

*Electronic Supplementary Information*

## **A Supramolecular Host Matrix for Preserving Fluorescence in the Solid-State**

Gargee Roy, Alisha Sengupta, Aakash Ravikant Likhari, Deepak Asthana\*  
*Ashoka University, Sonapat, Haryana, India.*

### **Table of Contents:**

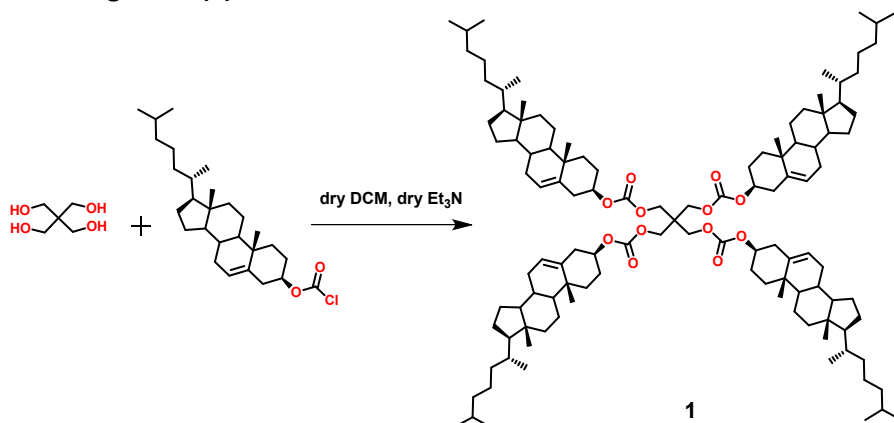
1. General information.....	S1
2. Experimental procedure for synthesis of compound <b>1</b> .....	S1-S2
3. Gelation of compound <b>1</b> .....	S2
4. Preparation of co-gel of <b>1</b> with fluorescent dyes.....	S2
5. Rheological Measurements of compound <b>1</b> and <b>1+perylene</b> co-gel .....	S3
6. BET Measurements of compound <b>1</b> and <b>1+perylene</b> co-gel.....	S4
7. Confocal Laser Scanning Microscopy of compound <b>1 + perylene</b> co-gel .....	S5
8. TEM images of compound <b>1 + perylene</b> co-gel.....	S5
9. Emission Spectra of <b>perylene</b> .....	S6
10. SSPL spectra of samples prepared by different methods.....	S6
11. Preparation of xerogel of <b>1</b> with fluorescent dyes.....	S7
12. Quantum Yield Measurements.....	S7
13. <sup>1</sup> H NMR spectrum of compound <b>1</b> .....	S8
14. MALDI-MS of compound <b>1</b> .....	S8
15. FT-IR of compound <b>1</b> .....	S9

## 1. General information

All the starting materials, reagents and requisite solvents were used as received. Pentaerythritol and cholesterol chloroformate were purchased from Sigma and TCI respectively. Dichloromethane (DCM), Methanol (MeOH) Ethanol (EtOH), N, N-dimethylformamide (DMF), Chloroform (CHCl<sub>3</sub>), n-hexane utilized in all the experiments were purchased from SRL Chemicals.

<sup>1</sup>H-NMR was recorded on a Bruker 400 MHz spectrometer. MALDI-MS was done using Bruker Daltonics FLEX-PC (Autoflex- TOF) and  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA) matrix. UV-Visible measurements were done using Agilent Cary 60 Spectrophotometer. Fluorescence measurements were conducted on Agilent Cary Eclipse Spectrophotometer. FT-IR measurements were performed using Agilent Cary 630 FT-IR Spectrophotometer equipped with ATR spectrometer. Elemental analysis was done using varioEL cube V4.0.11 Elementar Analysensysteme GmbH. Confocal Laser Scanning Microscopy was done using LSM900 (Carl Zeiss) and TEM images were taken using JEOL 2100F. SSPL measurements were done using HORIBA QuantaMaster QM-8450-22-C. Rheological measurements were done using TA instrument ARES G2. Quantum yields were calculated using Felix GX software on HORIBA Canada QM-8450-22-C instrument. Porosity measurements for xerogel samples were performed using BELSORP maxi (BELSORP- series) from Microtrac BEL Corp.

