Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Multi-Functional Materials through Self-Assembly of N-Alkyl Phenothiazine Linked Poly(Aryl Ether) Dendrons **

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Experimental

General information

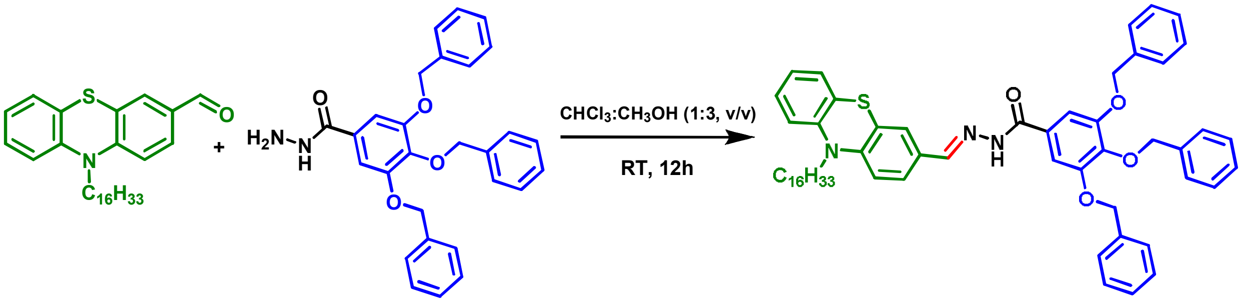
^1H and ^{13}C NMR data were collected on a Bruker 400 MHz spectrometer (^1H: 400 MHz; ^{13}C: 100 MHz). Mass spectra were recorded using Micromass Q-TOF mass spectrometer. IR spectrum was recorded using Jasco FT/IR-4100 spectrometer. The UV-Vis spectroscopic studies were carried using Jasco V-650 spectrophotometer. Emission studies were carriedoutusingJascoFP-6300 spectrofluorometer. The scanning electron microscopic studies were carried out using a FEI-Quanta Microscope. The transmission electron microscopic images were taken using JEM3010JEO, operated at 200 kV. Thin film on glass substrate was prepared from gelators solution(**D1** and **D2**)in THF/Hexane by spin-coating method using MILMAN SPN 2000 spin coating unit.Water contact angles (CA) of the thin films were measured with a deionized water droplet of 5 µL. The contact angles were determined by averaging values measured at six different points on each sample surface usingGBX digidrop goniometer. For ink purpose, ink pen, injector and capillary were used to write on different materials (color paper, chart paper and glass).

Materials:

The acyl hydrazides[1] and 10-hexadecyl-10*H*-phenothiazine-3-carbaldehyde[2] have been synthesized according to the literature procedure. All the starting materials were obtained from Aldrich or s.d. fine-chem. Pvt. Ltd. India. The used organic solvents were dried according to the standard procedures.

Experimental procedure for the synthesis of compound D1

A solution of 10-hexadecyl-10*H*-phenothiazine-3-carbaldehyde **1** (0.5 g, 0.0011 mole) in methanol was added drop wise to a $CHCl_3$ solution of compound **2a** (0.5 g, 0.0011 mole). The mixture was refluxed for about 12 hours. The resulting yellow precipitate was washed with methanol and filtered off by suction and dried under vacuum to yield the compound **3** (94 %). yellow solid; **m.p.**= 132-134 ^{0}C; **IR (KBr)**: υ3438, 2920, 1645, 1584, 1118, cm^{-1};**^{1}H NMR (400 MHz, DMSO-d$_6$) δ**: 0.85-0.88 (m, 3H, -C*H*$_3$), 1.22-1.25 (m, 24H, -C*H*$_2$), 1.39-1.41 (m, 2H,-C*H*$_2$), 1.70-1.73 (m, 2H, -C*H*$_2$), 3.93 (t, 2H, *J* = 6.4 Hz, -NC*H*$_2$), 5.06 (m, 2H, -OC*H*$_2$), 5.24 (m, 4H, -OC*H*$_2$), 7.00 (t, 1H, *J* = 7.4 Hz, Ar*H*), 7.06-7.12 (m, 2H, Ar*H*), 7.19 (d, 1H, *J* = 7.36 Hz, Ar*H*), 7.25 (t, 1H, *J* = 7.8 Hz, Ar*H*), 7.31-7.32 (m, 3H, Ar*H*), 7.39-7.43 (m, 6H, Ar*H*), 7.45-7.47 (m, 4H, Ar*H*), 7.52-7.54 (m, 5H, Ar*H*), 7.58 (d, 1H, *J* = 8.7 Hz, Ar*H*), 8.39 (s, 1H, C*H*=N), 11.7 (s,1H, CON*H*); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ:**13.91, 22.06, 25.92, 26.04, 28.22, 28.68, 28.76, 28.84, 28.92, 28.98, 31.26, 46.57, 70.46, 74.26, 106.86, 115.79, 116.06, 122.83, 122.87, 123.89, 125.06, 126.93, 127.14, 127.63, 127.65, 127.68, 127.71, 127.85, 127.93, 128.04, 128.14, 128.42, 128.59, 128.63, 136.75, 137.38, 140.05, 143.88, 146.25, 146.69, 152.05, 162.22; **MS (ES+)**: *m/z* Calcd for $C_{57}H_{65}N_3O_4S$: 888.21. Found: 910 [M+Na]$^+$; **EA (%)**calcd for $C_{57}H_{65}N_3O_4S$: C, 77.08; H, 7.38; N, 4.73. Found: C, 77.13; H, 7.43; N, 4.78.



