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Supporting Information

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Self-Assembly of Oligo(*p*-phenylenevinylene)s through Arene-Perfluoroarene Interaction: π-Gels with Longitudinally Controlled Fiber Growth and Supramolecular Exciplex Mediated Enhanced Emission

Sukumaran S. Babu, Vakayil K. Praveen, Seelam Prasanthkumar and Ayyappanpillai Ajayaghosh*

[*] S. S. Babu, Dr. V. K. Praveen, S. P. Kumar, Dr. A. Ajayaghosh

Photosciences and Photonics Group,

Chemical Sciences and Technology Division,

National Institute for Interdisciplinary Science and Technology

(NIIST), CSIR

Trivandrum 695 019 (India)

Fax: (+91) 471-249-1712

E-mail: ajayaghosh62@gmail.com

Description of Experimental Techniques

Gelation studies. The gelation studies were carried out as per reported procedures.[S1] A typical procedure for gelation studies is as follows: Gelation studies were carried out in glass vials of 1 cm diameter. A weighted amount of the compound in an appropriate solvent was placed in the vial, which was sealed and heated until the compound was dissolved. The solution was then allowed to cool. The gel formation was confirmed by the failure of the content to flow by inverting the glass vial. Repeated heating and cooling confirmed the thermal reversibility of gelation. The critical gelator concentration (CGC) is determined from the minimum amount of gelator required for the formation of a stable gel at room temperature.

Gel Melting Temperature (T_{gel}) Determination. The thermotropic behaviour of the gels formed by **5** in different solvents were investigated by dropping ball method.[S1] In dropping ball method, a steel ball (100 mg) was placed on the top of a 1 mL volume gel in a sealed glass vial. Then the gels were slowly heated, while the position of the ball on the top of gel is continuously observed, until the gel no longer bears the ball. The temperature at which the ball reaches the bottom of the vial is taken as the sol-gel phase transition temperature (T_{gel}).

Time Correlated Single Photon Counting (TCSPC). Fluorescence lifetimes and time resolved emission spectra (TRES) were measured using IBH (FluoroCube) time-correlated picosecond single photon counting (TCSPC) system. Solutions were excited with a pulsed diode laser (<100 ps pulse duration) at a wavelength of 440 nm (NanoLED-11) with a repetition rate of 1 MHz. The detection system consists of a microchannel plate photomultiplier (5000U-09B,Hamamatsu) with a 38.6 ps response time coupled to a monochromator (5000M) and TCSPC electronics (DataStation Hub including Hub-NL, NanoLED controller and preinstalled Fluorescence Measurement and Analysis Studio (FMAS) software). The fluorescence lifetime values were determined by deconvoluting the instrument response function with biexponential decay using DAS6 decay analysis software. The quality of the fit has been judged by the fitting parameters such as $\chi 2$ (<1.2) as well as the visual inspection of the residuals. All measurements were carried out in a 1 mm cuvette using a front face sample holder (5000U-04). For the TRES measurements the decay curves were measured at multiple emission wavelengths (450 to 700 nm) to construct a 3D dataset of counts versus time versus wavelength. Using the FMAS software, this 3D dataset was then sliced orthogonally to the time axis to produce 2D spectra of counts versus wavelength to visualize how the emission spectrum evolves during the fluorescence decay time.

Polarizing Optical Microscopy (POM). The POM studies were carried out using a Nikon HFX 35 A Optiphot equipped with a Linkan THMS 600 heating and freezing stage connected to Linkan TP 92 temperature programmer.

Rheological studies. Rheological measurements were conducted on an Anton Paar modular compact (MCR 150) stress controlled rheometer (Physica) equipped with a parallel plate geometry (20 mm diameter) with a striated cone and a rough plate to minimize the errors due to sliding of the gel layers. A hot solution of **5** (2×10^{-3} M) in *n*-decane was poured on to the Peltier kept at 20 °C and was allowed to form a uniform layer. Inorder to avoid the solvent evaporation the plate was properly covered.The gap between the cone and the plate was fixed between 0.25 mm.

Tables and Figures

Table S1. Critical gelator concentrations (CGC) of **5** in different solvents.

