Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Renewable resource-derived thixotropic self-assembled supramolecular gel: Magnetic stimuli responsive and real-time self-healing behaviour

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Experimental Section

Materials and Methods

All chemicals used for the synthesis of SG and MG were purchased from Sigma Aldrich, Merck, Alfa aesar and Avra chemicals and were used without further purification. All commercial solvents were dried and freshly distilled before use. We have used LR grade solvents for the compounds purification and AR grade solvents for gelation studies. The progress of the reaction was monitored by thin-layer chromatography (TLC) on pre-coated silica gel plates obtained from Merck. Column chromatography was performed on silica gel (100-200 meshes) purchased from Avra chemicals, India.

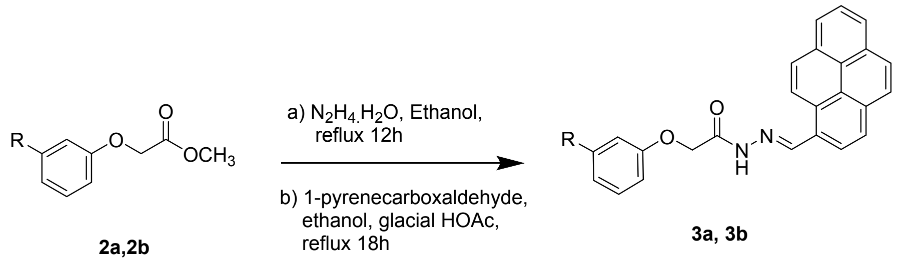
Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 MHz NMR spectrometer at 298 K in either $CDCl_3$ or $CDCl_3$ with few drops of DMSO-d_6. The ^{1}H and ^{13}C NMR chemical shifts were reported relative to TMS. Coupling constant (J) are denoted in Hz and chemical shifts (δ) in parts per million (ppm). Proton multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m). FT-IR spectra was recorded using Perkin Elmer spectrophotometer.

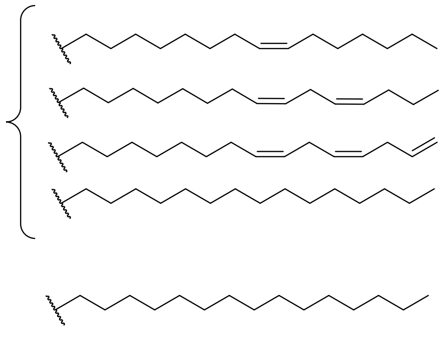
Synthesis

General procedure for the synthesis of 2-(3-alkylphenoxy)-N'-(pyren-1-ylmethylene)acetohydrazide, 3a and 3b

Methyl 2-(3-alkyl phenoxy)acetate, **2a** or **2b** (1 mmol), hydrazine hydrate (2 mmol) was refluxed in ethanol for about 12h. After completion of the reaction as identified using TLC, 1-pyrenecarboxaldehyde (1 mmol) and 1-2 drops of glacial acetic acid was added to the resultant mixture and further refluxed for about 8h. After completion of the reaction as identified using TLC, reaction mixture was then cooled to room temperature and yellow colored precipitated thus formed was filtered and dried under vacuum.



2a, 3a R=



2b,3b R=

Compound 3a: Yellow solid (75%);^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, J = 6.6 Hz, 3H), 1.24-1.32 (m, 18H), 1.58-1.60 (m, 4H), 2.63 (t, J = 7.8 Hz, 2H), 4.76 (s, 2H), 5.31-5.34 (m, 2H), 6.85-6.93 (m, 2H), 7.24-7.29 (m, 2H), 8.06-8.25 (m, 7H), 8.68-8.73 (m, 2H), 9.26 (s, 1H), 9.73 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.55, 157.12, 147.84, 145.35, 132.99, 131.21, 130.49, 129.67, 128.88, 128.70, 127.38, 126.19, 126.07, 125.79, 125.66, 125.01, 124.51, 122.71, 122.09, 115.00, 111.78, 67.38, 36.02, 31.93, 31.39, 29.69, 29.54, 29.37, 22.70, 14.14.

