

An *all-organic steroid-D- π -A* modular design drives ferroelectricity in supramolecular solids and nano-architectures at RT

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Experimental Details:

General: All chemicals were obtained from Sigma Aldrich or Spectrochem India and were used as received. Thin layer chromatography (TLC) was carried out on aluminium plates coated with silica gel mixed with fluorescent indicator having particle size of 25 μm and was sourced from Sigma Aldrich. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer in $\text{DMSO}-d_6$ with TMS as standard. Infra Red spectra were recorded in KBr pellet using Varian 3100 FT-IR instrument. The circular dichroism (CD) spectra were performed in THF solvent using Applied Photophysics-Chirascan Circular Dichroism Spectrometer.

Theoretical Calculations: The geometry optimization was done using HF level 6-31G (d,p) basis set in gas phase in Gaussian 03 program.

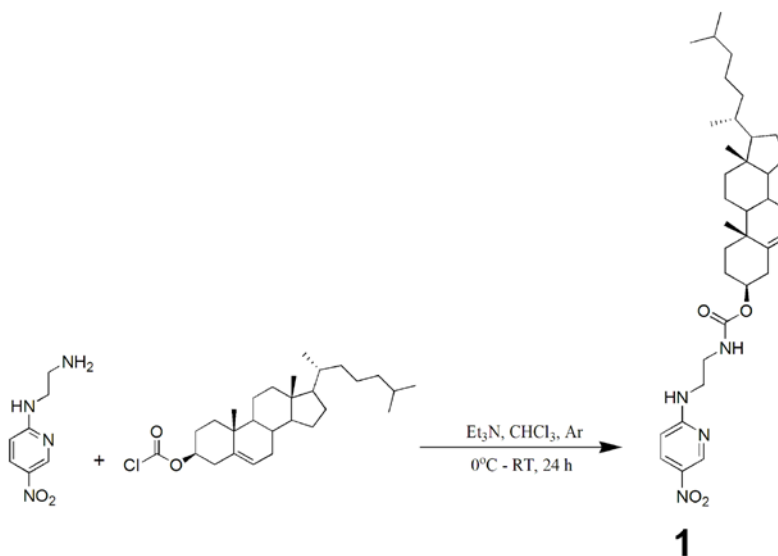
SEM Images: The morphologies of the xerogels were investigated in a field emission scanning electron microscope (FE-SEM) apparatus (JEOL, JSM-6700F). The samples were platinum coated with thickness of 40 nm by sputtering technique in argon atmosphere and were observed at a voltage of 5 kV. The investigated gel samples were **1** (0.5 wt% gel in THF/MeOH 1:12), **2** (1 and 2 wt% gel in glacial Acetic Acid), and **3** (3 wt% gel in $\text{CHCl}_3/\text{CS}_2$ 1:3).

Second Harmonic Generation (SHG) Measurements: Q-switched Nd:YAG laser of fundamental wavelength 1064 nm (Spectra Physics, PROLAB 170, pulse width 10 ns and repetition rate 10 Hz) was used as the source of light for measuring the SHG efficiency of the compounds with respect to similar grain size KDP. The energy of the laser beam was kept at 2.60 mJ/pulse. The beam was focused onto a glass capillary, using a converging lens of 200 mm focal length. The incoherently scattered SH photons were collected in the transverse direction using a combination of a monochromator and a photomultiplier tube. The second harmonic signal was then sampled, averaged over 512 shots and was recorded in a digital storage oscilloscope.

Dielectric Measurements: The dielectric constant measurement was performed using an impedance analyzer HP 4192A.

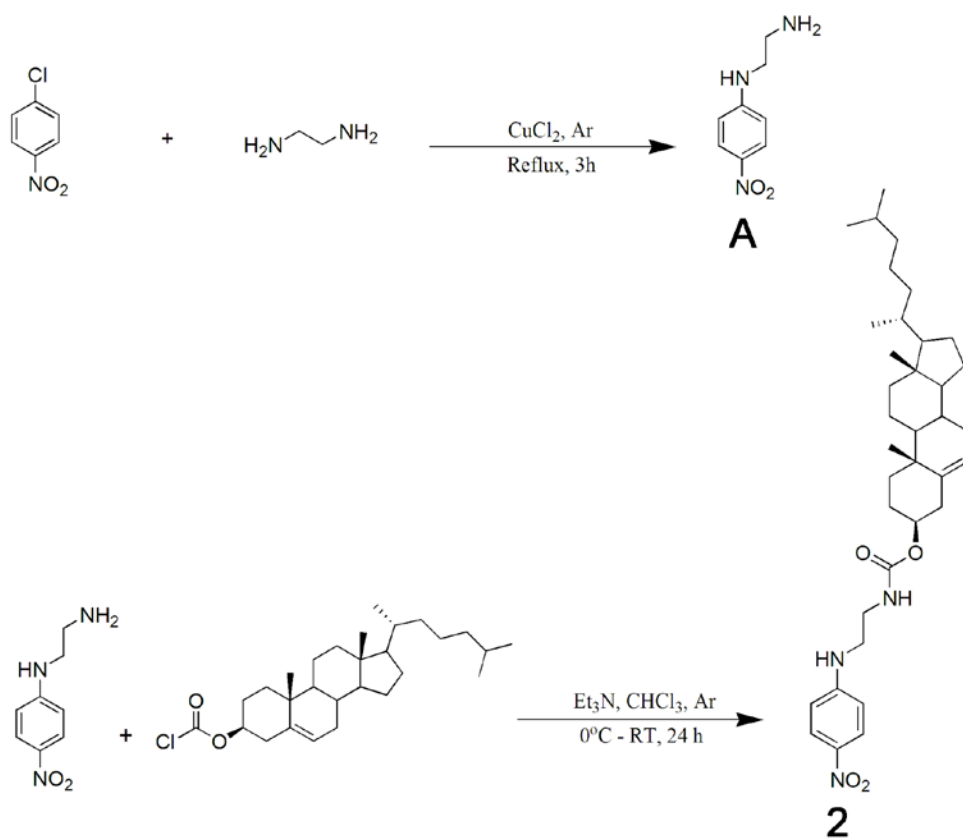
Measurement of Electric Hysteresis loop: The measurement of ferroelectric properties was done using a Radiant Technologies ferroelectric tester (model Premier Precision II). The measurements were done at room temperature with powder sample in pellet form immersed in an insulating oil. The powder sample (**1**) was pressed uniaxially at 2 ton pressure to yield a uniform disk pellet of 3 mm diameter and 1.56 mm in thickness. The samples of compound **2**, compound **3** and **3** (xerogel) were prepared by applying 5 kg/cm^2 pressure to yield pellets of 3 mm in diameter and 1.33, 0.82 and 1.25 mm in thickness, respectively. The obtained pellets were subsequently turned to a electrode using Ag paste.

Synthesis of 1:



Synthetic Procedure for 1 -In a 100 mL round bottomed flask cholesterylchloroformate (4.10 g, 8.80 mmol) was taken in 60.0 mL of dry chloroform. The solution was cooled to 0°C under argon atmosphere. Subsequently 2-(2-aminoethylamino)-5-nitro pyridine (2.01 g, 10.9 mmol) and 2.0 ml of Et₃N was added to this solution and stirred for 24 h. The reaction mixture was gradually brought to room temperature. After completion of reaction the reaction mixture was washed with water, dried over NaSO₄ and solvent was evaporated using rotary evaporator. The product was purified by washing it with methanol (5 x 30 mL) and dried under vacuum to obtain product as pale yellow solid: Yield- 69%. R_f = 0.526 (9:1 CHCl₃/MeOH). Melting point: 173 °C. ¹H NMR (500 MHz, DMSO-*d*₆, 296 K, TMS): δ = 8.89 (s, 1H, Py); 8.18 (br, m, 1H, HN); 8.09 (d, 1H, Py); 7.17 (br, m, 1H, HN-CO); 6.56 (d, 1H, Py); 5.32 (m, br, 1H, HC=C); 4.30 (br, m, 1H, CH-O); 3.44 (m, 2H, CH₂); 3.15 (m, 2H, CH₂); 2.15–2.27 (m, 2H, CH₂); 1.76-1.97 (m, 5H); 0.83-1.53 (m, 33H); 0.65 (s, 3H, CH₃); ¹³C NMR (125 MHz, DMSO-*d*₆, 296 K, TMS): δ = 162.07, 147.08, 140.32, 135.00, 132.27, 122.25, 73.61, 56.66, 56.18, 50.06, 42.40, 39.44, 38.77, 37.09, 36.60, 36.18, 35.62, 31.95, 31.84, 28.35, 28.19, 27.82, 24.32, 23.70, 23.07, 22.83, 21.08, 19.44, 19.06, 12.16; FTIR (KBr Pellet): 3410 (ν_{NH}), 3325 (ν_{NH}), 2942 (ν_{CH2}), 2869 (ν_{CH3}), 1694 (ν_{CO}), 1609 (ν_{COO}), 1530 (ν_{NO2}), 1468, 1334, 1296, 1114 cm⁻¹. Anal Calcd. For C₃₅H₅₄N₄O₄: C 70.67, H 9.15, N 9.42; Found: C 70.73, H 9.09, N 9.49.