Solvent	**CGC in mM**	**CGC in Wt%**	**Nature of the Gel**
n-Decane	0.72	0.20	Stable, Opaque
n-Hexane	0.75	0.24	Stable, Opaque
Cyclohexane	0.76	0.21	Stable, Opaque
Benzene	0.85	0.21	Stable, Opaque
Toluene	0.97	0.23	Stable, Opaque
p-Xylene	1.09	0.20	Stable, Opaque
Chloroform	2.23	0.32	Stable, Opaque
Dichloromethane	2.60	0.41	Stable, Opaque
N,N-dimethylaniline	2.65	0.42	Stable, Opaque
Tetrahydrofuran	-	-	Soluble

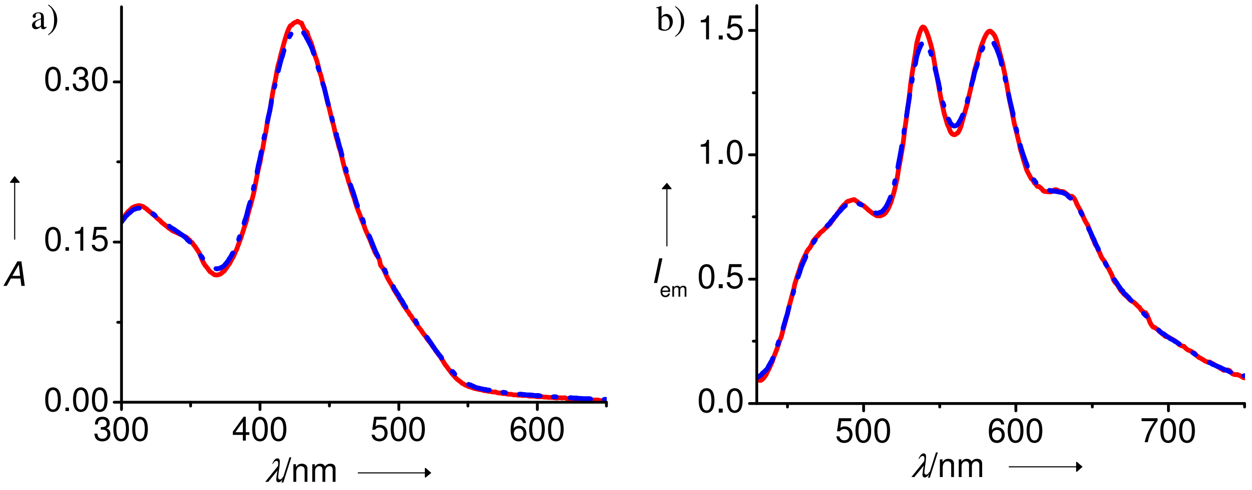

Figure S1. a) Absorption and b) emission changes of **5** before (———) and after (-·-·-) UV irradiation (365 nm) in *n*-decane for 48 hours (1 x 10^{-4} M).

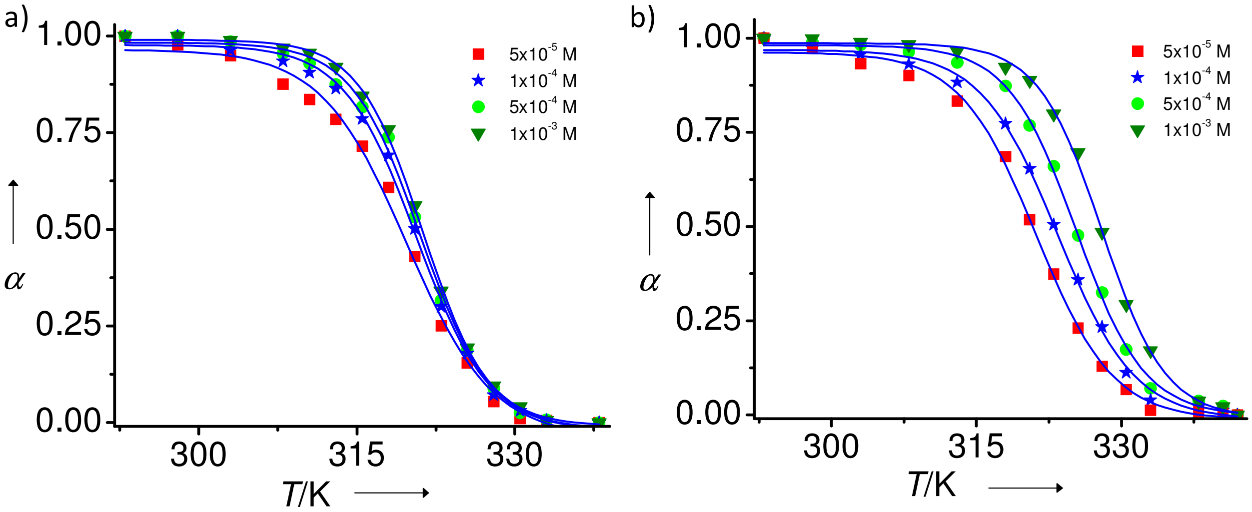

Figure S2. Plots of aggregate fraction (α) vs temperature for a) **4**, b) **5** in *n*-decane at different concentrations (data points obtained from variable temperature emission measurements).[S2]