1

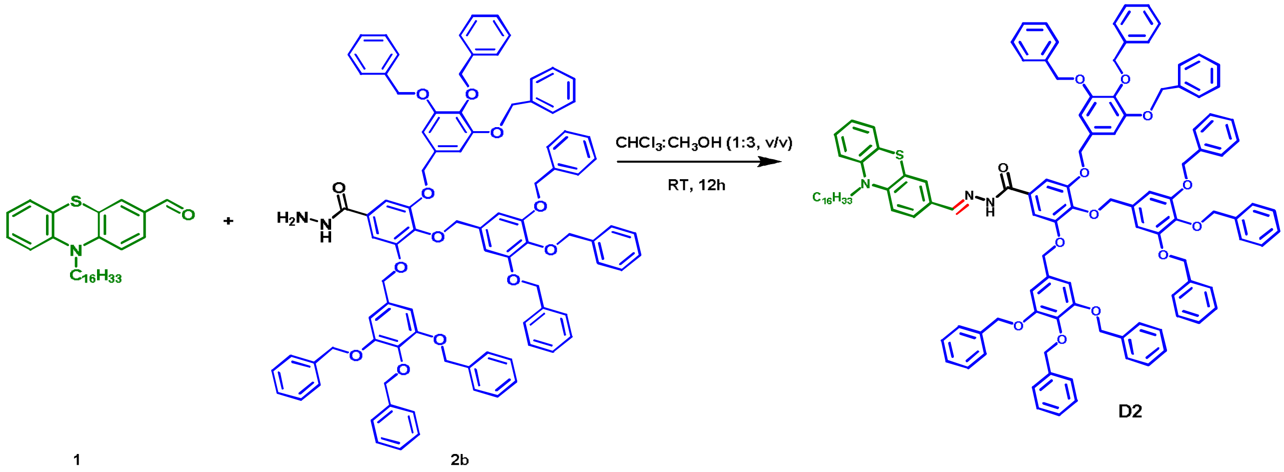
2a

D1

Scheme S1. Synthesis of compound **D1**

Experimental procedure for the synthesis of compound D2

A solution of 10-hexadecyl-10*H*-phenothiazine-3-carbaldehyde **1** (0.5 g, 0.0011 mole) in methanol was added drop wise to a $CHCl_3$ solution of compound **2b** (1.56 g, 0.0011 mole). The mixture was refluxed for 12 hours. The resulting precipitate was washed with methanol and filtered off by suction and dried under vacuum to yield the compound **4** (92 %); yellow solid; **m.p**.= 150-152 ^{0}C; **IR (KBr)**: ʋ3438, 2926, 1642, 1583, 1114 cm^{-1}; **^{1}H NMR (500 MHz, DMSO-d$_6$) δ**: 0.86 (t, 3H, *J* = 7.1 Hz, -C*H*$_3$), 1.09 (t, 1H, *J* =7.0 Hz, -C*H*$_2$), 1.22-1.25 (m, 22H, -C*H*$_2$), 1.41-1.42 (m, 2H, -C*H*$_2$), 1.73 (t, 2H, *J* =6.45 Hz, -C*H*$_2$), 2.57 (m, 1H, -C*H*$_2$), 3.94 (t, 2H, *J* =6.5 Hz, -NC*H*$_2$), 4.74 (m, 2H, -OC*H*$_2$), 4.80 (m, 4H, -OC*H*$_2$), 4.86 (m, 4H, -OC*H*$_2$), 5.03 (m, 8H, -OC*H*$_2$), 5.12 (m, 2H, -OC*H*$_2$), 5.22 (m, 4H, -OC*H*$_2$), 6.90 (m, 2H, Ar*H*), 6.96-7.03 (m, 5H, Ar*H*), 7.08-7.12 (m, 2H, Ar*H*), 7.18-7.20 (m, 1H, Ar*H*), 7.21-7.22 (m, 1H, Ar*H*), 7.22-7.23 (m, 2H, Ar*H*), 7.24-7.25 (m, 4H, Ar*H*), 7.26- 7.27 (m, 4H, Ar*H*), 7.27-7.28 (m, 2H, Ar*H*), 7.29 (m, 11H, Ar*H*), 7.31-7.32 (m, 7H, Ar*H*), 7.33-7.34 (m, 7H, Ar*H*), 7.38-7.39 (m, 8H, Ar*H*), 7.50-7.52 (m, 3H, Ar*H*), 7.57 (d, 1H, *J* =8.35 Hz, Ar*H*), 8.40 (s, 1H, C*H*=N), 11.73 (s, 1H, CON*H*); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ:**14.42, 22.56, 26.39, 26.53, 28.91, 29.17, 29.24, 29.33, 29.40, 29.47, 31.75, 40.88, 47.06, 70.40, 70.60, 71.23, 74.65, 74.72, 106.81, 107.07, 123.37, 127.91, 128.0, 128.05, 128.07, 128.15, 128.21, 128.26, 128.31, 128.41, 128.45, 128.69, 128.78, 132.99, 137.15, 137.23, 137.31, 138.13, 144.41, 152.54, 152.76, 162.64; **MS (ES+):** *m/z*Calcd for $C_{120}H_{119}N_3O_{13}S$: 1841.85. Found: 1864 [M+Na] $^+$;C, 78.19; H, 6.51; N, 2.28. Found: C, 78.13; H, 6.58; N, 2.34.