Synthesis of 2:

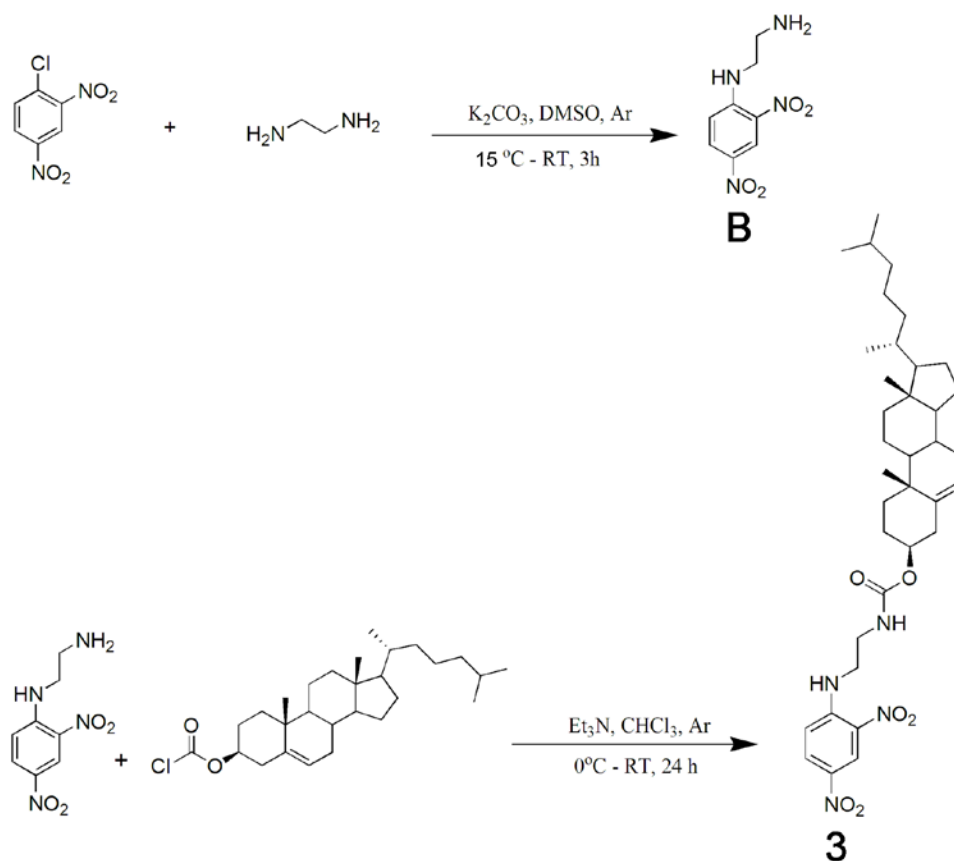


Synthetic Procedure for A- In a 100 ml round bottomed flask, p-nitrochlorobenzene (24.0 g, 152.32 mmol) was added to a solution of anhydrous CuCl_2 (1.9 g, 14.07 mmol) in 42.8 mL (639.75 mmol) of ethylenediamine and mixture was refluxed for 3 hours under argon atmosphere. After completion of reaction the reaction mixture was cooled and 260 ml of water was added, stirred for 15 minutes, and filtered. Precipitate was recrystallized from boiling water and dried under vacuum to obtain product as orange solid: Yield- 48%. $R_f = 0.52$ (9:1 $\text{CHCl}_3/\text{MeOH}$). Melting point: 150 °C.^a

Synthetic Procedure for 2- In a 100 mL round bottomed flask cholesterylchloroformate (2.62 g, 5.83 mmol) was taken in 80.0 ml of dry chloroform and cooled to 0 °C under argon atmosphere. Subsequently **A** (0.95 g, 5.25 mmol) and 1.2 ml of Et_3N was added to this solution and stirred for 24 hours. The reaction mixture was washed

with water, dried over NaSO₄ and solvent was evaporated using rotary evaporator. The crude product was purified by washing it with methanol (5 x 30 mL) and dried under vacuum to obtain pure product as yellow solid: Yield-85%. R_f = 0.684 (9:1 CHCl₃/MeOH). Melting point: 172 °C. ¹H NMR (500 MHz, DMSO-*d*₆, 296 K, TMS): δ = 7.99 (s, 2H, Ar); 7.19-7.31 (br, m, 2H, HN); 6.65 (d, 2H, Ar); 5.33 (s, br, 1H, HC=C); 4.31 (br, m, 1H, CH-O); 3.22 (m, 2H, CH₂); 3.13 (m, 2H, CH₂); 2.25 (m, 2H, CH₂); 1.78-1.97 (m, 5H); 0.97-1.54 (m, 33H); 0.65 (s, 3H, CH₃); ¹³C NMR (125 MHz, DMSO-*d*₆, 296 K, TMS): δ = 154.99, 140.30, 136.44, 126.57, 122.28, 111.30, 73.69, 56.66, 56.17, 50.06, 42.40, 39.44, 38.76, 37.09, 36.60, 36.18, 35.62, 34.67, 31.95, 31.84, 28.34, 28.19, 27.82, 25.26, 24.32, 23.70, 23.06, 22.83, 21.08, 19.44, 19.06, 12.15; FTIR (KBr Pellet): 3421 (ν_{NH}), 3342 (ν_{NH}), 2937 (νCH₂), 2869 (νCH₃), 1707 (νCO), 1605 (νCOO), 1499 (νNO₂), 1469, 1326, 1259 cm⁻¹. Anal Calcd. For C₃₆H₅₅N₃O₄: C 72.81, H 9.34, N 7.08; Found: C 72.75, H 9.45, N 7.13.

Synthesis of 3:



Synthetic Procedure for B- In a 100 ml round bottomed flask, 1-chloro-2,4-dinitrobenzene (7.610g, 37.5 mmol) was dissolved in 40 ml of dry DMSO and was cooled to 15 °C with stirring. A 21.03 g of K_2CO_3 was added to this solution and stirred. Subsequently ethylenediamine (63 ml, 940.0 mmol) was added to this solution and was stirred

for 3 hours. The reaction mixture was poured into the ice and stirred vigorously. The yellow precipitate was filtered and washed with water, dried under vacuum. Yield- 49%. $R_f = 0.52$ (9:1 $\text{CHCl}_3/\text{MeOH}$). Melting point: 135 °C. FTIR (KBr Pellet): 3340.24 (ν_{NH}), 3310.97 (ν_{NH}), 3091.35, 1619, 1520, 1421, 1347, 1328, 1316 cm^{-1} .^b

Synthetic Procedure for 3- In a 100 mL round bottomed flask cholesterylchloroformate (3.50 g, 7.79 mmol) was taken in 100.0 ml of dry chloroform. The solution was cooled to 0 °C under argon atmosphere. Subsequently **B** (2.64 g, 11.6 mmol) and 1.6 ml of Et_3N was added to this solution and stirred for 24. The reaction mixture was washed with water, dried over NaSO_4 and solvent was evaporated using rotary evaporator. The solid thus obtained was purified by washing with MeOH: Yield- 80%. $R_f = 0.736$ (9:1 $\text{CHCl}_3/\text{MeOH}$). Melting point: 174 °C. ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 267 K, TMS): $\delta = 8.89$ (m, 1H, NH); 8.86 (s, 1H, Ar); 8.26 (d, 1H, Ar); 7.26-7.30 (br, m, 2H); 5.31 (s, br, 1H, $\text{HC}=\text{C}$); 4.30 (br, m, 1H, $\text{CH}-\text{O}$); 3.58 (m, 2H, CH_2); 3.23 (m, 2H, CH_2); 2.20 (m, 2H, CH_2); 1.73-1.82 (m, 5H); 0.83-1.50 (m, 33H); 0.65 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$, 267 K, TMS): $\delta = 148.97, 140.26, 135.46, 130.61, 130.22, 123.96, 122.30, 115.69, 73.80, 56.66, 56.17, 50.05, 43.40, 42.40, 39.44, 38.69, 37.06, 36.59, 36.18, 35.61, 31.95, 31.83, 28.28, 28.18, 27.82, 24.32, 23.70, 23.07, 22.83, 21.08, 19.44, 19.06, 12.15$; FTIR (KBr Pellet): 3438 (ν_{NH}), 3320 (ν_{NH}), 2940 (ν_{CH_2}), 2869 (ν_{CH_3}), 1715 (ν_{CO}), 1615 (ν_{COO}), 1506 (ν_{NO_2}), 1469, 1311, 1259, 1139, 1008 cm^{-1} . Anal Calcd. For $\text{C}_{36}\text{H}_{54}\text{N}_4\text{O}_6$: C 67.68, H 8.52, N 8.77; Found: C 67.75, H 8.59, N 8.75.

References:

- (a) Linsker, F.; Evans, R. L. *J. Org. Chem.* **1945**, 10, 283-285.
- (b) Twieg, R.; Azema, A.; Jain, K., Cheng, Y. Y. *Chem. Phys. Lett.* **1982**, 92, 208-211.