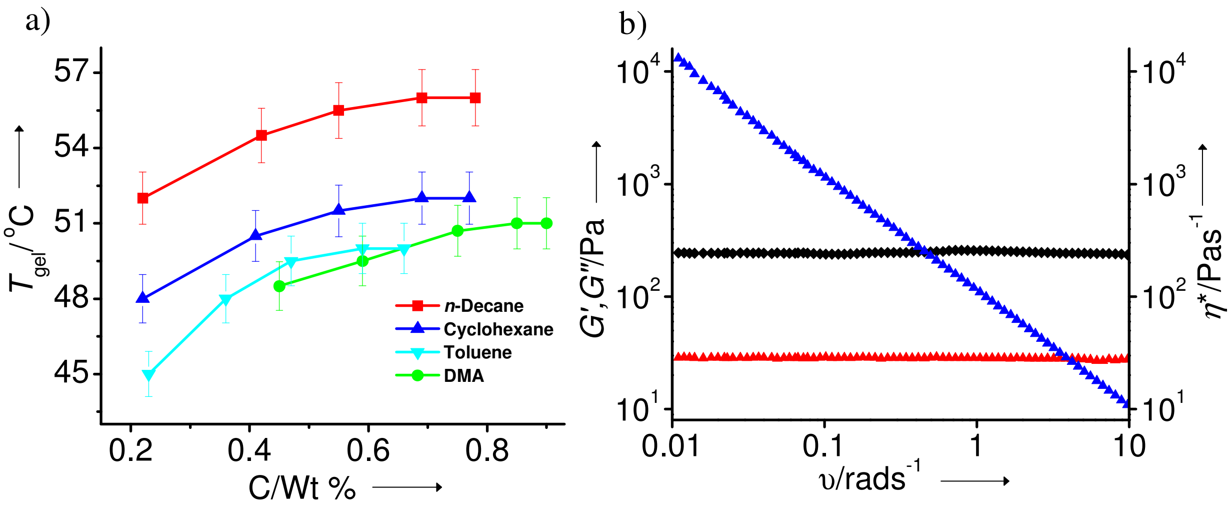

Figure S3. (a) Gel melting temperatures (T_{gel}) vs concentration of **5** in different solvents (data points are obtained by dropping ball method) and (b) plot of elastic modulus (*G'*), viscous modulus (*G"*) and complex viscosity (η*) vs angular frequency (υ) on double logarithmic scale for a 2 x 10^{-3} M gel of **5** in *n*-decane at 20°C at a shear strain = 5%.[S3]

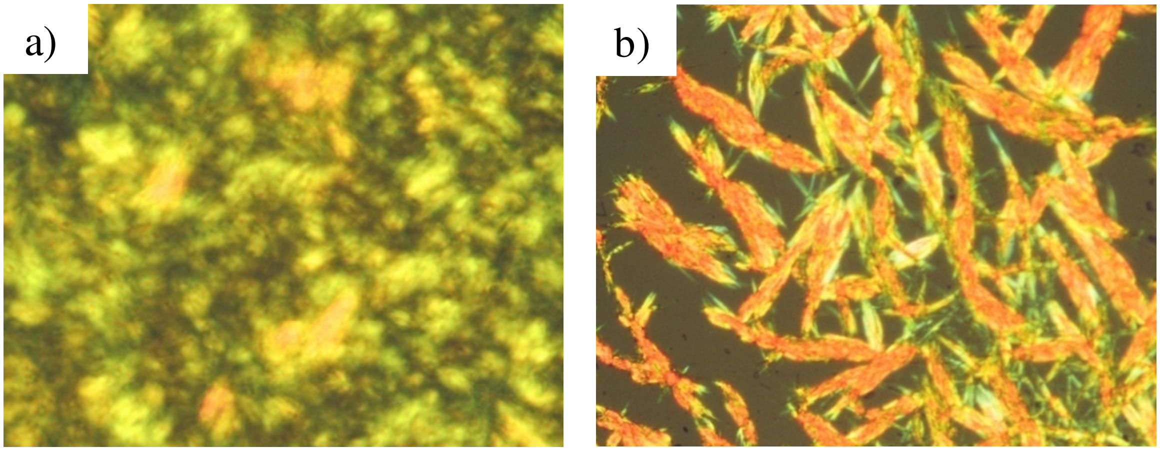

Figure S4. POM images of (a) aggregates of **4** and (b) gel of **5** in *n*-decane (0.72 mmol) (40x).

