scanning Calorimetry

Figure 3. DSC traces at 5 °C/min of the first cooling (top) and second heating (bottom) scans of compound (1). In the cooling scan crystallization occurred at 45.55 °C (1.834 J/g). In the heating scan two endothermic transitions were observed: 50.38 °C (1.284 J/g) and 73.46 °C (1.398 J/g).

Figure 4. DSC traces at 5 °C/min of the first heating (top), first cooling (middle) and second heating (bottom) scans of compound (2).
Polarized Optical Microscopy

Samples of compounds (1) and (2) were examined between glass plates under crossed polarizers, while heated on a hot stage at 10 °C/min.

Figure 5. Optical polarized texture exhibited by the mesophase of (2) obtained by heating to 115 °C (200x).

Figure 6. Optical polarized texture exhibited by the mesophase of (1) obtained by quenching to room temperature after heating to 100 °C (200x).