Table-1: SHG Experiment using Kurtz-Perry Method:

	KDP	Compound 1	Compound 2	Compound 3 (Xerogel)
Signal (mV)	33	1.8	3.6	1.5

Table-2: Effect of Field variation on P-E Hysteresis curves studied with crystalline solid samples for **1-3** and xerogels prepared from the nano-architecture of **3**:

Compound 1

Voltage (kV)	P_s (μC/cm²)	P_r (μC/cm²)	E_c (kV/cm)
0.31	0.124	0.041	0.07
0.62	0.241	0.089	1.37
0.94	0.363	0.148	2.08
1.56	0.624	0.265	3.67
2.34	0.926	0.417	5.53
3.12	1.240	0.570	7.56

Compound 2

Voltage (kV)	P_s (μC/cm²)	P_r (μC/cm²)	E_c (kV/cm)
0.66	0.248	0.053	1.02
1.33	0.511	0.128	2.44
1.99	0.777	0.227	4.13
2.66	1.040	0.380	6.36

Compound 3

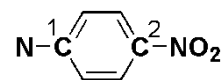
Voltage (kV)	P_s (μC/cm²)	P_r (μC/cm²)	E_c (kV/cm)
0.41	0.144	0.037	1.3
0.82	0.286	0.071	2.3
1.23	0.427	0.148	4.8

Compound 3 (**Xerogels** prepared from the nano-architectures)

Voltage (kV)	P_s (μC/cm²)	P_r (μC/cm²)	E_c (kV/cm)
1.25	0.498	0.234	3.9

Table-3: Theoretical calculation using HF 6-31G (d,p), Gauussian 03 program:

Compound	D (debye)	L (nm)	HOMO (eV)	LUMO (eV)	NBO (Hartree)			
					N	C ¹	C ²	NO ₂
1	5.78	2.89	-8.001	2.013	-0.697	0.559	-0.102	-0.292
2	8.80	2.86	-8.436	2.149	-0.703	0.295	-0.031	-0.292
3	7.45	2.90	-8.028	1.496	-0.683	0.334	-0.036	-0.272



D: Dipole Moment, L: Molecular Length; Numbering scheme for NBO calculations:

References:

1. Frisch, M. J. et. al. *Gaussian 03W*, revision E.01; Gaussian Inc.: Wallingford, CT, 2007.

Table-4: Organogelation tests: G_{RT}- Gel at RT, G_F- Forms Gel when cooled under fridge, G_S- Gel on sonification, G*- Gel like, S- Solution.

Compound 1

Solvent	10 wt%	5.0 wt%	3.0 wt%	2.0 wt%	1.0 wt%
Acetic Acid	G _{RT}	G _S	G _S	G _S *	S
THF/MeOH (1:12)	-	-	G _{RT}	G _{RT}	G _{RT}
DMF/MeOH (1:14)	-	-	G _{RT}	G _{RT}	G _{RT}

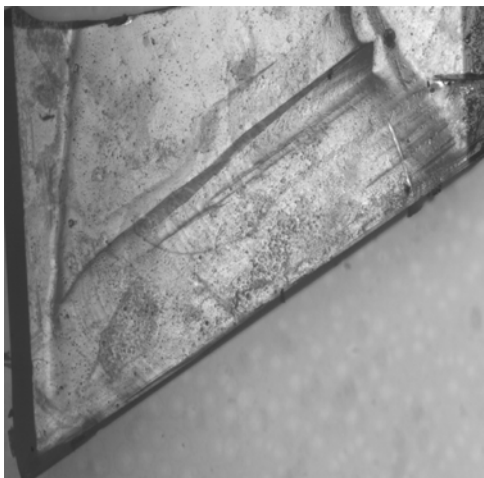
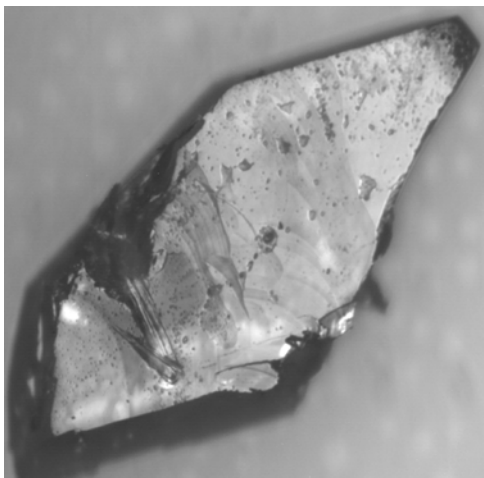
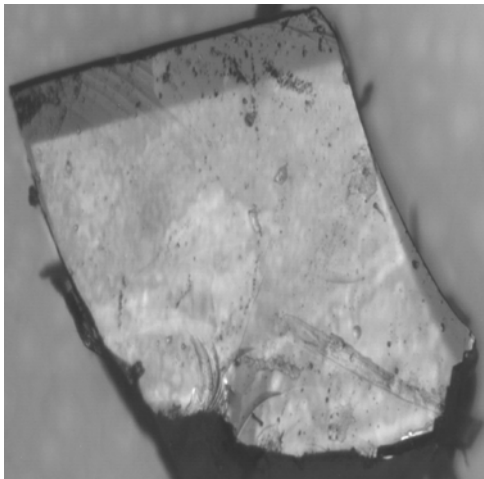
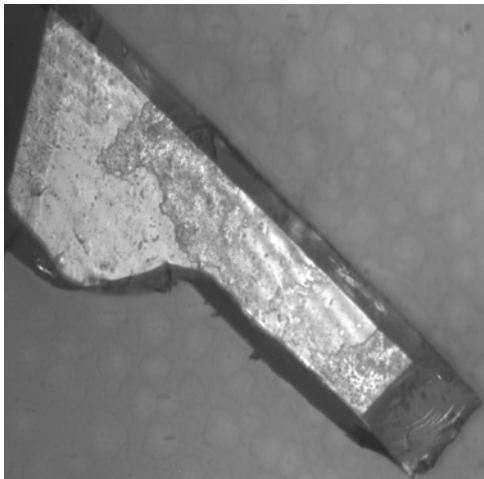
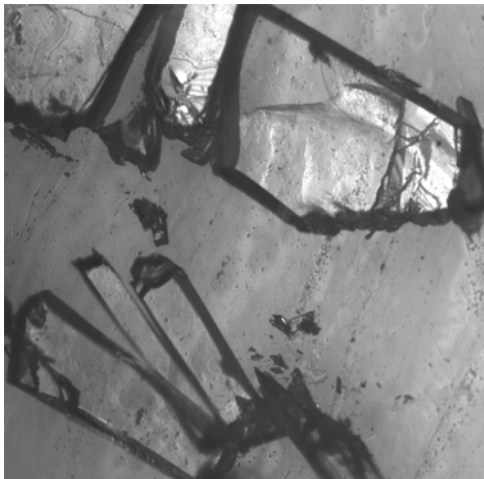
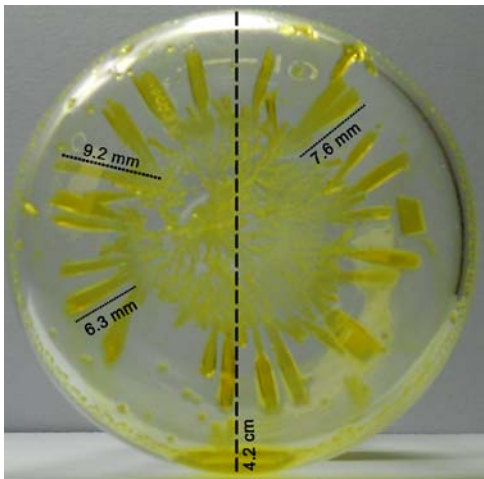
Compound 2

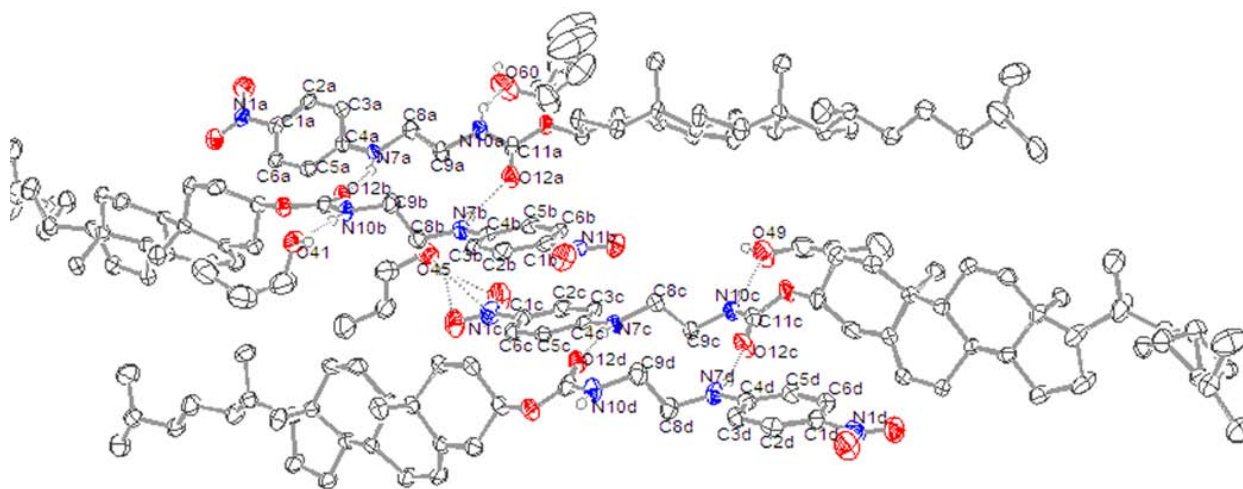
Solvent	3.0 wt%	2.0 wt%	1.0 wt%	0.5 wt%	0.25 wt%
MeOH	-	-	G _{RT}	P	-
CCl ₄	-	G _F	G _F	G _F	S
Acetic Acid	-	G _{RT}	G _S	S	-
THF/MeOH (1:9)	-	G _{RT}	G _{RT}	G _F	G _F
CHCl ₃ /MeOH (1:9)	-	G _{RT}	G _{RT}	G _F	G _F
CHCl ₃ /n-Hexane (1:9)	-	G _{RT}	G _F	G _F	S