## 2. Synthesis of the gelator (1)



Pentaerythritol (0.4 g, 2.94 mmol) was taken in a 250 ml round-bottomed flask. To it, anhydrous DCM (60 ml) was added and dissolved under inert atmosphere. Dry triethyl amine (1.8 ml, 12.93 mmol) was added dropwise and the reaction mixture was stirred for 15 minutes. To the reaction mixture, cholesterol chloroformate (5.8 g, 12.93 mmol) was added under ice-cold condition and the resultant mixture was stirred for 3 hours. After completion of the reaction, the crude product was washed with water/DCM. Organic layer was collected and dried over anhydrous sodium sulphate, filtered off and then evaporated using a rotary evaporator. The crude product obtained was further purified using column chromatography over silica gel (hexane:DCM) to give the product **1** as white solid. (Yield= 94%)

**MS(MALDI):** Calculated: C<sub>117</sub>H<sub>188</sub>O<sub>12</sub> (Molecular Weight=1785.41), Found: [M+K]<sup>+</sup>: 1824.52

**CHN Analysis:** Calculated (%) C, 78.65; H, 10.61; N, 0. Found (%) C, 78.68; H, 10.441; N, 0.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 300 K)  $\delta$ (ppm): 5.42 (s, 4H), 4.50 (m, 4H), 4.23 (s, 8H), 2.33-2.48 (m, 8H), 1.81-2.08 (m, 21H), 1.43-1.72 (m, 41H), 1.23-1.41 (m, 16H), 1.06-1.23 (m, 27H), 1.02-1.06 (m, 16H), 0.87-0.96 (m, 32H), 0.74-0.64 (s, 11H)

### 3.1 Gelation tests

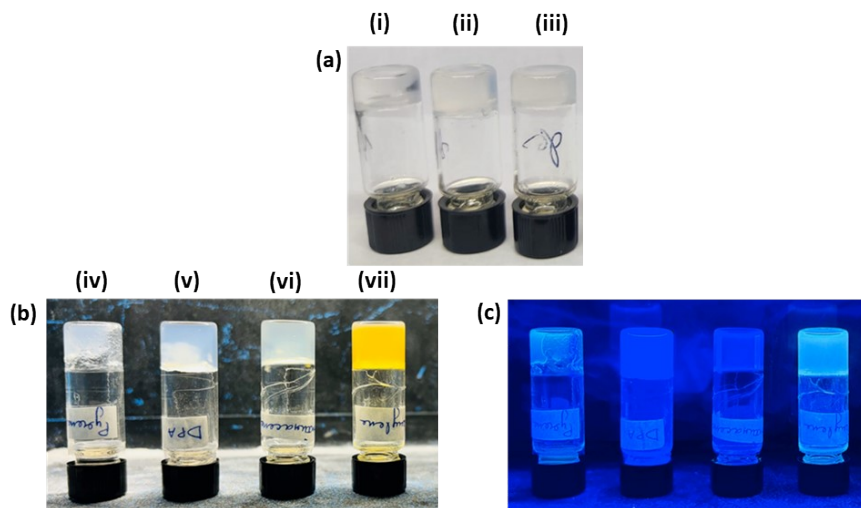
The gelation tests for compound **1** were performed using heat-cool method. In a typical procedure, gelator (**1**) was taken in the selected solvent and was heated until a clear solution was obtained. The solution was then allowed to cool at room temperature (undisturbed). In most cases gelation was observed within a few minutes, which was confirmed by inversion of the vial. Following table shows the gelation results in selected solvents:

Solvent	Weight%
Hexane	0.6 <sup>a</sup>
Chloroform: methanol (1:1)	0.25 <sup>b</sup>
Hexane: ethanol (1:3)	0.6 <sup>c</sup>
DMF: ethanol (1:1)	0.5 <sup>c</sup>
DMF: methanol (1:1)	1.0 <sup>c</sup>