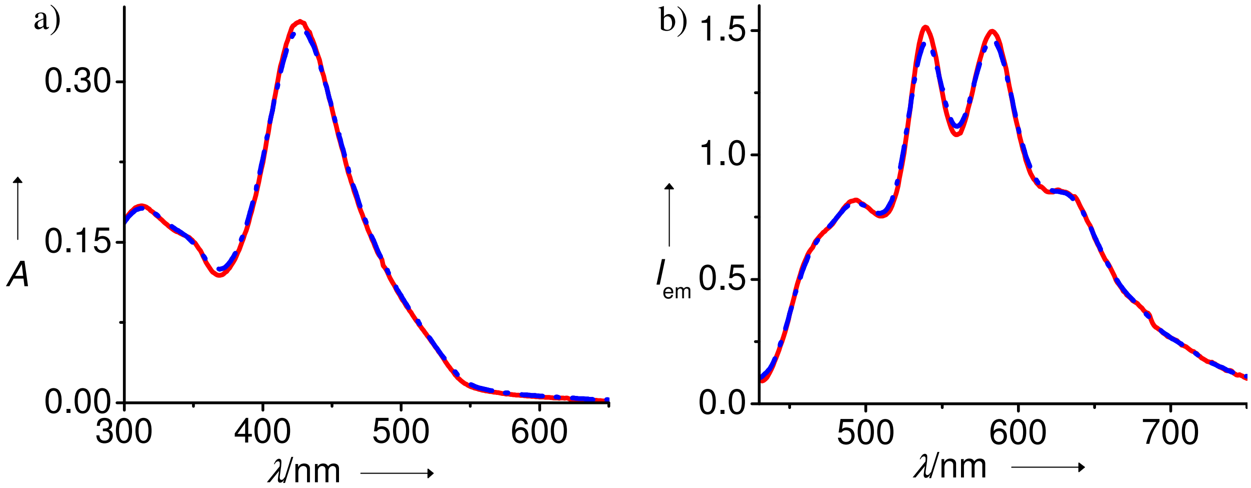

Figure S5. a) Absorption and b) emission changes of **5** (8.3 x 10^{-5} M) before (——) and after (·—·—) addition of DMA (0.83 M) in *n*-decane solution (λ_{ex} = 415 nm).

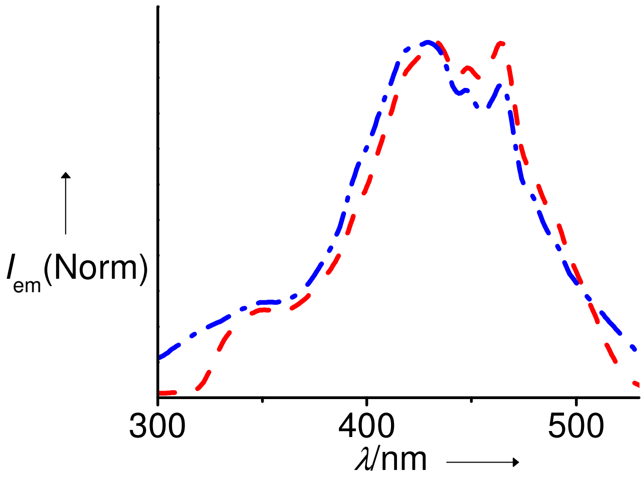

Figure S6. Excitation spectra of **5** (8.3 x 10^{-5} M) before (·—·—) and after (— — —) addition of DMA (0.83 M) in *n*-decane solution (λ_{ex} = 300-555 nm, λ_{em} = 565 nm).