Compound 3

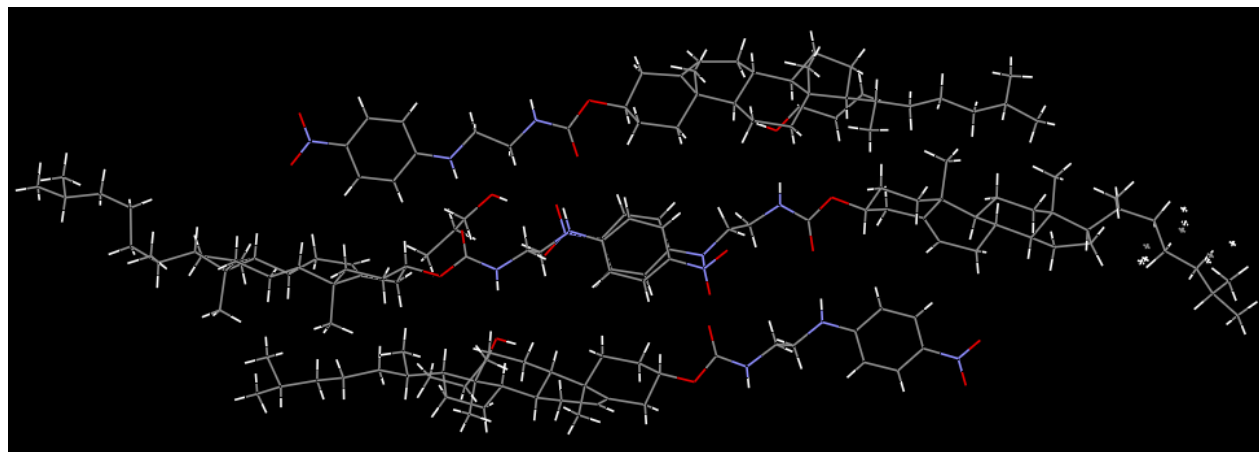
Solvent	10 wt%	5.0 wt%	3.0 wt%	2.0wt%
CHCl ₃	GRT	S	-	-
THF/MeOH (1:9)	-	-	-	G _{RT}
CHCl ₃ /MeOH (1:12)	-	-	G _{RT}	S
CHCl ₃ /n-Hexane (1:9)	-	-	G _{RT}	S
CHCl ₃ /Cyclohexane (1:9)	-	-	G _{RT}	S

Photographs of Single Crystals of compound **2**



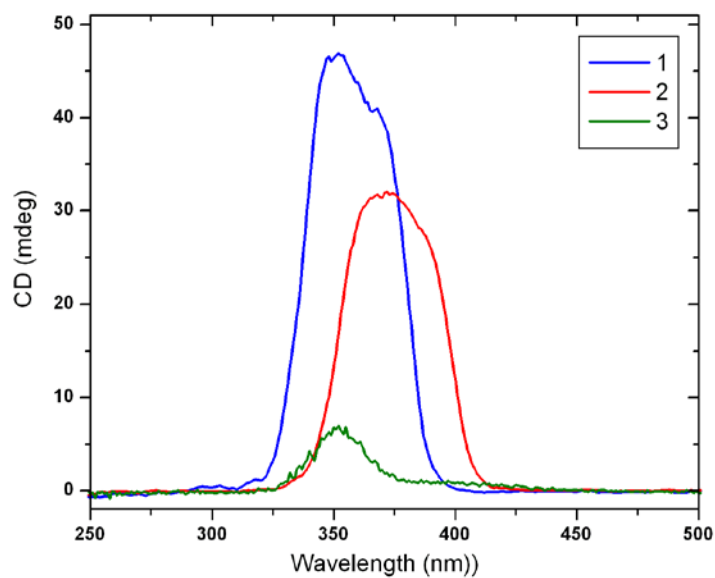


SI 1: ORTEP diagram showing the thermal ellipsoids of compound **1** showing the intermolecular H-bonding to form the rings, π - π stacking and the four solvent molecules.



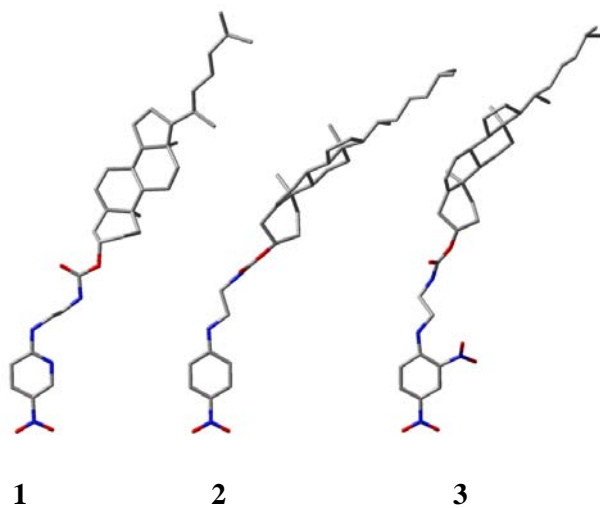
SI 2: A top view of the crystal structure depicting that the amino nitro-phenyl rings make a specific angle and are tilted while undergoing the π - π stacking interactions.

CD Spectra of compounds 1, 2 and 3:



SI 3: CD spectra of compound **1** (2.24×10^{-3} M), **2** (1.49×10^{-3} M) and **3** (1.50×10^{-3} M) in THF.

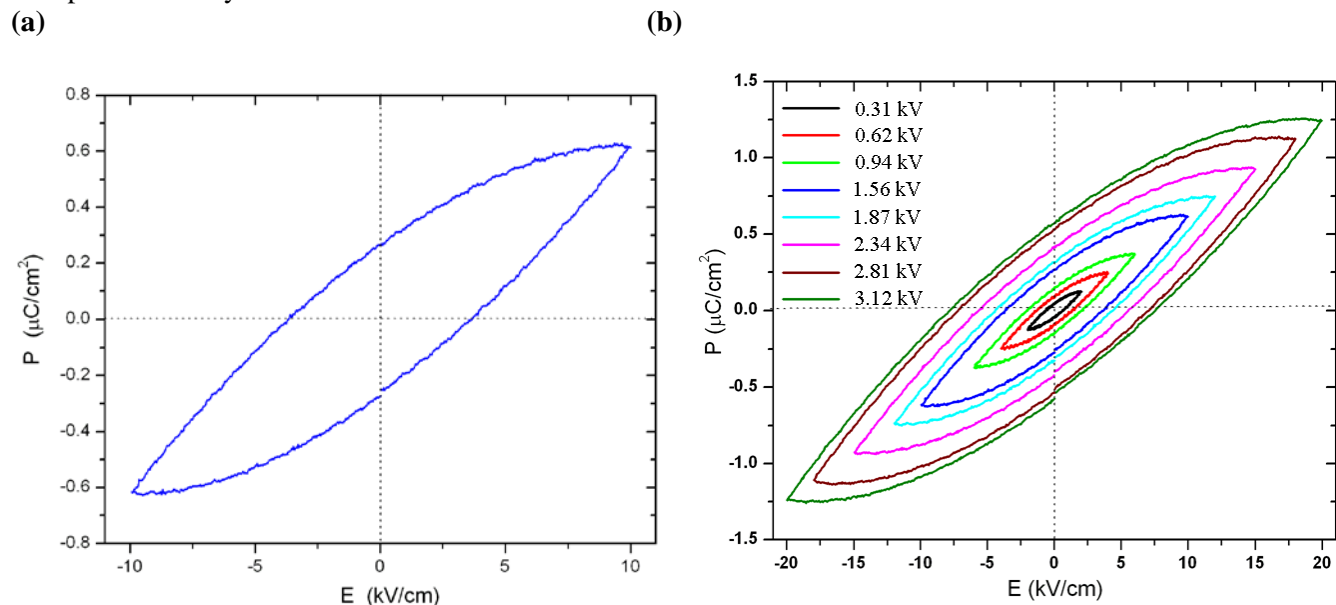
Optimized geometry of 1, 2 and 3:



SI 4: The geometry optimized molecular structures of the compounds **1**, **2**, and **3**. Optimization was carried out at HF level using 6-31G (d,p) basis set in gas phase with Gaussian 03 program.

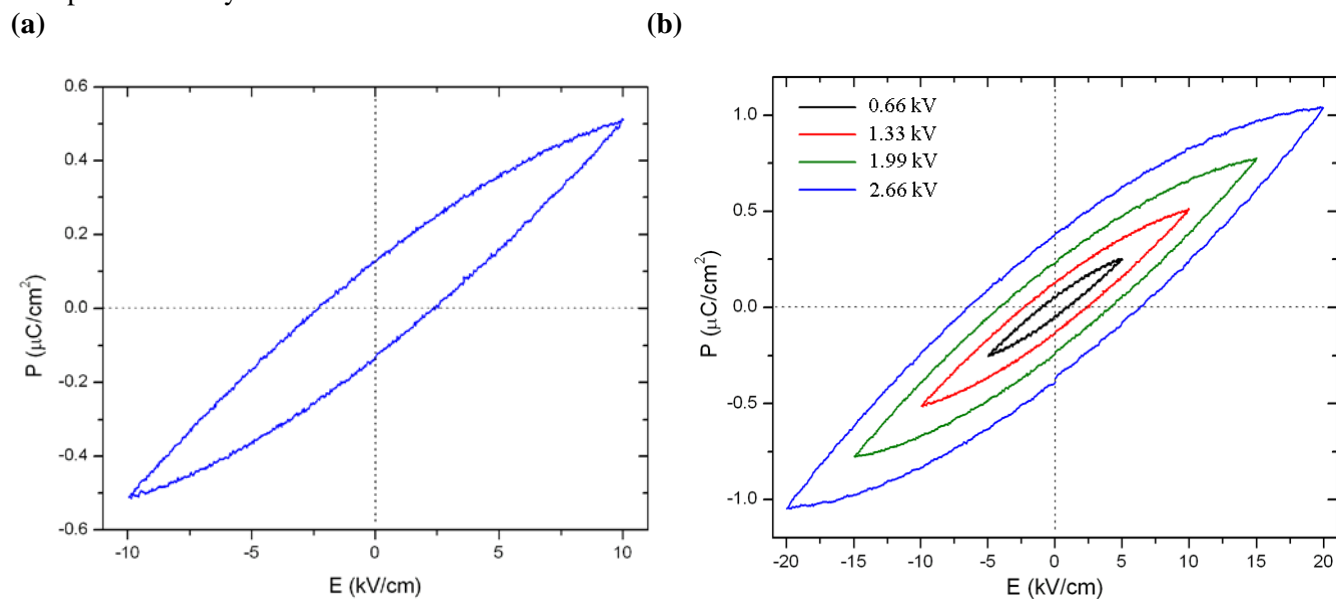
P-E Hysteresis Measurements:

Compound **1** in crystalline solid form:



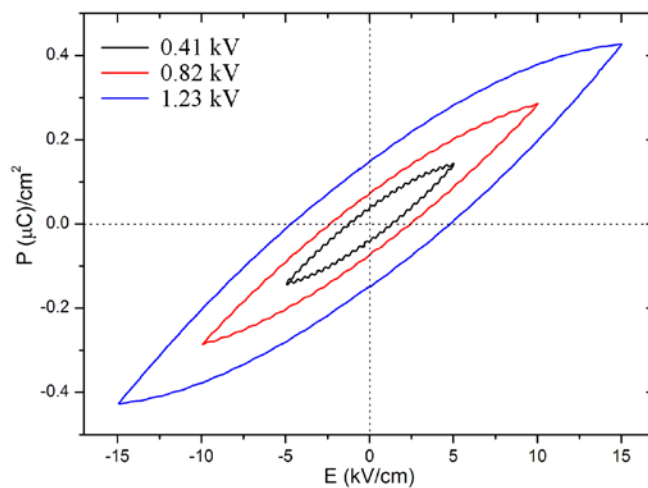
SI 5. (a) P-E hysteresis measurement at voltage 1.56 kV and frequency 1Hz, (b) at different voltages from 0.31-3.12 kV.

Compound **2** in crystalline solid form:



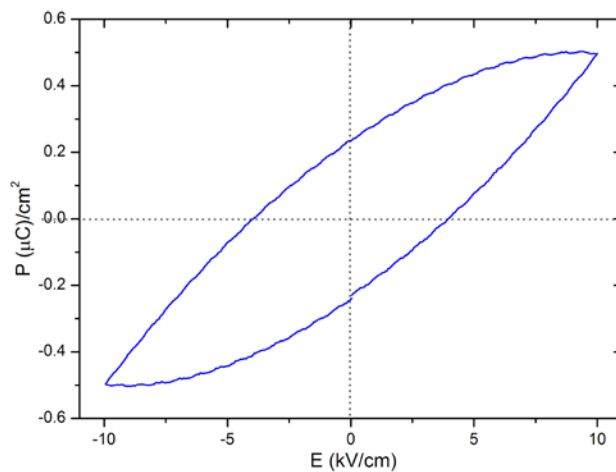
SI 6: (a) P-E hysteresis measurement at voltage 1.33 kV and frequency 1Hz, (b) at different voltages from 0.66-2.66 kV and frequency 1Hz.

Compound **3** in crystalline solid form:



SI 7: P-E hysteresis measurement at voltages 0.41, 8.20 and 1.23 kV.

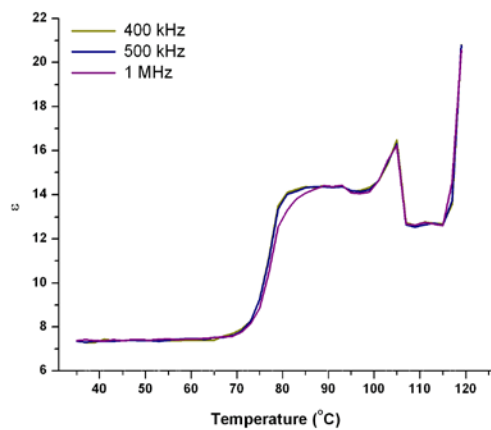
Compound **3** in xerogel form prepared from the nano-architecture of **3**



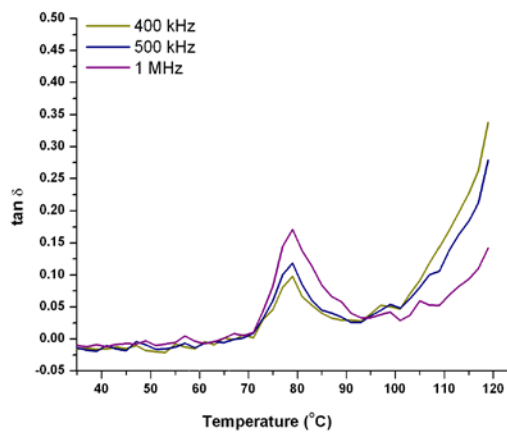
SI 8: (a) P-E hysteresis measurement at voltage 1.25 kV.

Dielectric constant measurement:

(a)



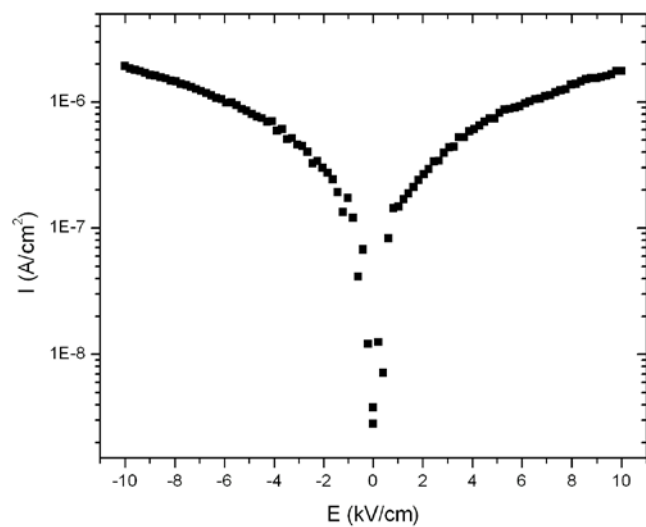
(b)



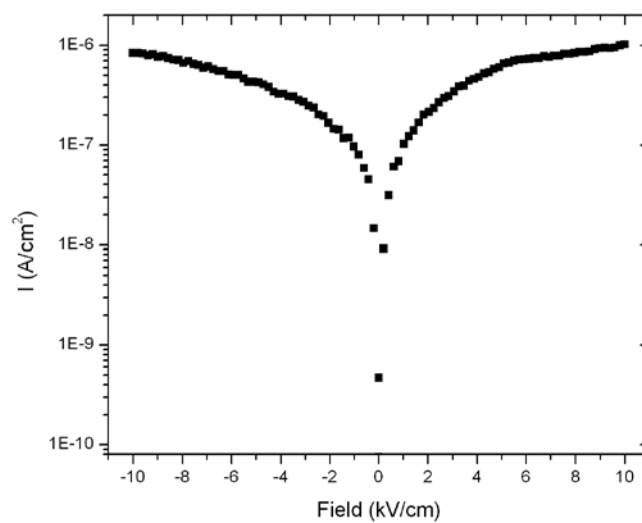
SI 9: Dielectric constant measurement of (a) compound **1** and (b) compound **2** at different frequencies.

Leakage current measurement of 1-3:

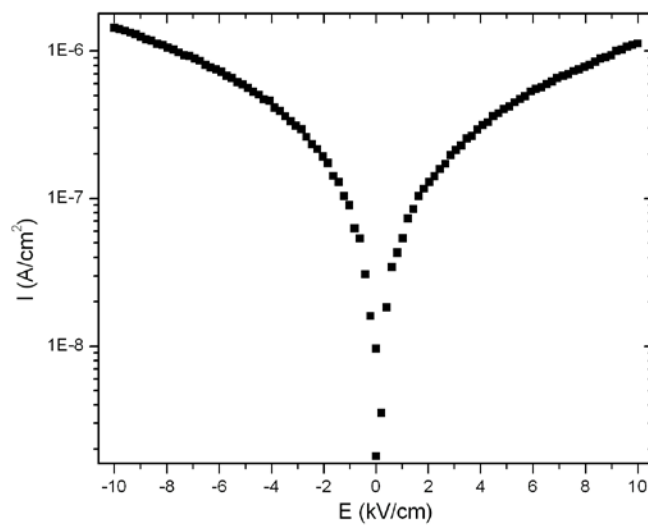
(a)



(b)



(c)

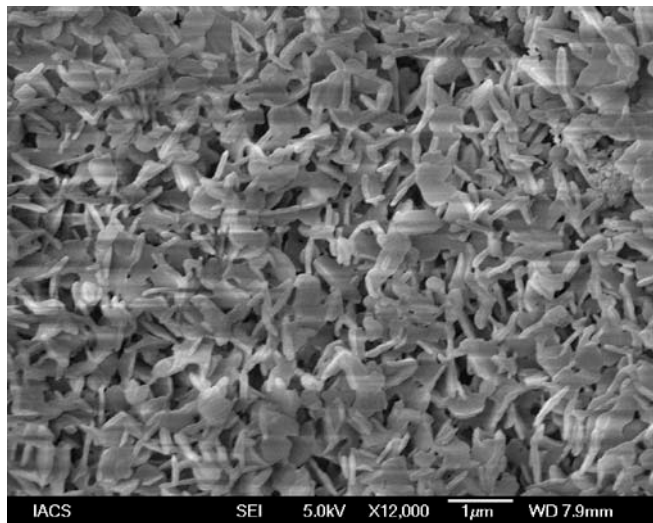


SI 10: Leakage current measurement of (a) compound **1**, (b) compound **2** and (c) compound **3**.