Compound 3b: Pale yellow solid (87%);^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.80 (t, J = 6.9 Hz, 3H), 1.14-1.35 (m, 29H), 2.53-2.58 (m, 2H), 4.69 (s, 2H), 6.77-6.86 (m, 2H), 7.17-7.24 (m, 2H), 7.94-8.19 (m, 7H), 8.54-8.66 (m, 2H), 9.17 (s, 1H), 9.67 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.97, 163.96, 146.98, 143.57, 142.47, 131.33, 129.44, 128.47, 128.15, 128.10, 127.62, 127.51, 127.41, 126.39, 125.63, 125.45, 125.24, 124.94, 124.64, 124.23, 123.99, 123.89, 121.32, 120.48, 114.20, 110.95, 66.57, 64.55, 39.60, 39.32, 39.05, 38.76, 38.49, 34.95, 30.84, 30.36, 30.30, 28.60, 28.46, 28.28, 21.61, 13.13.

Gelation Studies and gel-to-sol melting temperature, T_g

A known amount of gelator was mixed with appropriate amount of solvent in a sealed vial, and the system was heated to 80-100 ^{o}C until the solid get dissolved. By this procedure the solvent boiling point becomes higher than that under standard atmospheric pressure. The resulting solution was slowly allowed to cool to room temperature, and gelation was visually observed by inverting the test tube. A gel sample thus obtained which exhibited no gravitational flow in inverted tube is denoted as "G". The gelation studies were systematically studied in different organic solvents such as dodecanol, decanol, octanol, ethanol and toluene etc. and also with oils such as hazelnut oil, sesame oil, jojoba oil, olive oil, heavy paraffin, light paraffin, etc. Gel melting temperature was determined by flow of gel by test tube inversion method. Above the gelation temperature, the gel phase becomes solution phase, but could be returned to their original gel state upon cooling. Gel was prepared in a 5 mL glass vial as described above, the vial was immersed in the oil-bath 'upside down' and the vial was slowly heated. The temperature at which the gel melted down to solution was recorded as T_g.

Morphological analysis

Morphology of self-assembled gels, SG and MG were identified using a JEOL JEM 2100 F FETEM instrument. Small quantity of self-assembled gels, SG and MG was dispersed in 1 mL of acetone and drop casted the resultant solution on HRTEM grid.

Fluorescence measurements

Absorption spectra was measured with an Evolution 220 UV-vis spectrophotometer. The spectra was recorded in the continuous mode between 200 and 700 nm, with a wavelength increment of 1 nm and a bandwidth of 1 nm. Emission behavior of SG and MG were studied using JASCO spectrofluorometer FP-8200 by fixing the excitation value as 350 nm. The selection of excitation wavelength depends up on the absorbance maximum displayed by SG and MG in paraffin oil. For fluorescence titration experiments, 2 mL of initial volume of solution (1 X 10^{-5} M) was titrated with piecemeal addition of 100 μL of heavy paraffin oil.

Small angle X-ray diffraction studies

A small portion of a gel sample formed by SG and MG was transferred into a sample holder and coated like a thin film. The XRD measurement was performed on XPert-PRO Diffractometer system.

Preparation of MG

A typical procedure for the preparation of MG is as follows: 2 mg of gelator, 3a was dissolved in 2 mL of heavy paraffin, then 2 mg of Fe3O4 nanopower was added followed by sonicated for 5 min. The sealed vial was heated until the compound was dissolved and allowed to cool to room temperature.

Rheological measurements

The mechanical properties of gel were investigated using a stress controlled rheometer (Anton Paar 302 rheometer) equipped with a steel-coated parallel-plate geometry (25 mm diameter). A small amount of gel sample (1 % wt/v) was placed between the two parallel plates with a gap of 1 mm. Firstly, we carried out the amplitude sweep measurement to collect the information about the linear viscoelastic range which is directly proportional to the mechanical strength of the gel sample. Then, the storage modulus, G', and the loss modulus, G'', were monitored as a function of frequency sweep from 0.1 to 300 rad s^{-1}. Self-healing nature of gel was investigated by performing step strain experiments (For SG, 100% and 0.05% strain, and for MG 100% and 0.01% strain were applied alternatively) at 23 ^{o}C.