**Table S1:** Gelation conditions for gelator **1** (a= transparent gel, b=opaque gel, c= semi-transparent gel).

### 3.2 Preparation of 1+dye co-gels

The condition for formation of gel along with the dye was as follows: 5 mg of **1** and 1.5 mg of the corresponding fluorescent dyes (anthracene, pyrene, perylene and DPA) was taken in a 2 ml screw cap vial, and 0.5 ml of 1:1 hexane:ethanol solvent mixture was added. Mixture was heated to form a clear solution. The solution was then cooled at room temperature and within a couple of minutes, gelation was noted.

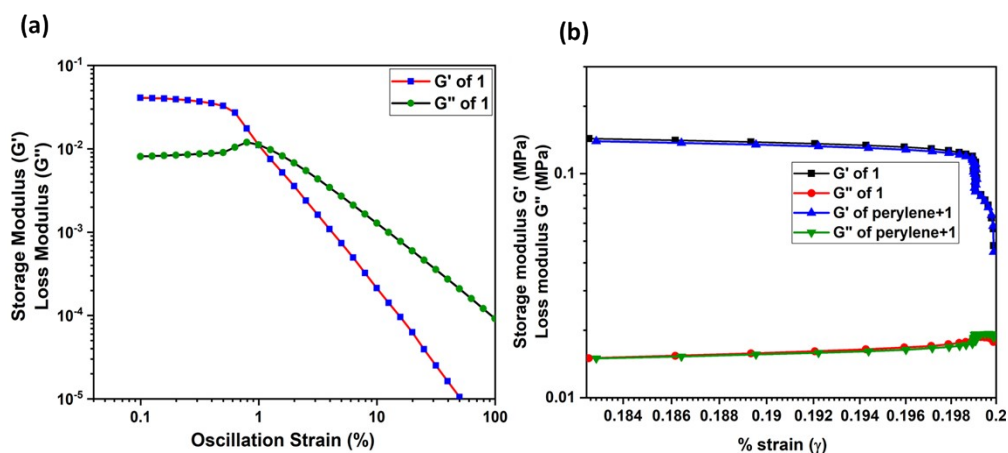


**Figure S1:** Images of the (a) gel in hexane (i), 1:1 hexane: ethanol (ii), 1:1 DMF: ethanol (iii), (b) gelator + dye (under normal light) [ pyrene (**4**), DPA (**5**), anthracene (**6**), perylene (**7**)] (c) dyes under UV light (order remains the same as above).

### 3.3 Rheological Studies

The rheological experiments were carried out in cone and plate geometry (diameter= 25 mm, 0.1 rad) on the rheometer plate using TA instruments Rheometer ARES G2. A 1 wt% hexane:ethanol (1:1) gel sample of **1** (1 wt%) and co-gel **1+dye** (perylene) containing 0.3 equivalents of dye was used to collect the data. The frequency sweep experiment was performed as a function of angular frequency (0.1 - 100 rad/s) at fixed strain of 0.2% at 25 °C, with respect to the amplitude sweep experiments, showing a linear viscoelastic region (LVR) between 0.1-0.4 strain%. Above 1% oscillation strain, the gel-like properties of compound **1** begins to decrease and the compound begins to flow.