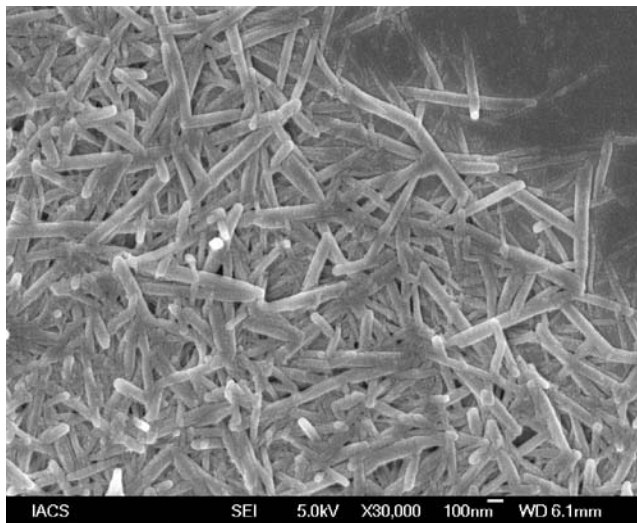
SEM Images of the nano-architectures formed by 1-3:

SEM images showing various nano-architectures ranging from, nano-platelets, nano-rods, nano-helical ribbons, nano-sheets:

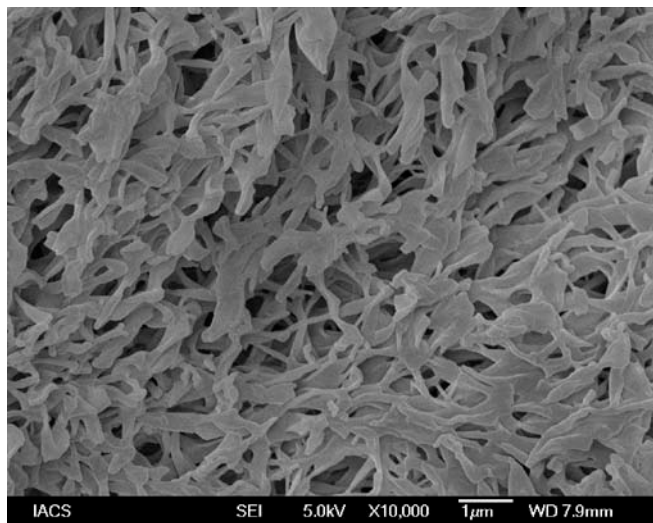
(a)



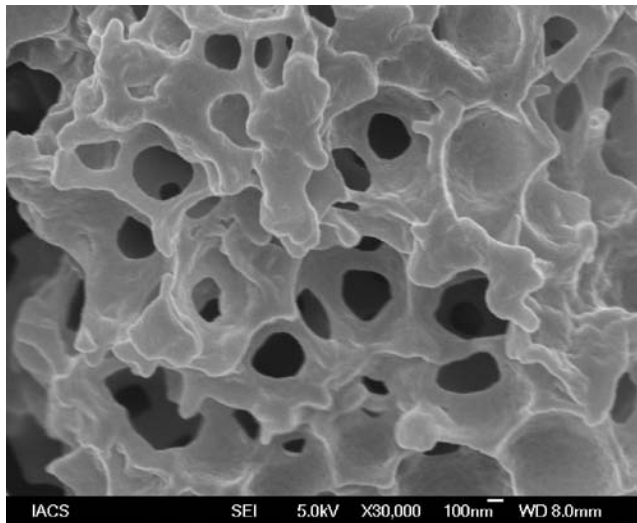
(b)



(c)

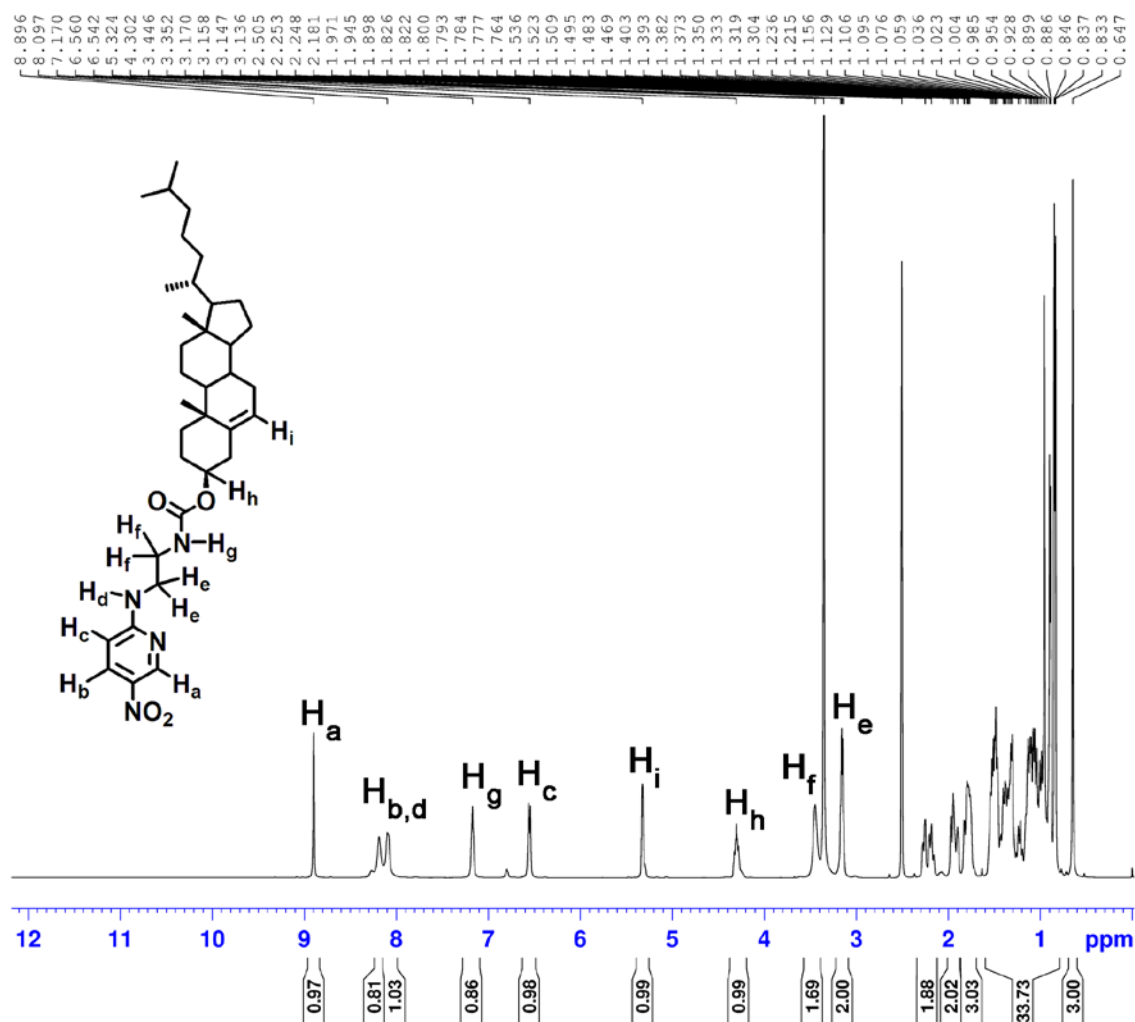


(d)



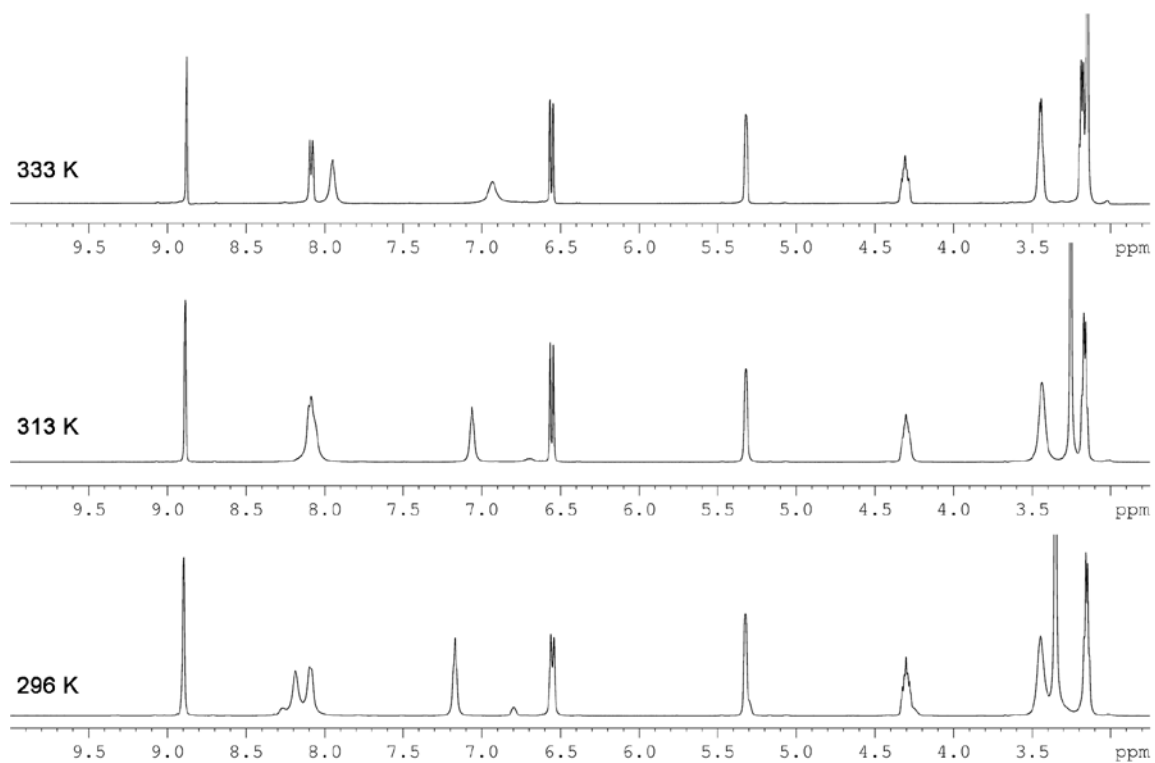
SI 11: (a): Xerogel **1**, 0.5 wt% gel in THF/MeOH 1:12); (b) Xerogel **2**, 1 wt% gel in glacial Acetic Acid and (c) Xerogel **2** (1 wt% and 2 wt% gel in glacial Acetic Acid), and (d) Xerogel **3** (3 wt% gel in $\text{CHCl}_3/\text{CS}_2$ 1:3).