Scheme S2. Synthesisof compound **D2**

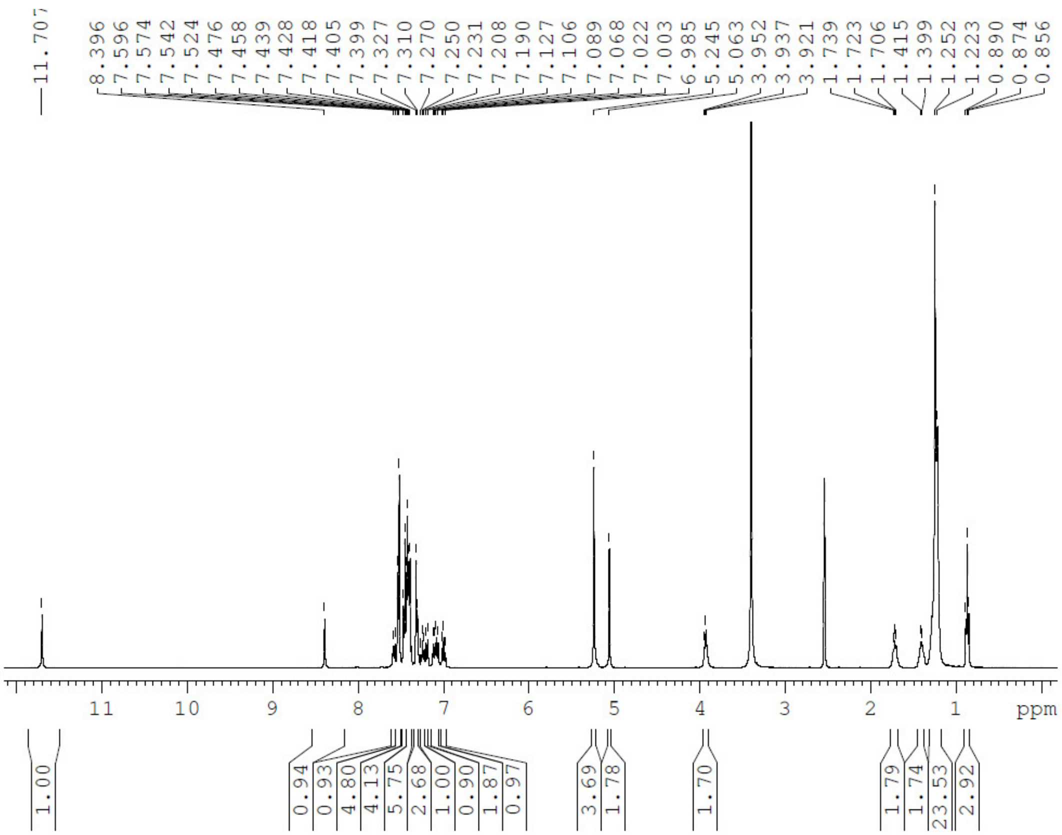


Figure S1. ^{1}H NMR spectrum of compound **D1**in DMSO-d_6

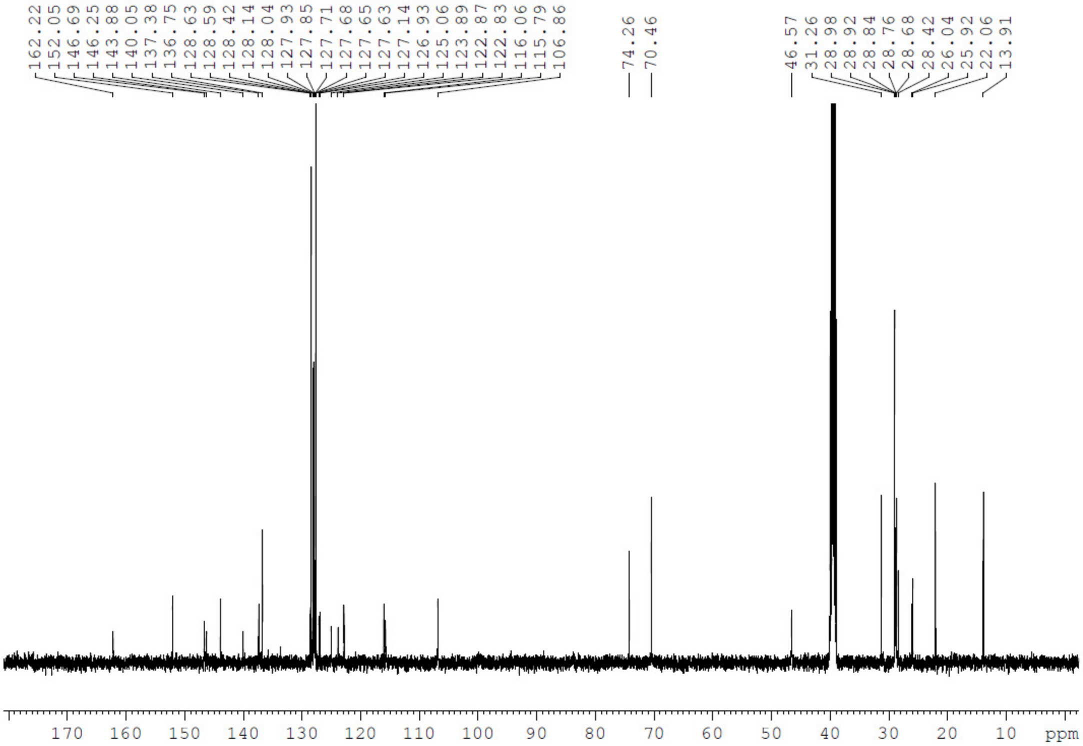


Figure S2. ^{13}C NMR spectrum of **D1**in DMSO-d_6

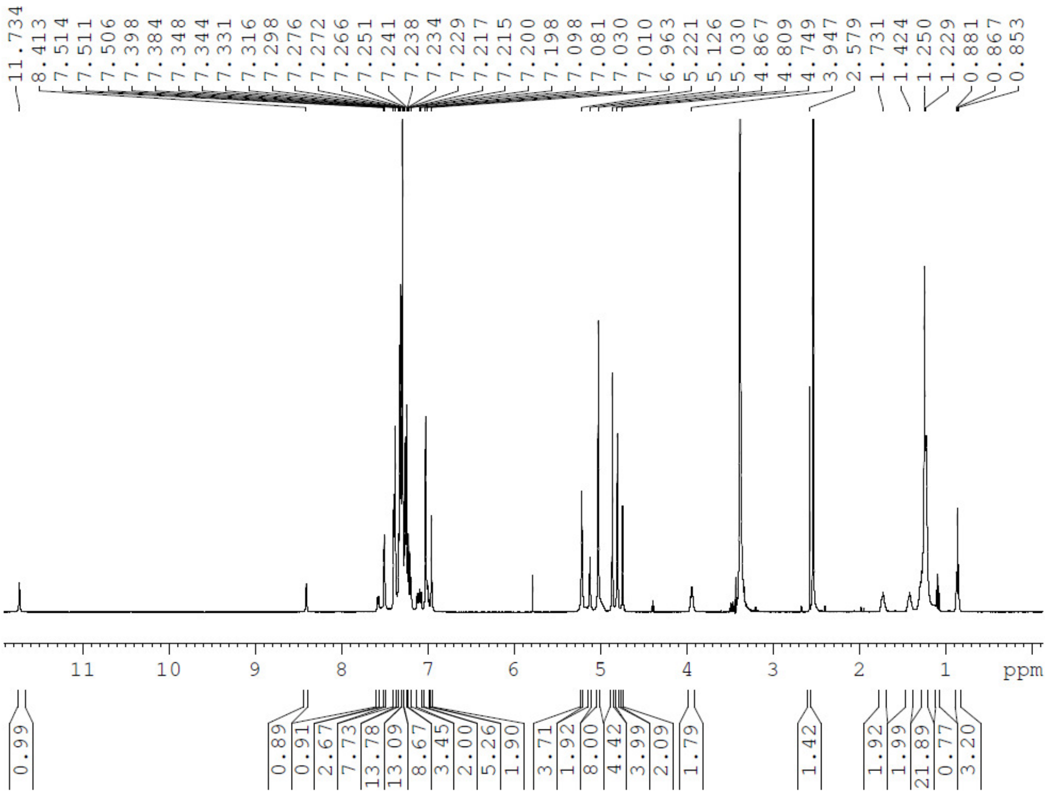


Figure S3. ^{1}H NMR spectrum of compound **D2**in DMSO-d_6

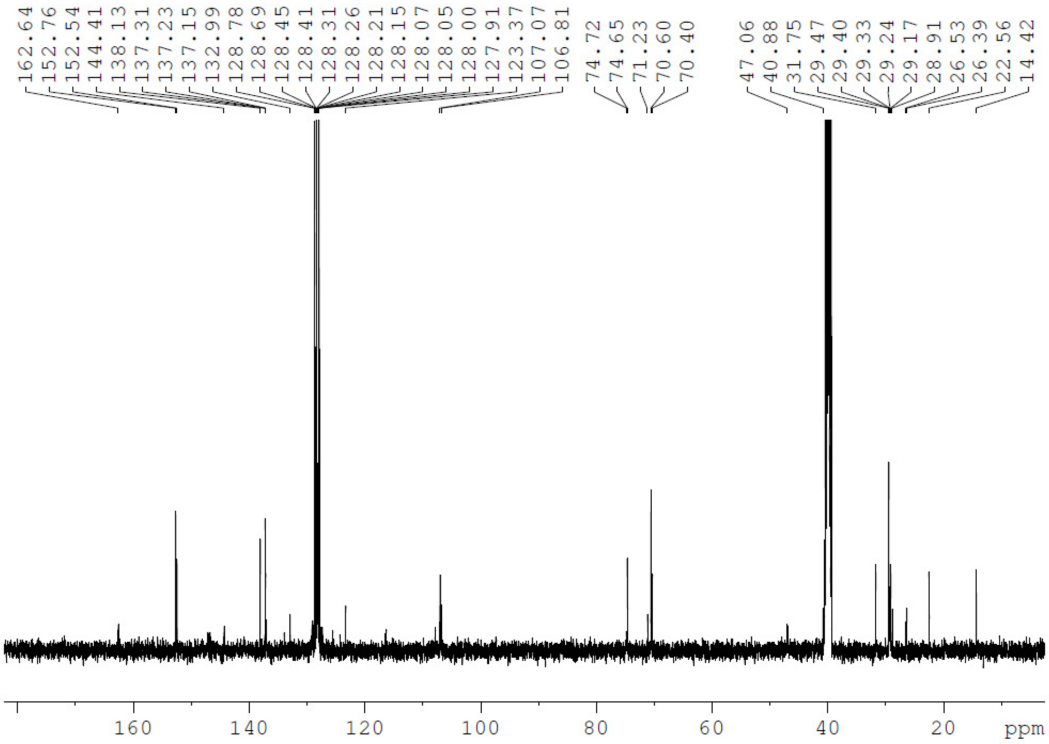