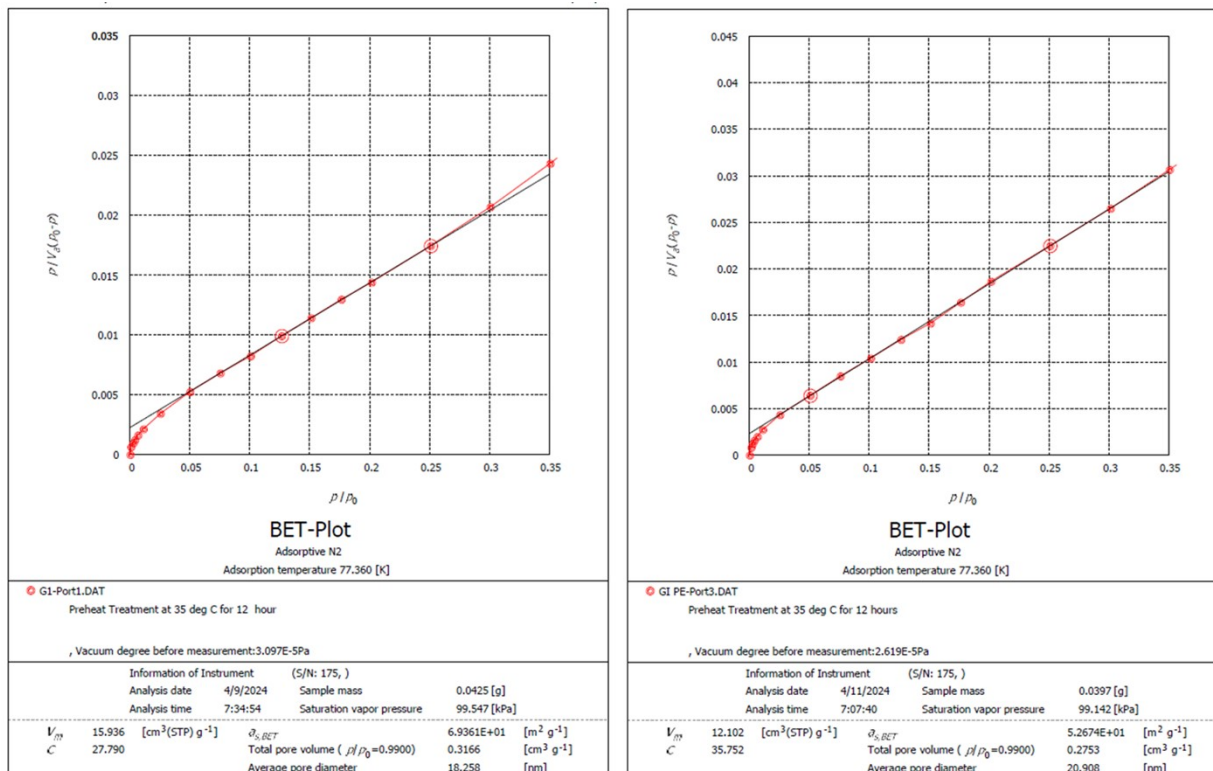
The  $G'$  and  $G''$  ( $G' > G''$ ) showed a plateau region, which is a notable feature of viscoelastic materials. The value of  $G'$  for both the organogels was seen to be in the order of  $10^6$  Pa, which shows a relatively high mechanical strength. Also, both samples gel and **1+dye** co-gel exhibit nearly similar  $G'$  values, which shows that there is no loss in the rigidity and overall strength of the gelator even upon the inclusion of the dye. The oscillatory strain sweep experiments were also carried out for both the organogels. Gradual increase in the applied strain led to decrease in both  $G'$  and  $G''$  and at around 0.19% strain, sudden decrease in  $G'$  indicates the gel-to-sol transition.



**Figure S2:** Plots showing variation in  $G'$  and  $G''$  with respect to (a) amplitude sweep, and (b) applied oscillatory strain for gelator **1**.

### 3.4 BET Studies

The adsorption and desorption capacity of the xerogels **1** and **1 + perylene** to nitrogen was tested using BELSORP maxi (BELSORP- series) from Microtrac BEL Corp. The porosity, average pore size, and specific surface area of the xerogels were calculated from the adsorption and desorption change curves through degassing at 35 degrees.