500 MHz ^1H NMR Spectrum of Compound 1:



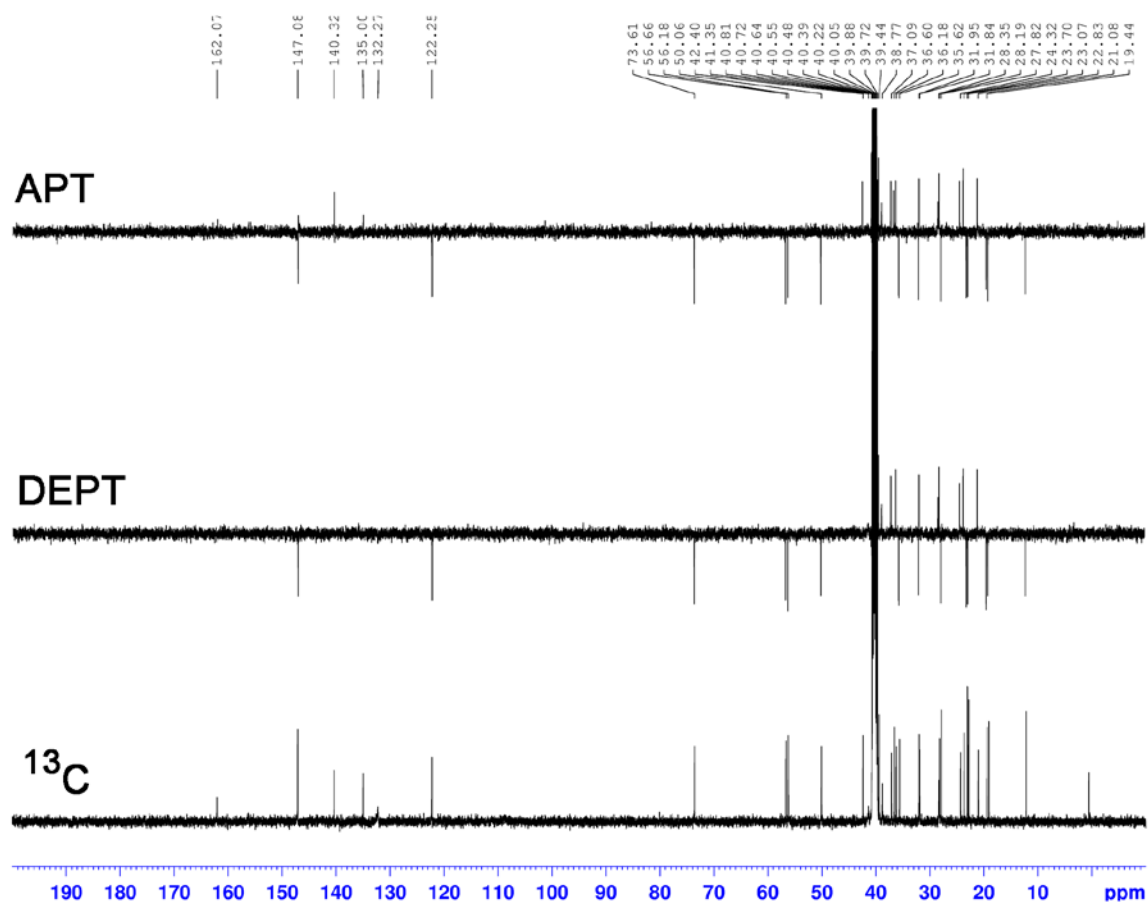
SI 12: 500 MHz ^1H NMR Spectrum of Compound 1 in $\text{DMSO}-d_6$, 296 K

VT 500 MHz ^1H NMR Spectra of Compound 1:



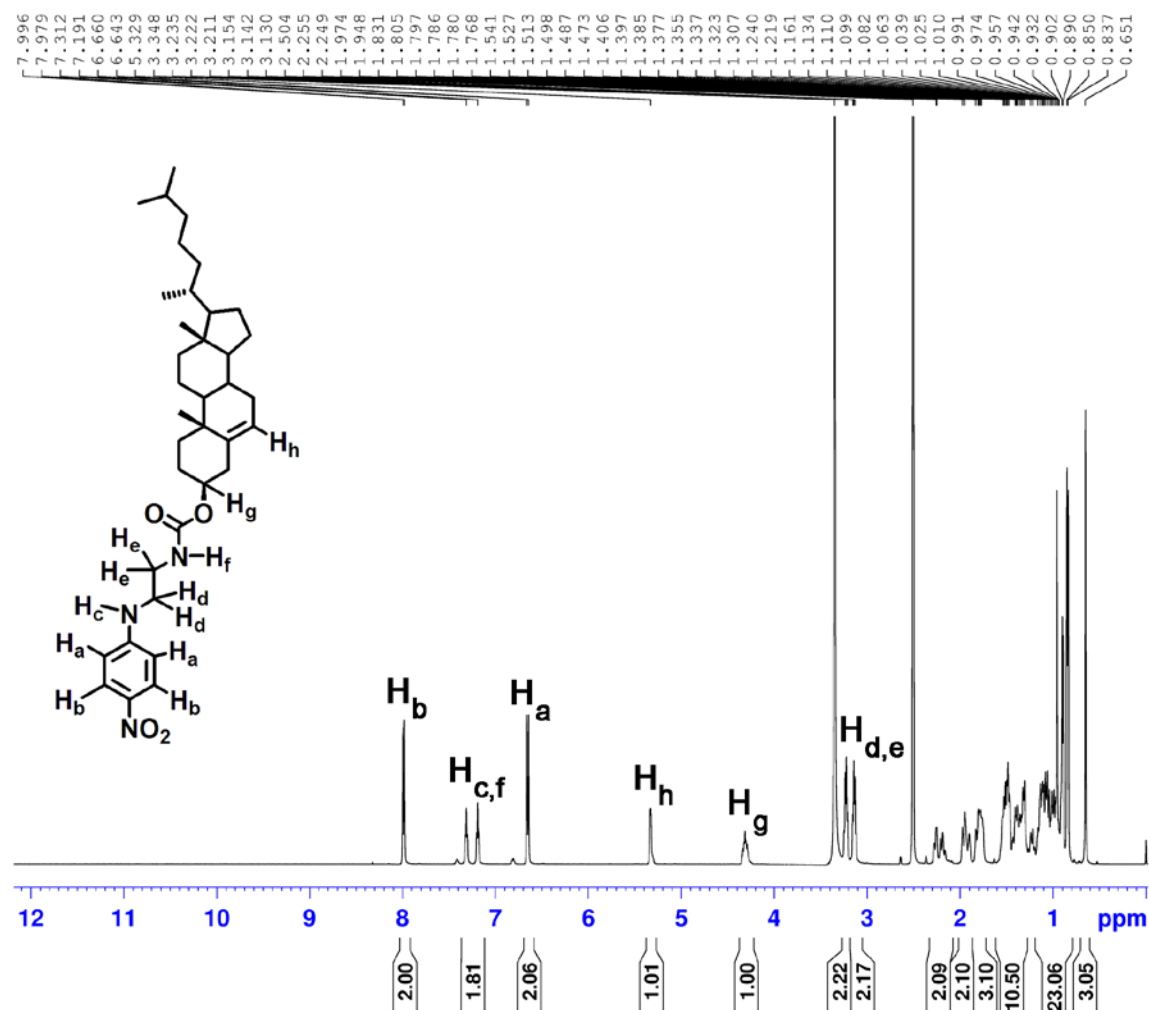
SI 13: 500 MHz ^1H NMR Spectrum of Compound 1 ($\text{DMSO-}d_6$) at variable temperatures