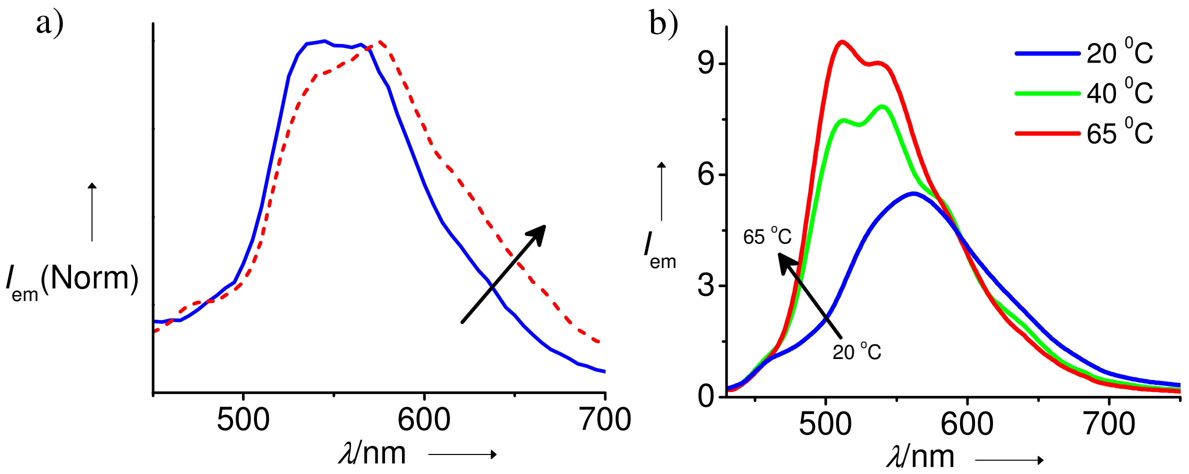

Figure S7. Time resolved emission spectra of **4** at 56 ps (——) and 1.1 ns (– – –) after the excitation at 440 nm at 20°C in *n*-decane (8.3 x 10^{-5} M). b) Variable temperature emission changes of **5** (8.3 x 10^{-5} M) in the presence of 0.83 M DMA at 20°C (——), 40°C (——), 65°C (——) in *n*-decane.

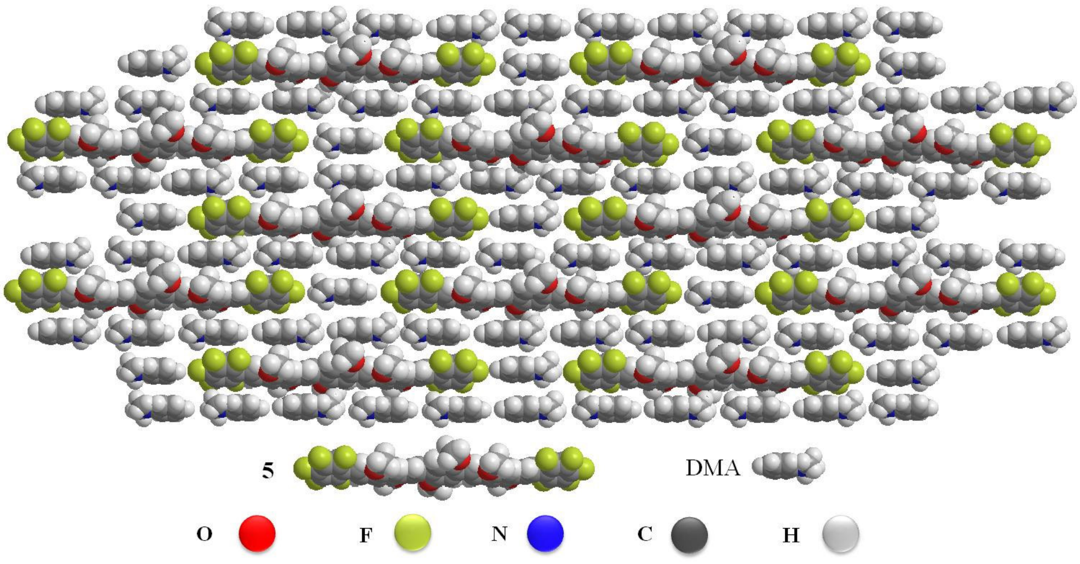

Figure S8. Proposed molecular packing of **5** in presence of DMA in the gel state. This model has been arrived taking into consideration of the previous reports on the crystal packing of fluorinated distyryl derivatives. Gelation of **5** in DMA indicates the intercalation of the solvent within the brickwall type self-assembly. The proposed supramolecular structure is ideally suited for exciplex formation when excited as observed in the case of **5 +** DMA in *n*-decane.

References.

S1. S. J. George, A. Ajayaghosh, *Chem. -Eur. J.* **2005**, *11*, 3217-3227.

S2. a) P. Jonkheijm, F. J. M. Hoeben, R. Kleppinger, J. van Herrikhuyzen, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2003**, *125*, 15941-15941; (b) J. J. Apperloo, R. A. J. Janssen, P. R. L. Malenfant, J. M. J. Fréchet, *Macromolecules* **2000**, *33,* 7038-7043.

S3. a) S. Yao, U. Beginn, T. Gress, M. Lysetska, F. Würthner, *J. Am. Chem. Soc.* **2004**, *126*, 8336-8348; (b) F. M. Menger, A. V. Peresypkin, *J. Am. Chem. Soc.* **2003**, *125*, 5340-5345.