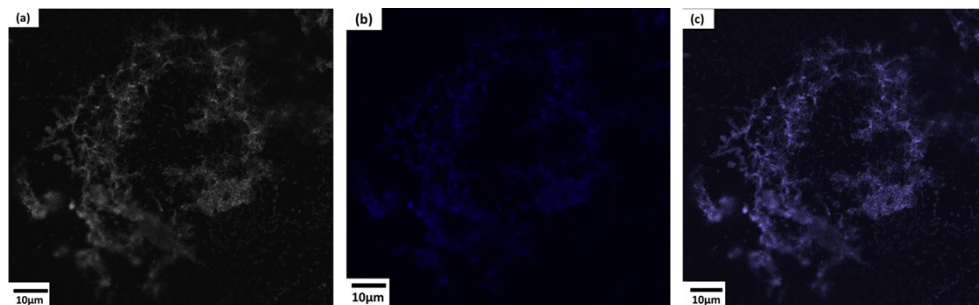
**Figure S3:** BET plots obtained with hexane:EtOH (1:1) xerogel of **1** and **1+perylene** with respect to relative saturation of pressure.

Name of Sample	BET Surface Area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Average Pore Radius (nm)
Gelator <b>1</b>	69.361	0.3166	9.129
Gelator <b>1 + perylene</b>	52.674	0.2753	10.454

**Table S2:** Table showing difference in surface area, pore volume and average pore radius between xerogel **1** and **1+perylene** (1:1 Hexane: EtOH).

### 3.5 Confocal Laser Scanning microscopy (CLSM) images

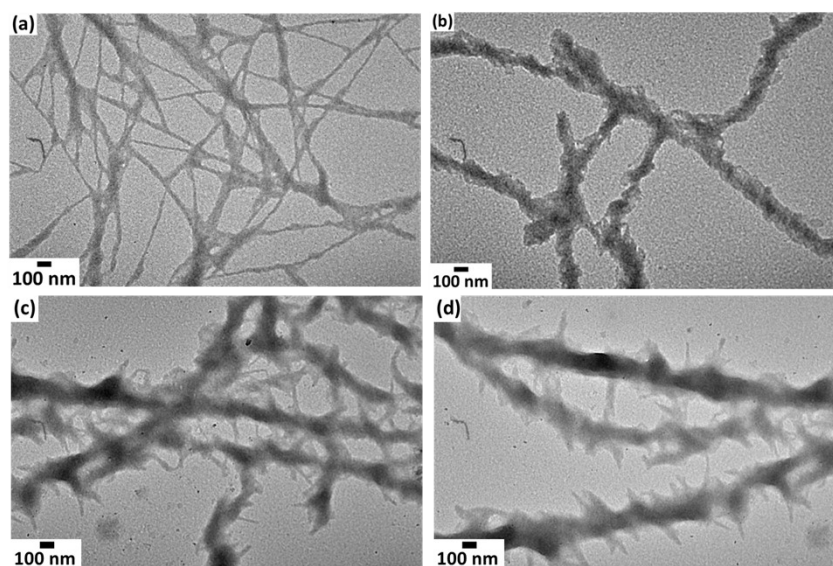
CLSM experiments were carried out with a LSM900 (Carl Zeiss) with a 63X/1.4: oil objective. The fluorescent probe perylene was excited with a 405 nm laser line (diode). The fluorescence was acquired with GaAsP detector in the ranges 415 nm-470 nm. Viscous (gel-like) sample of **1+perylene** dye (in 1:1 hexane: ethanol (0.25 wt%)) was drop casted on TEM grid and was used for viewing. Grid was placed on a pre-cleaned glass slides and was dried under vacuum for 24 hours. Samples were visualized through confocal microscopy for a period of 20 minutes to evaluate the morphology of the dye within the gel matrix.



**Figure S4:** CLSM images of the **1+ Perylene** co-gel in hexane+ethanol (1:1). (a) DIC image (grayscale); (b) Fluorescence image (upon blue excitation of 410 nm); (c) Overlay of both the fluorescent and grayscale image.