Macroscopic self-healing studies

Self-healing experiment was carried out using freshly prepared SG and MG. In order to differentiate SG from MG, a trace amount of rhodamine B was added to SG. When these two gels were placed one over the other, an immediate healing action started and this phenomenon was visualized by naked eye. Self-healing of SG-to-SG or SG-to-MG in water was carried out by using freshly prepared SG and MG pieces. When these gel pieces were placed in water, they experience repulsive force from water (hydrophilic/lipophilic character) and self-healing occurs.

Self-healing of SG-to-MG in response to magnetic field: On application of magnetic field of strength 0.556T, the MG aligned themselves uniformly and self-heal themselves.

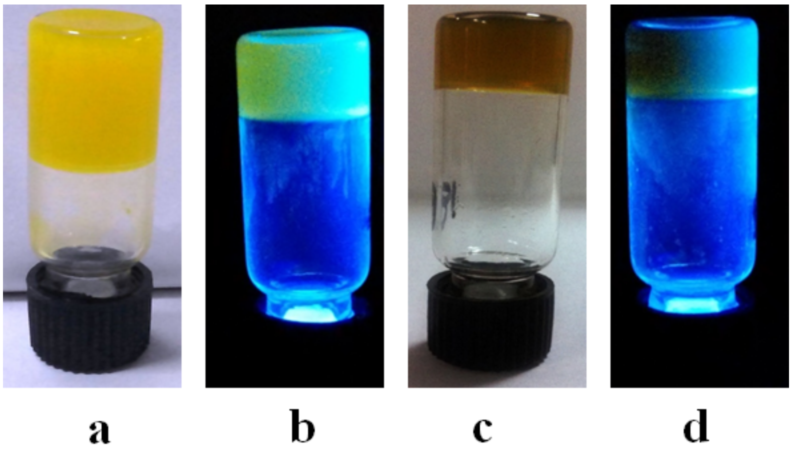


Figure S1. Images of SG and MG gel in day and UV light.(a) SG under day light ; (b) SG under UV light; (c) MG under day light and (d) MG under UV light

Table S1. Vegetable oil/Solvent used for gelation studies

S.No	**Oil/Solvent**	**3a**	**CGC(%)**	**3b**	**CGC(%)**
1	Hazelnut	S	-	P(slow)	-
2	Sesame	S	-	S	-
3	Jojoba	G	0.67	P	-
4	Olive	G	1.00	S	-
5	Soyabean	G	1.00	S	-
6	Linseed	S	-	S	-
7	Light paraffin	G	0.29	G	0.75
8	Heavy paraffin	G	0.18	G	0.75

9	Dodecanol	P	-	P	-
10	Decanol	P	-	P	-
11	Ethanol	P	-	P	-
12	Octanol	P	-	P	-
13	Toluene	PG	-	S	-
14	Acetonitrile	P	-	P	-
15	Acetone	S	-	S	-
16	THF	S	-	S	-
17	Ethyl acetate	P	-	P	-
18	DMF	S	-	S	-
19	DMSO	S	-	S	-
20	DMF+WATER	G	0.8	G	2.5

S – Soluble; I – Insoluble; P – Precipitation; PG – Partial gel formation; G- Gellation