Figure S4. ^{13}C NMR spectrum of compound **D2**in DMSO-d_6

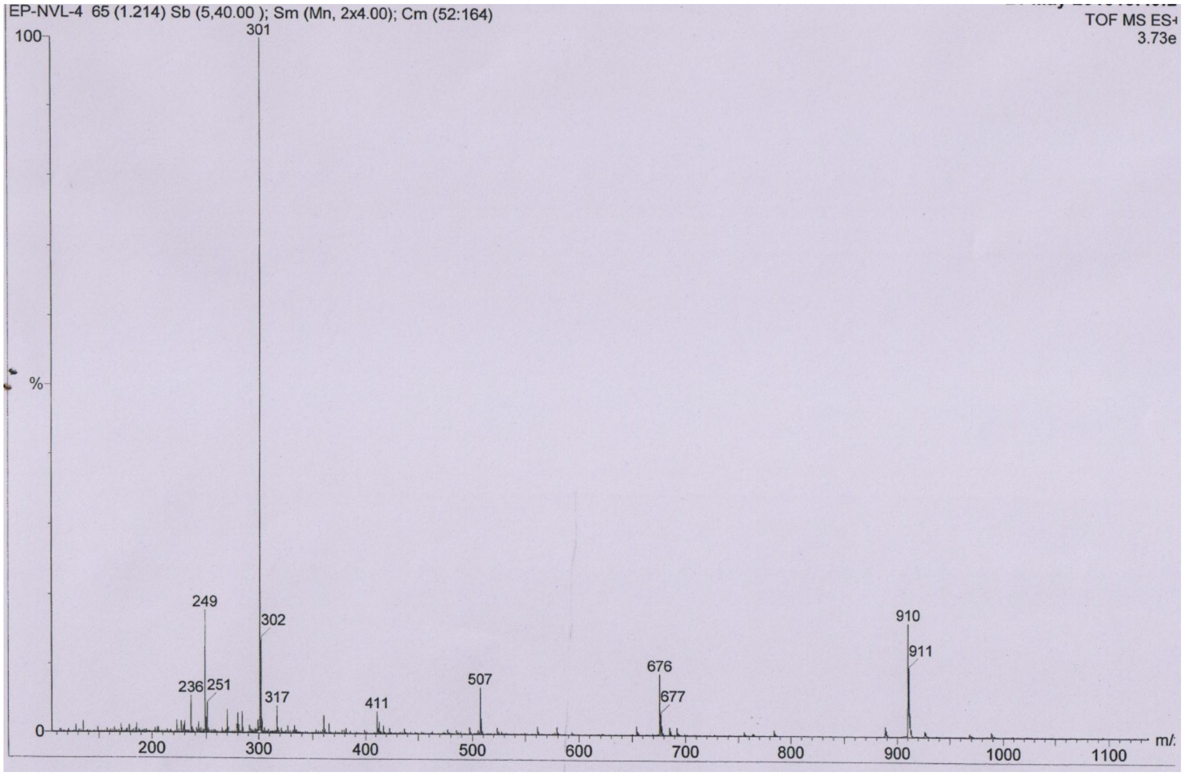


Figure S5. ESI Mass spectrum of **D1**

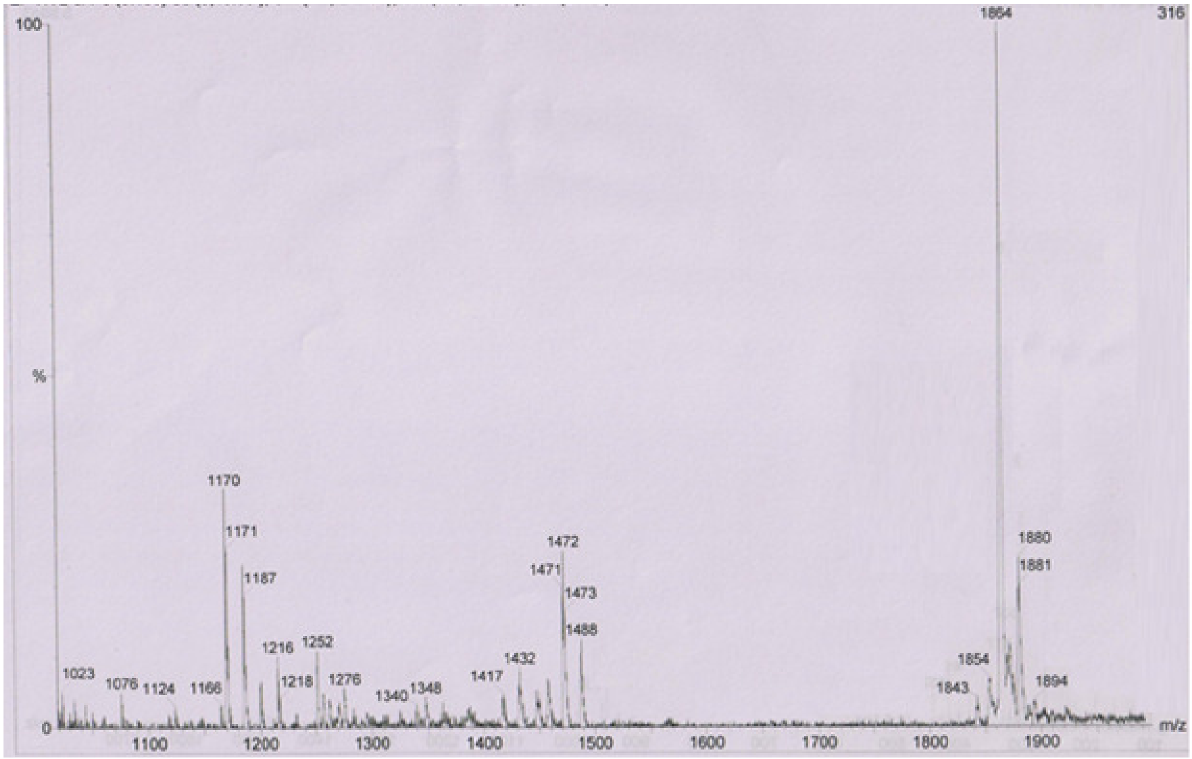


Figure S6. ESI Mass spectrum of **D2**

Critical gel concentration: The gelator was found to be initially homogeneous in these solvents after warming the solution. After 45 seconds, the solution becomes gel at room temperature.