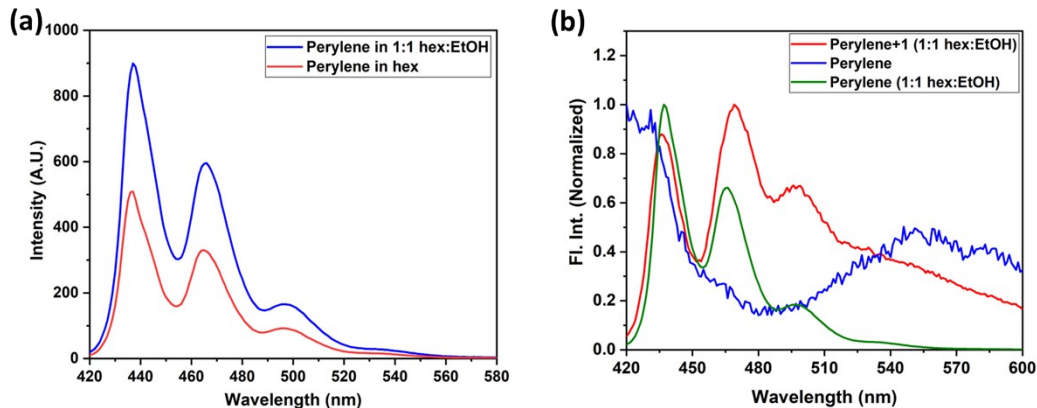
### 3.6 Transmission Electron Microscopy (TEM) images of 1+perylene co-gel

TEM images were obtained using a JEOL 2100F instrument. Samples were prepared by dip-coating method. Copper-based TEM grids were prepared dipping it once into the gel (0.25 wt%) samples and were dried under vacuum for 24 hours before taking the images.



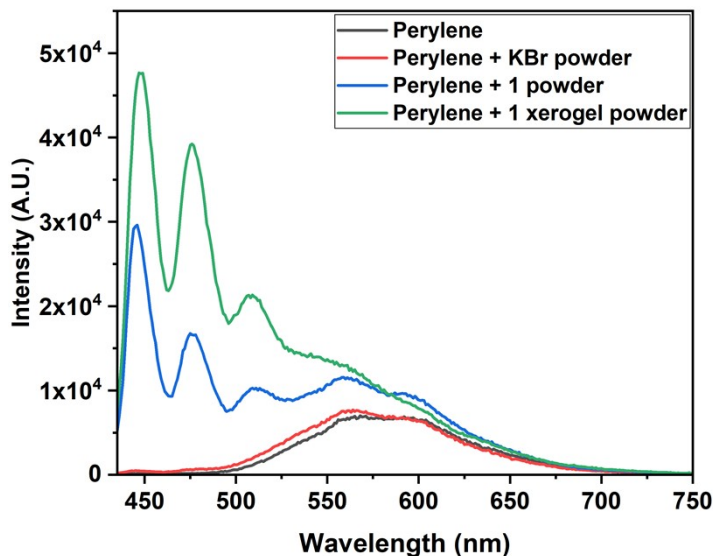
**Figure S5:** Pictures (a & b) showing TEM images of **1+ Perylene** co-gel in hexane:ethanol (1:1); (c & d) TEM images obtained from gel of **1** in hexane:ethanol (1:1).

### 3.7 Emission spectrum of perylene



**Figure S6:** Plots (a) showing room temperature emission spectrum of perylene solutions [1 μM] in hexane and 1:1 hexane:ethanol ( $\lambda_{\text{ex}} = 410$  nm). Plot (b) shows the normalized emission spectrum ( $\lambda_{\text{ex}} = 410$  nm) of perylene solution (green), emission spectrum of perylene powder (blue), and xerogel powder of perylene+1 co-gel (red).