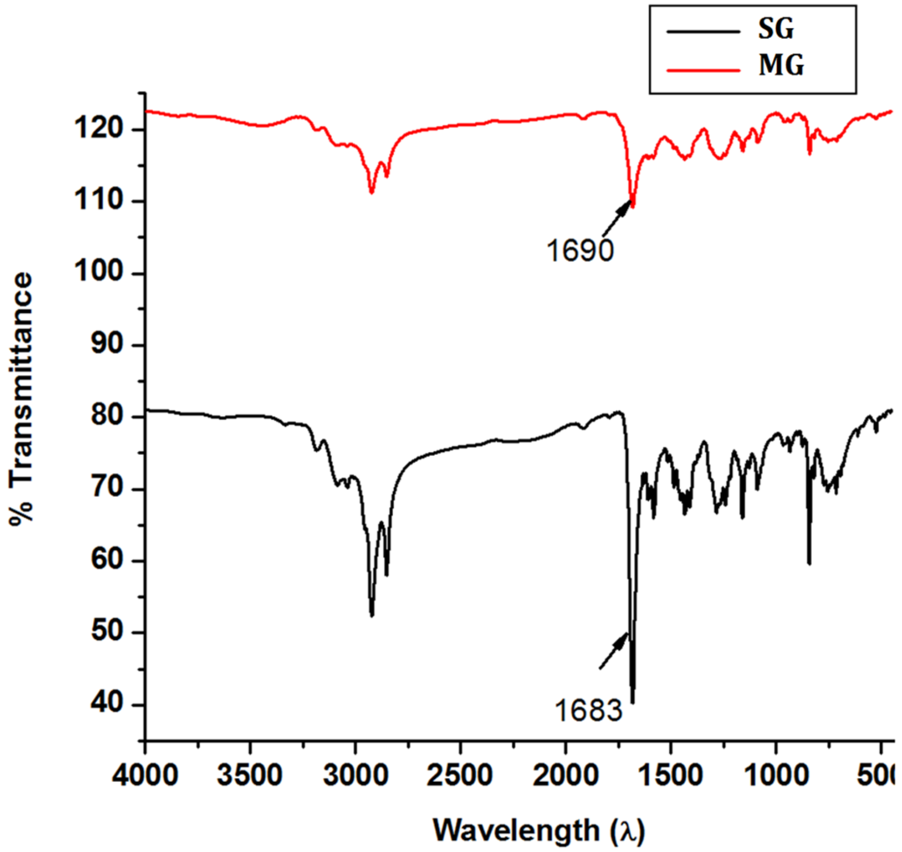


Figure S2. FT-IR spectra of SG and MG.

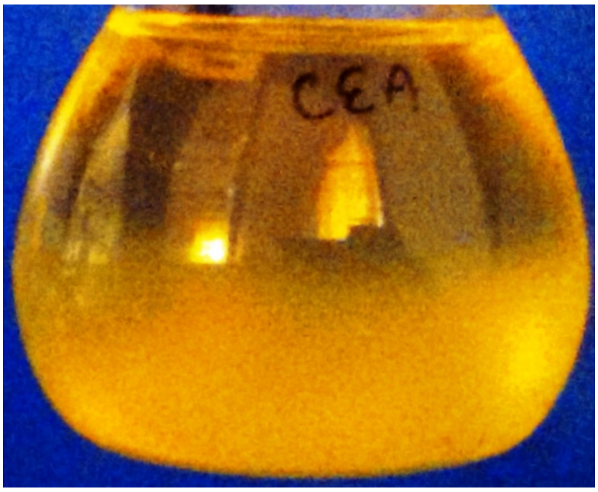


Figure S3. Self-assembly of SG in heavy paraffin oil.