Table S1: Gelation properties and critical gel concentrations (CGCs) of **D1** and **D2** in various organic solvents and mixture of solvents at 35^{o}C.G=Gelation, S= Solution, P=Precipitation, P.G= Partial gelation, I- insoluble.

Solvent	**D1**(mg/ml)	**Solvent**	**D2**(mg/ml)
Hexane	G (9)	Hexane	G (7)
Diesel	G (9)	Diesel	G (7)
Petrol	G (10)	Petrol	G (8)
Silicone oil	G (11)	Silicone oil	G (8)
Pump oil	G (11)	Pump oil	G (9)
Sunflower oil	G (9)	Sunflower oil	G (7)
Coconut oil	G (13)	Coconut oil	G (10)
water	I	water	I
Chloroform	S	Chloroform	S
THF	S	THF	S
DCM	S	DCM	S
$CHCl_3$:Hexane (1:1)	G (10)	$CHCl_3$:Hexane (1:1)	G (8)
THF:Hexane (1:1)	G (10)	THF:Hexane (1:1)	G (8)
DCM:Hexane (1:1)	G (11)	DCM:Hexane (1:1)	G (8)
Acetone:Hexane	G (10)	Acetone:Hexane	G (8)
Benzene	G (13)	Benzene	G (11)
Toluene	G (11)	Toluene	G (9)
Xylene	G (10)	Xylene	G (8)

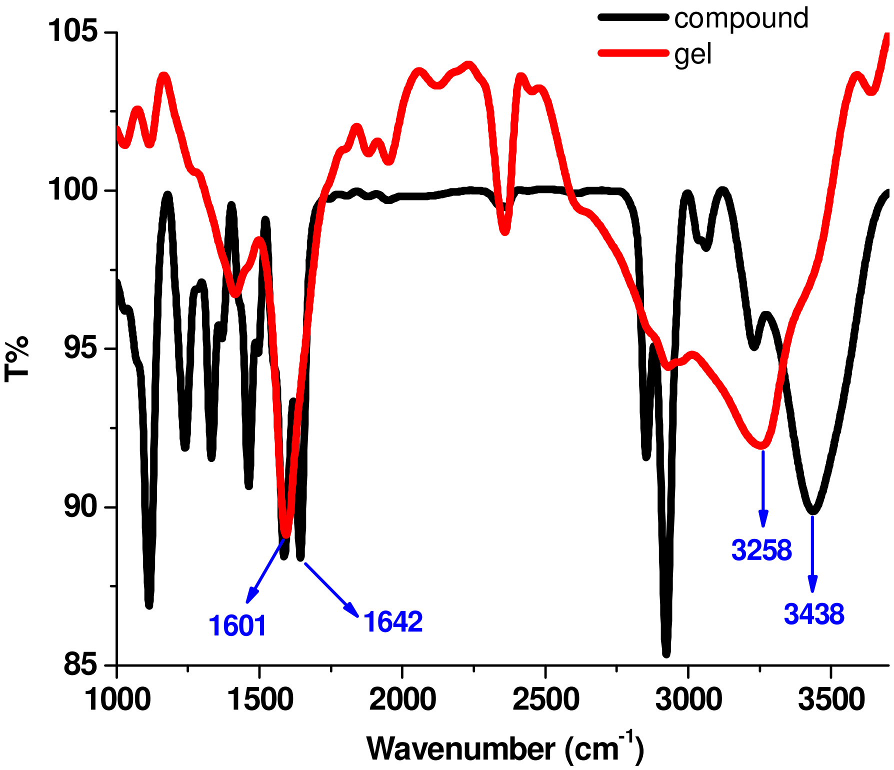
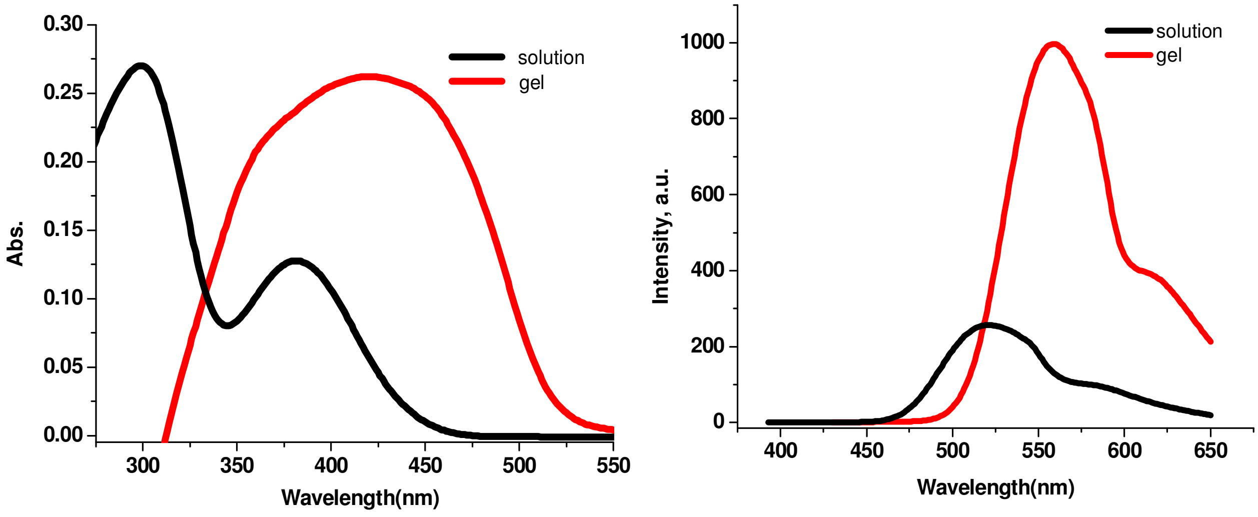
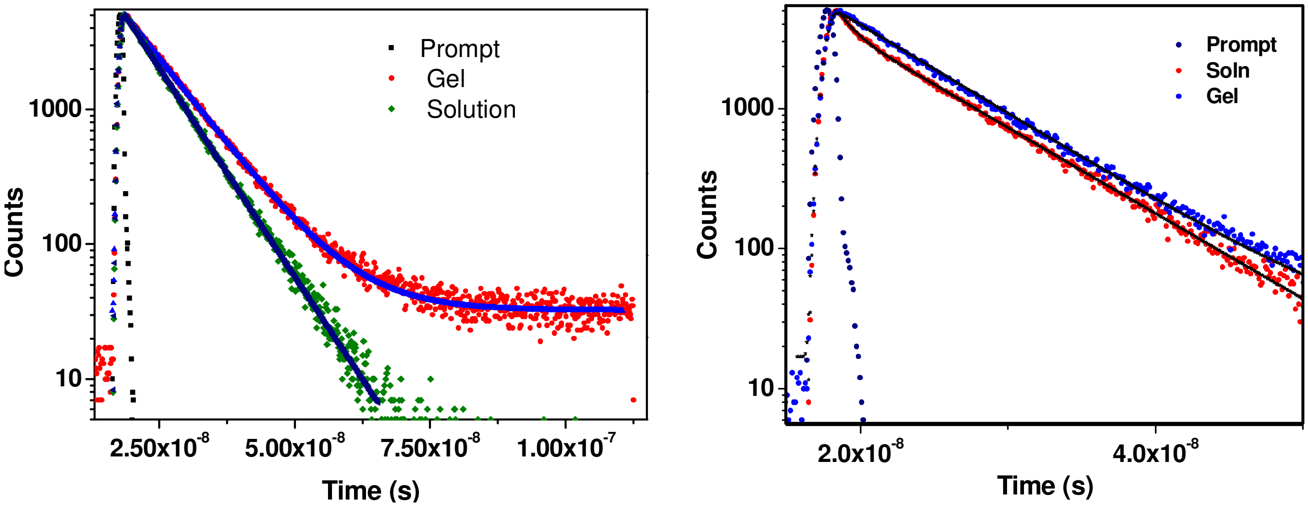