### 3.8 SSPL spectra of samples prepared by different methods

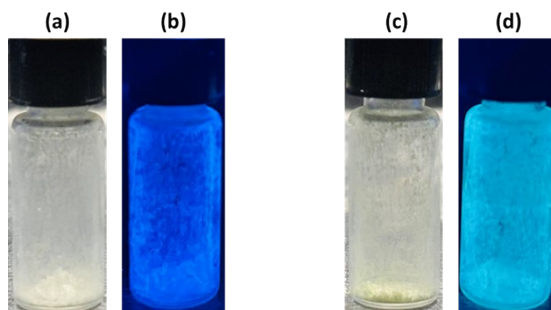


**Figure S7:** SSPL spectra obtained from powder samples of perylene, perylene mixed with KBr, perylene and gelator mixed mechanically, and 1+perylene xerogel ( $\lambda_{\text{ex}} = 410$  nm).



### 3.9 Preparation of xerogel of 1+ dyes co-gels

Xerogel of the (1 + Dye) co-gels were prepared in following manner: Co-gel obtained from 1 + Dye mixture was flash frozen using liquid nitrogen for about an hour. Frozen sample was then dried under slow vacuum to ensure complete removal of solvent. The solid gel obtained was further tested for photoluminescence.



**Figure S8:** Xerogel images of 1+ anthracene in regular light (a), and long wavelength UV light. Images (c & d) of 1+ pyrene xerogel under normal light and under long wavelength UV light, respectively.

### 3.10 Quantum Yield Measurements

Absolute quantum yield method was used to calculate the quantum yield of the respective xerogels mentioned below using Felix GX software on a HORIBA QuantaMaster QM-8450-22-C instrument. It should be noted that this absolute method for calculating the emission quantum yield has an estimated error of  $\pm 5\%$ .<sup>1,2</sup>

$$\text{Quantum Yield} = \frac{E_c - [(1 - A) \times E_b]}{L_a \times A}$$

$$A = 1 - \left( \frac{L_c}{L_b} \right)$$

where,  $E_c$  = Total number of photons emitted in the emission wavelength region

$E_b$  = Total number of photons emitted by reflected light

$L_b$  = Total number of photons after absorption of reflected light

$L_c$  = Total number of photons not absorbed by the fluorescent species under direct excitation.

$A$  = Sample absorbance in integrating sphere



### 3.11 Characterization

#### $^1\text{H-NMR}$ Spectrum of **1**

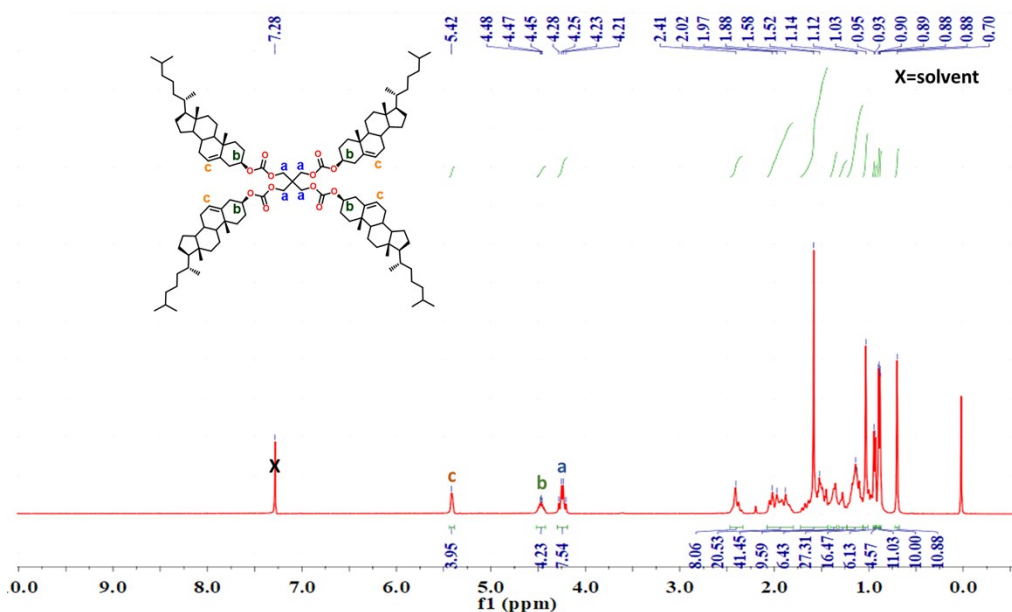


Figure S9: 400MHz  $^1\text{H-NMR}$  Spectrum of Compound **1** in  $\text{CDCl}_3$ , 300 K.