Copies of NMR spectra for 3a and 3b

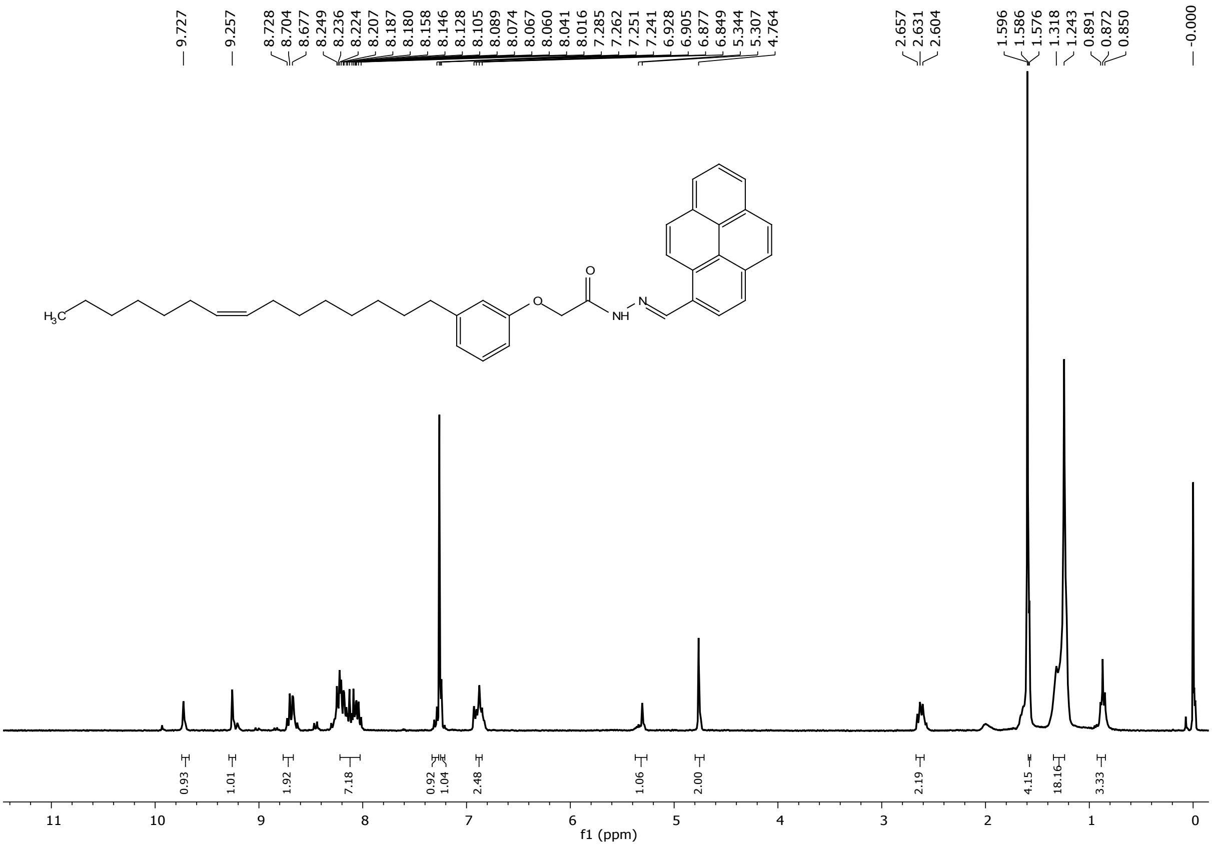


Fig S4: ^{1}H NMR of compound 3a