Figure S7. FT-IR spectra of the xerogel from **D2** (8 mg/mL) in $CHCl_3$/Hexane (1/1, v/v) and compound **D2** before gelation



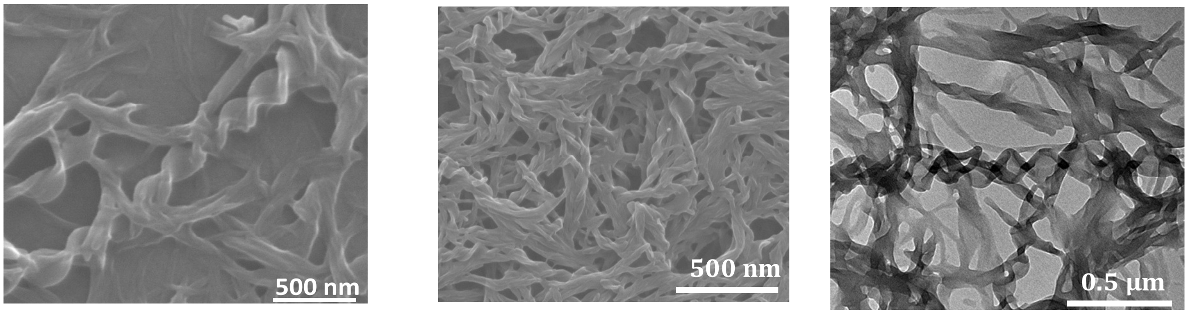
a **b**

Figure S8. (a) UV-visible spectra of compound **D1** in solution and gel phase, and (b) Emission spectra of compound **D1** in solution (λ_{exc}= 385 nm) and gel phase (λ_{exc} = 420 nm).



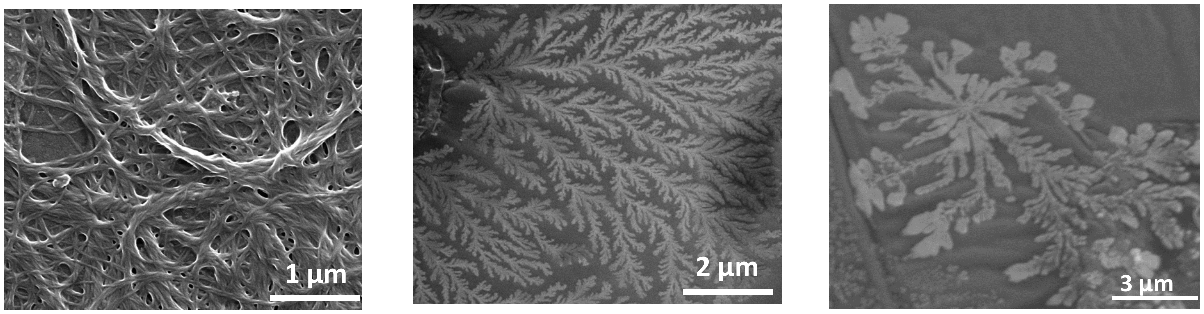
a b

Figure S9. (a) Life time plot of compound **D1** in solution and gel state and (b) Life time plot of compound **D2** in solution and gel state.



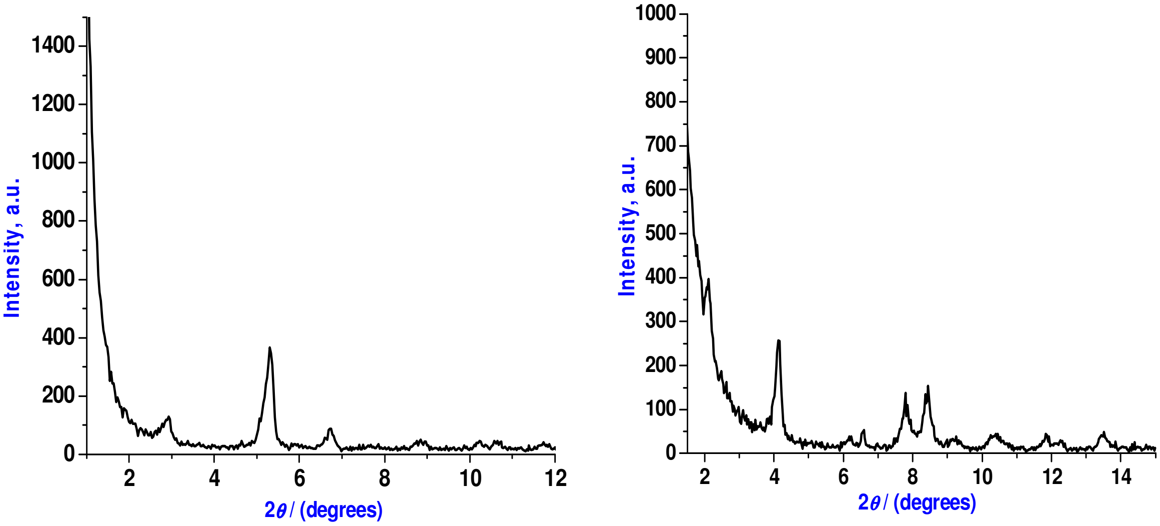
a b c

Figure S10. SEM images of xerogels from (a) **D2** in hexane, (b) **D1** and (c) TEM image of xerogel from **D1** in hexane