#### Mass Spectrum of **1**

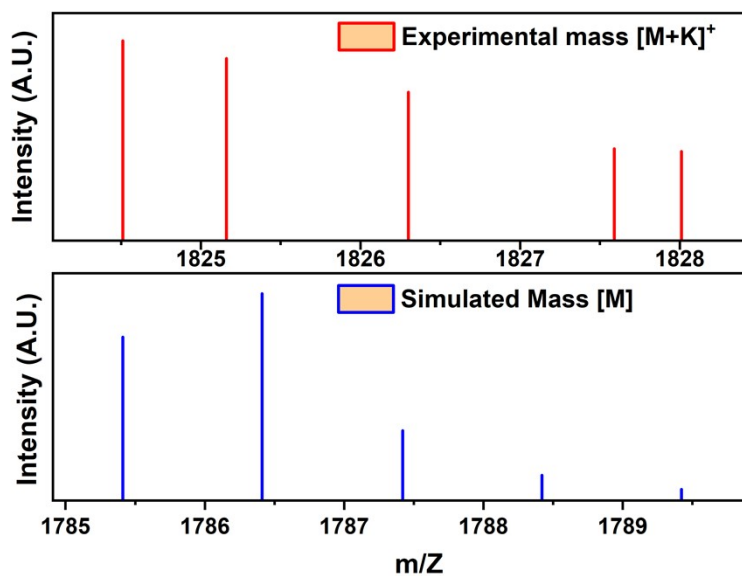


Figure S10: MALDI-MS of spectrum of **1**.

## FT-IR Spectrum of 1

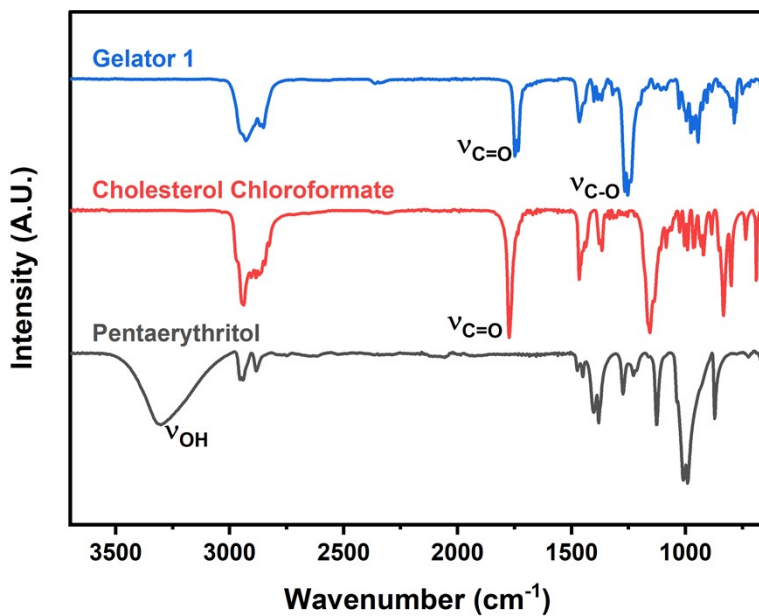


Figure S11: FT-IR Spectra of starting materials and gelator (1).

## References:

1. [https://static.horiba.com/fileadmin/Horiba/Application/Materials/Material\\_Research/Quantum\\_Dots/quantumyieldstrad.pdf](https://static.horiba.com/fileadmin/Horiba/Application/Materials/Material_Research/Quantum_Dots/quantumyieldstrad.pdf)
2. C. Würth, M. Grabolle, J. Pauli et al. Relative and absolute determination of fluorescence quantum yields of transparent samples. *Nat Protoc*, 2013, **8**, 1535–1550.