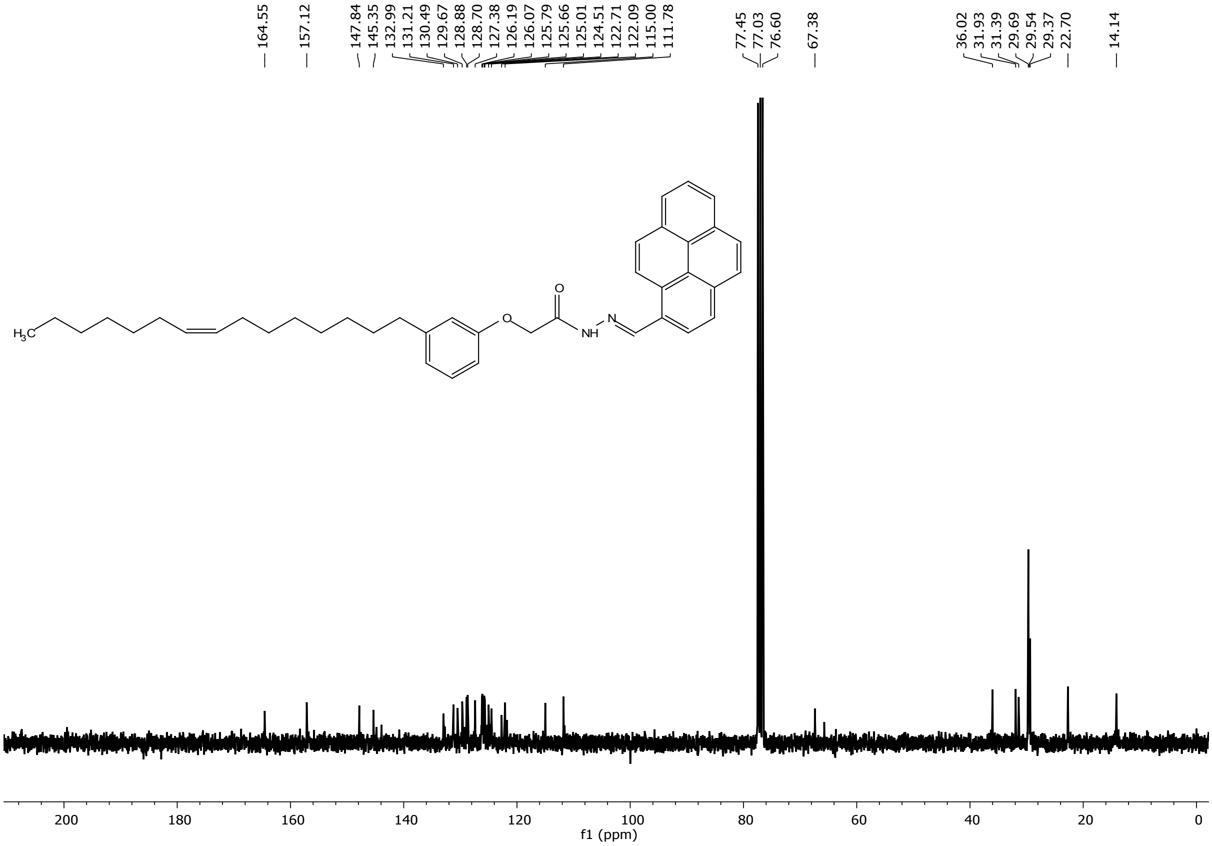


Fig. S5: ^{13}C NMR of compound 3a

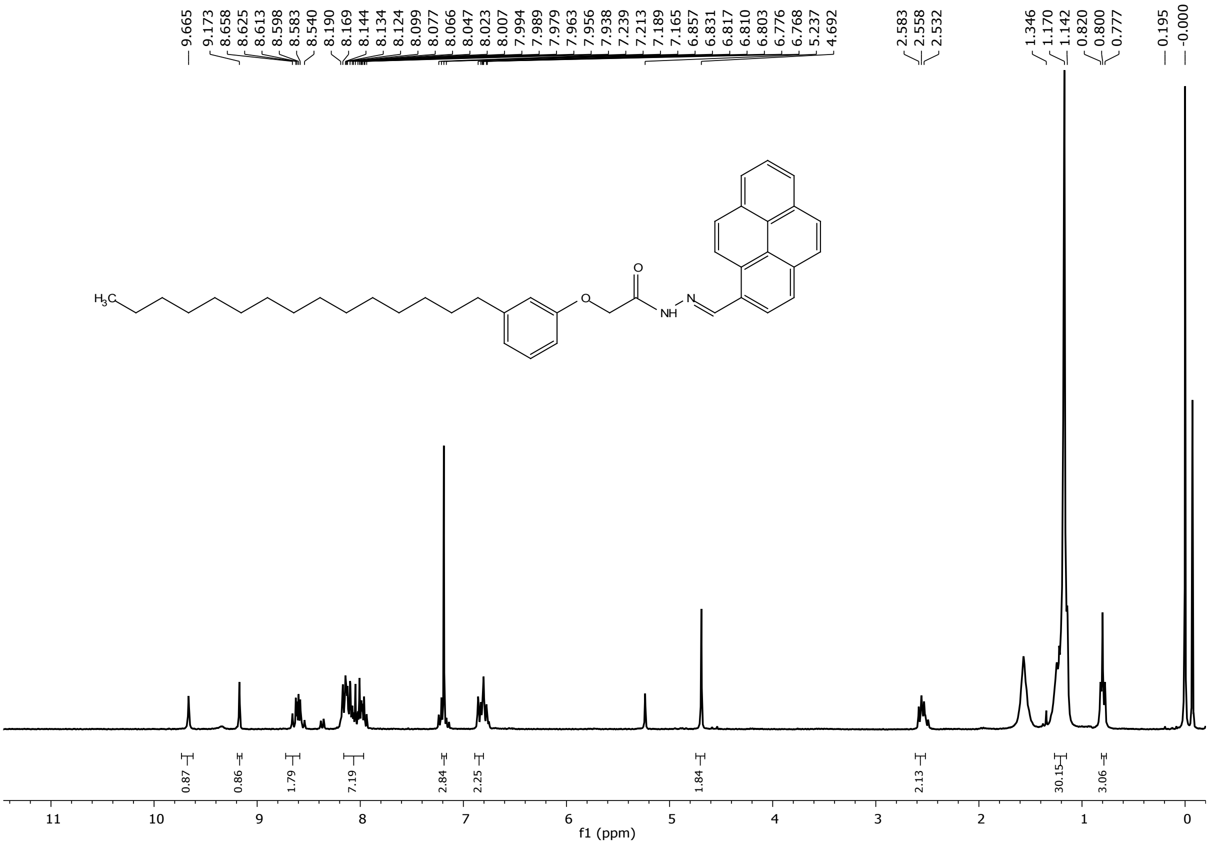