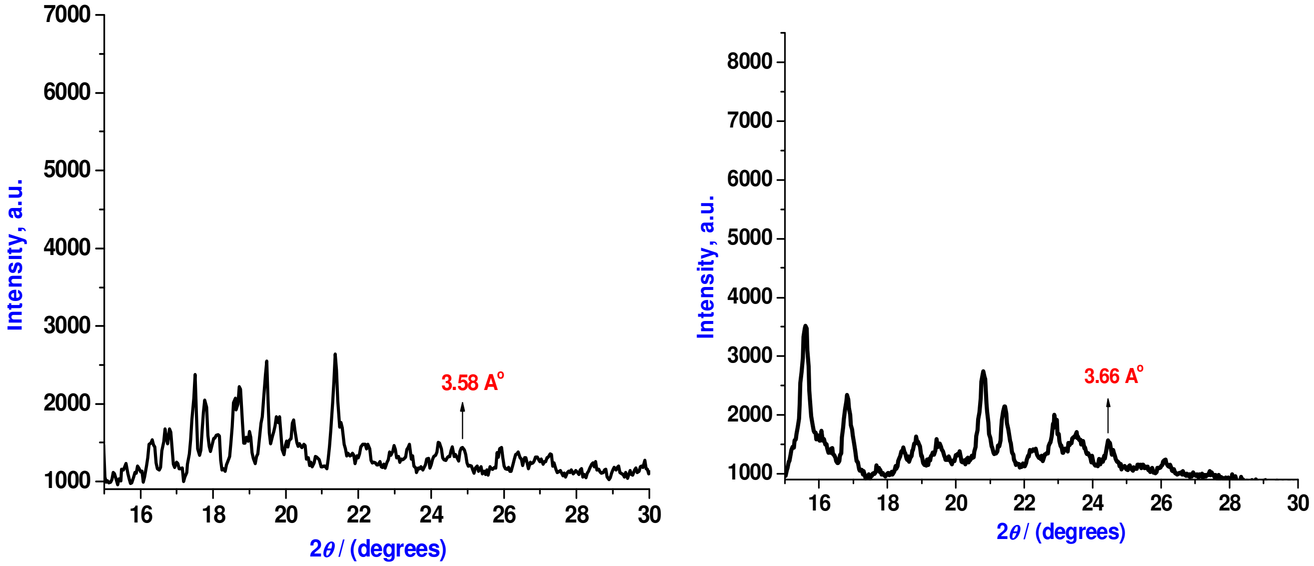
a **b** **c**

Figure S11. SEM images of xerogels from (a) **D2**in $CHCl_3$/Hexane (b) **D2** in THF/Hexane and (c) **D1** in THF/Hexane



a **b**

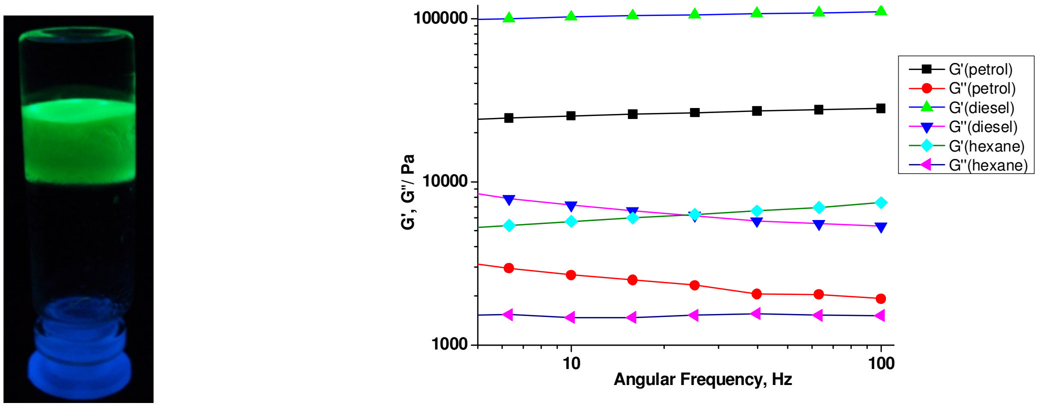
Figure S12. Powder-XRD patterns of gels from (a) **D1** and (b) **D2** in hexane



a

b

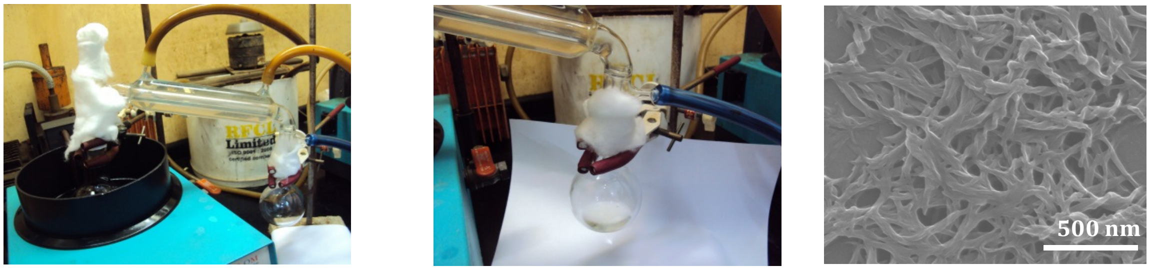
Figure S13. Wide angle powder-XRD patterns of gels from (a) **D1** and (b) **D2** in hexane



a

b

Figure S14. (a) Phase selective gelation from compound **D1** in 1:1 mixtureof diesel and water and (b) Rheology of gels from compound **D1**in petrol, hexane and diesel

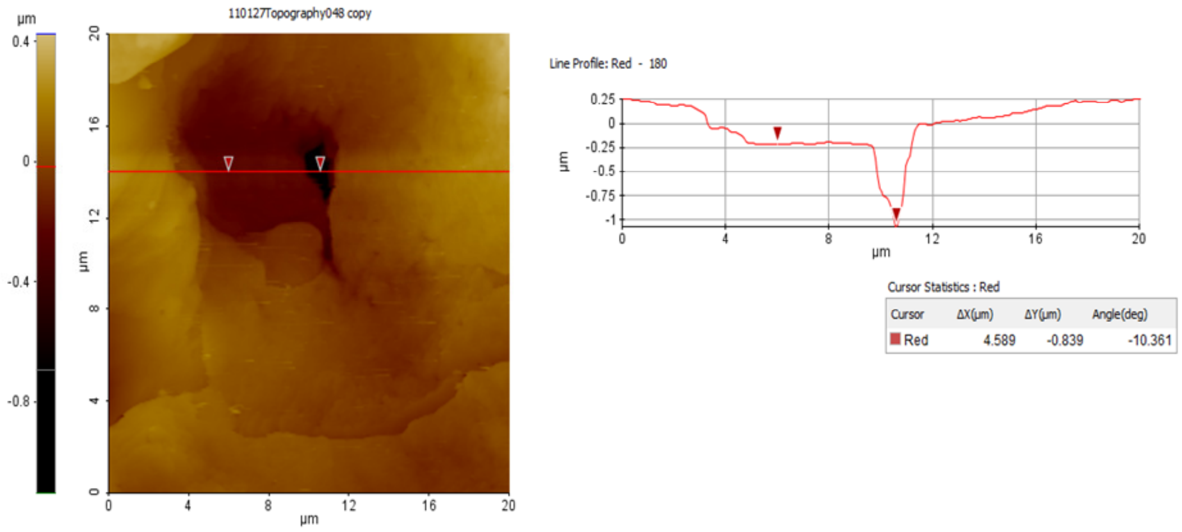


a **b** **c**

Figure S15. (a) Vacuum distillation of the oil gel from compound **D2**, (b) Recovered diesel from the gel and (c) SEM image of the gel from recovered compound **D2** from 5th cycle.