Fig. S6: ^{1}H NMR of compound 3b

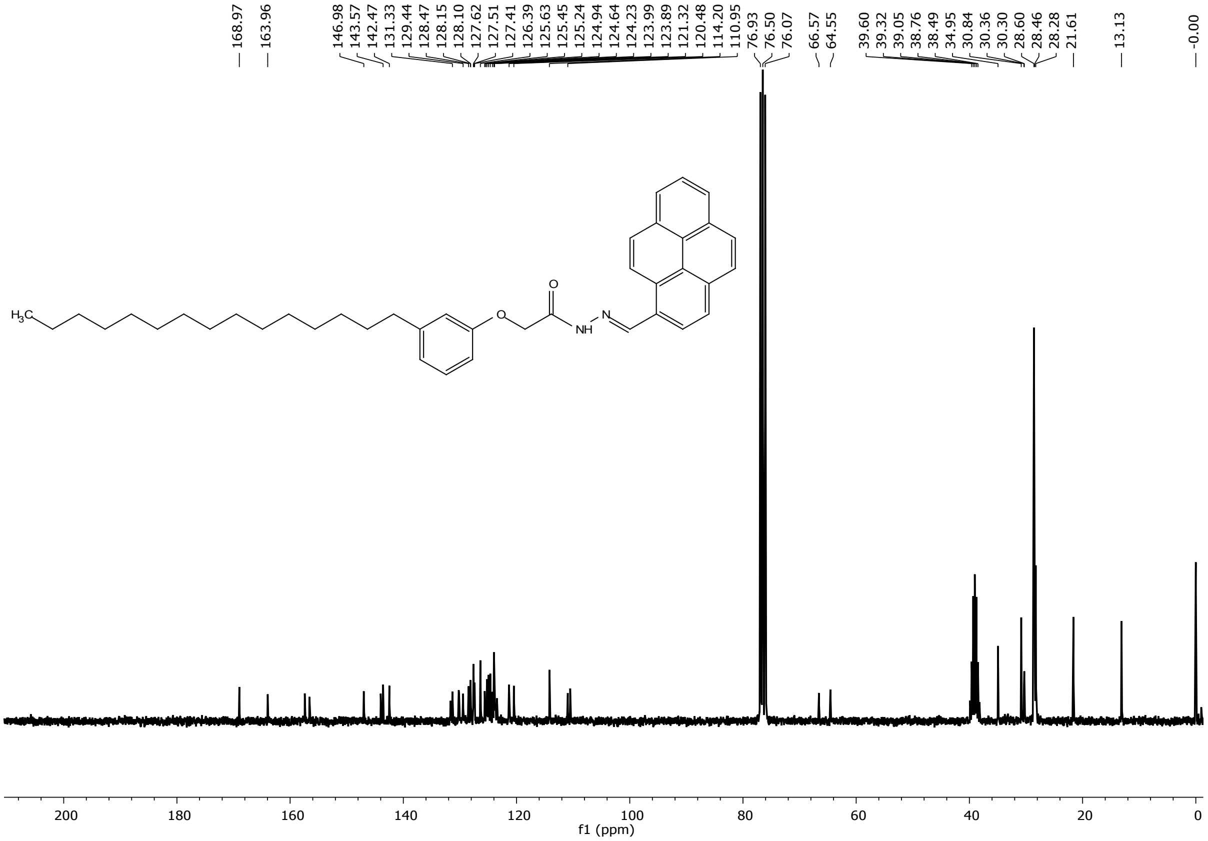


Fig S7: ^{13}C NMR of compound 3b