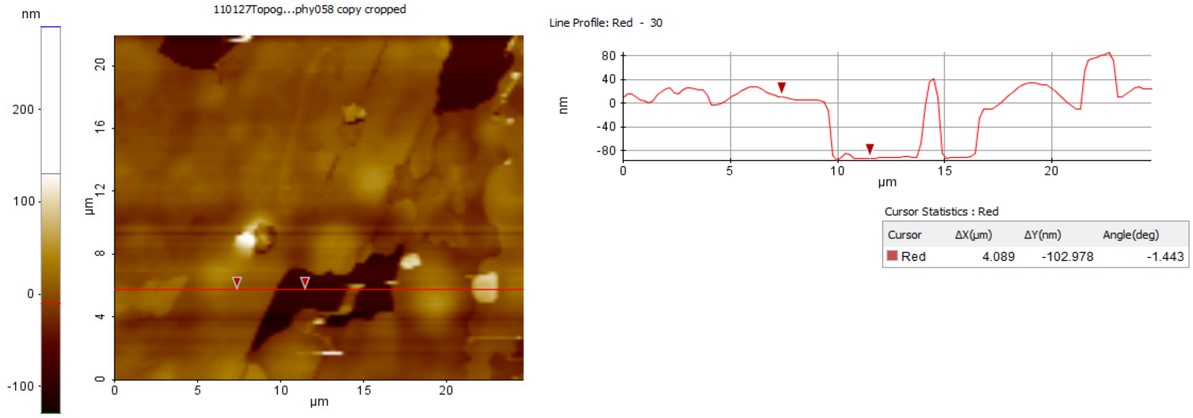
a **b**

Figure S16.(a) Selective gel kind of thin layer formation from compound **D1** in diesel layer floating on sea water under UV illumination, (b) Photograph of transparent thin film of oil gel



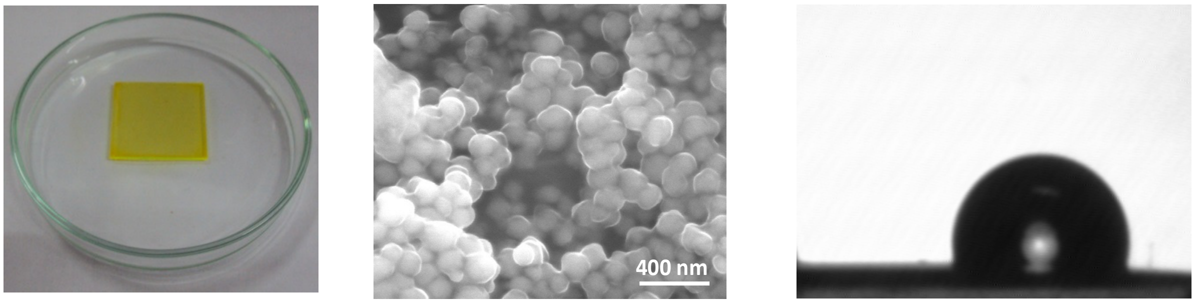
Cursor	ΔX(µm)	ΔY(µm)	Angle(deg)
🟥 Red	4.589	-0.839	-10.361

Figure S17. AFM image of the thin film from compound **D1**



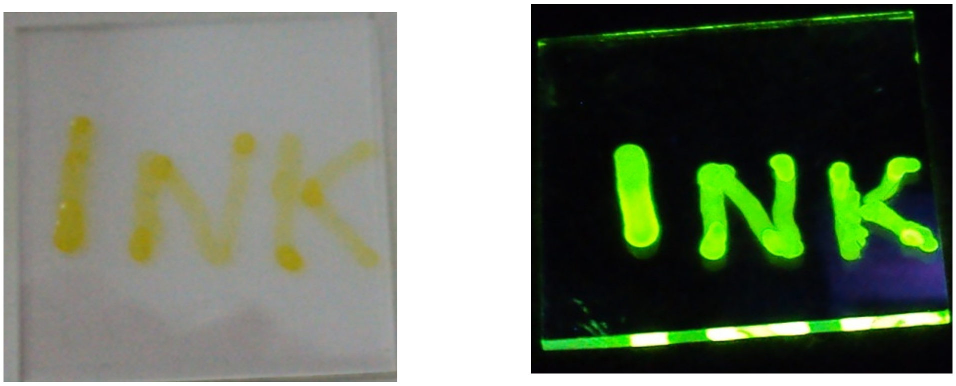
Cursor	ΔX(µm)	ΔY(nm)	Angle(deg)
🟥 Red	4.089	-102.978	-1.443

Figure S18. AFM image of the thin film from compound **D2**



a **b** **c**

Figure S19. (a) Formation of thin film on glass substrate from compound **D1**inTHF/hexane, (b) SEM image of thin film and (c) Contact angle (97.4 ± 2^0) photograph of thin film with deionized water.



a **b**

Figure S20. The word INK (from compound **D1**) written by an injector on glass substrate (a) under visible light Illumination, (b) under UV light illumination

References

[1] (a) P. Rajamalli, E. Prasad, *New J. Chem*. **2011**, *35*, 1541; (b) P. Rajamalli, E. Prasad,*Org. Lett*. **2011**, *13*, 3714; (c) P. Rajamalli, E. Prasad, *Soft Matter* **2012**, *8*, 8896; (d) P.Rajamalli, E. Prasad, *Langmuir* **2013**, *29*, 1609; (e) P. Rajamalli, S. Atta, S. Maity, E.Prasad, *Chem. Commun*. **2013**, *49*, 1744; (f) P. Rajamalli, P.S. Sheet, E. Prasad, *Chem.Commun.***2013**, *49*, 6758; (g) P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson,G. M. Whitman, *J. Am. Chem. Soc.* **1957**, *79*, 3416.

[2] J. Lee, J. Kwak, K.C.Ko,J. H. Park, J.H.Ko, N.Park,E. Kim, D. H.Ryu, T.K.Ahn, J. Y. Lee, S. U. Son, *Chem. Commun.***2012**, *48*, 11431.