125 MHz ^{13}C , DEPT-135 and APT NMR Spectra of Compound 1:



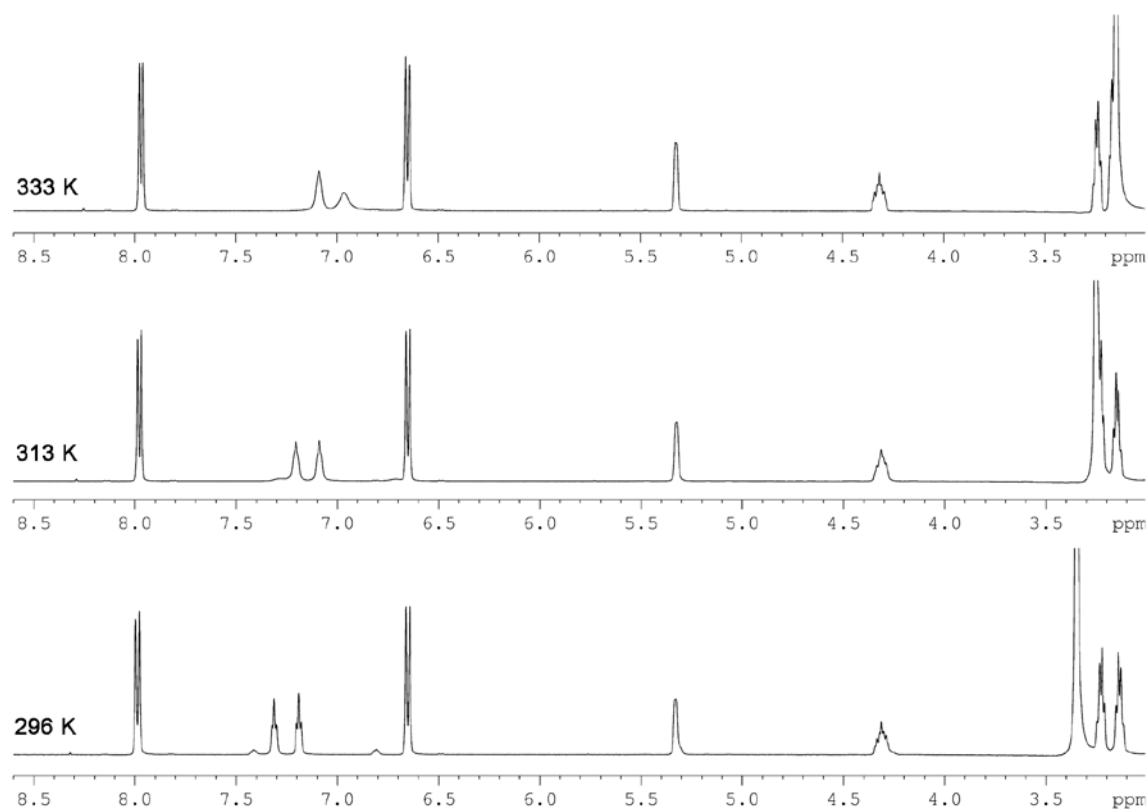
SI 14: 125 MHz ^{13}C , DEPT-135 and APT NMR Spectra of Compound 1 in DMSO- d_6

500 MHz ^1H NMR Spectrum of Compound 2:



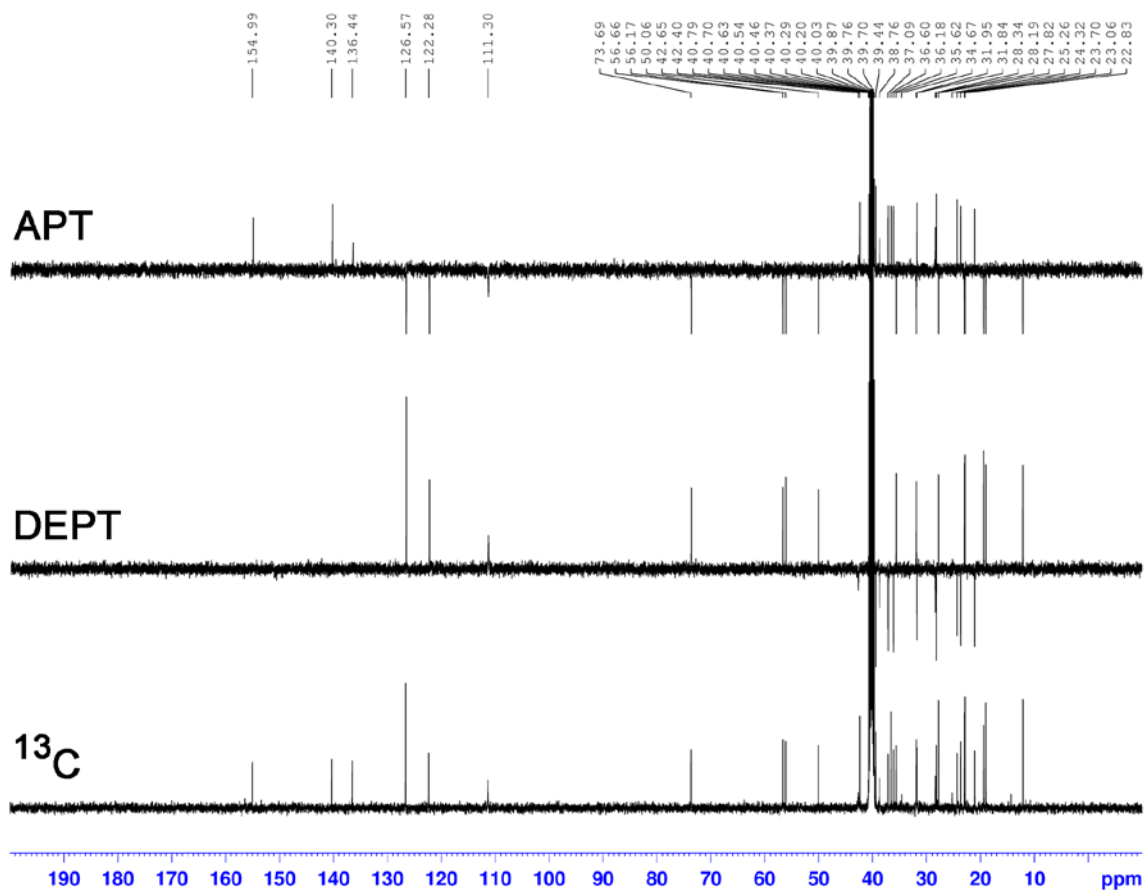
SI 15: 500 MHz ^1H NMR Spectrum of Compound 2 in $\text{DMSO}-d_6$, 296 K

VT 500 MHz ^1H NMR Spectra of Compound 2 ($\text{DMSO-}d_6$):



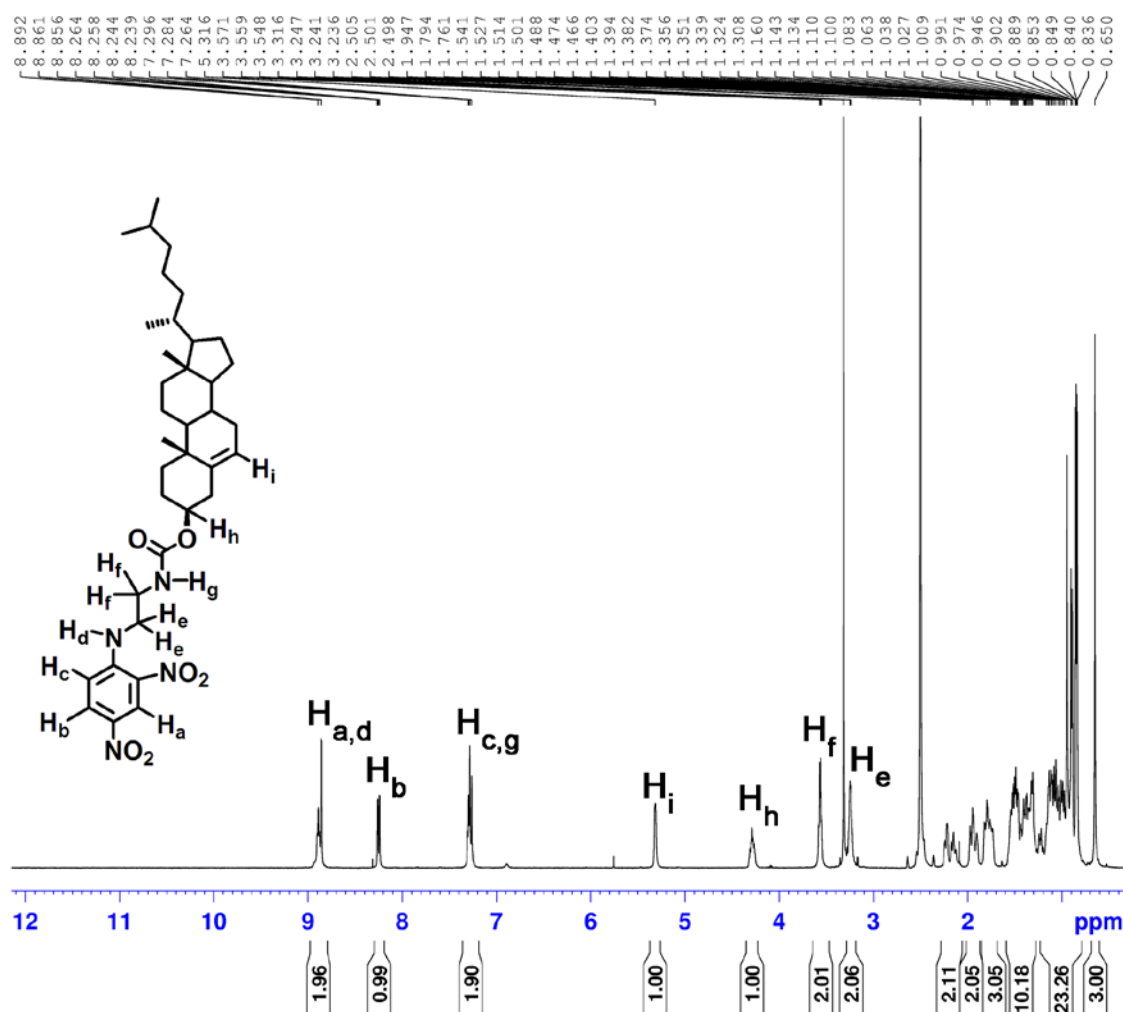
SI 16: 500 MHz ^1H NMR Spectra of Compound 2 ($\text{DMSO-}d_6$) at variable temperatures

125 MHz ^{13}C , DEPT-135 and APT NMR Spectra of Compound 2:



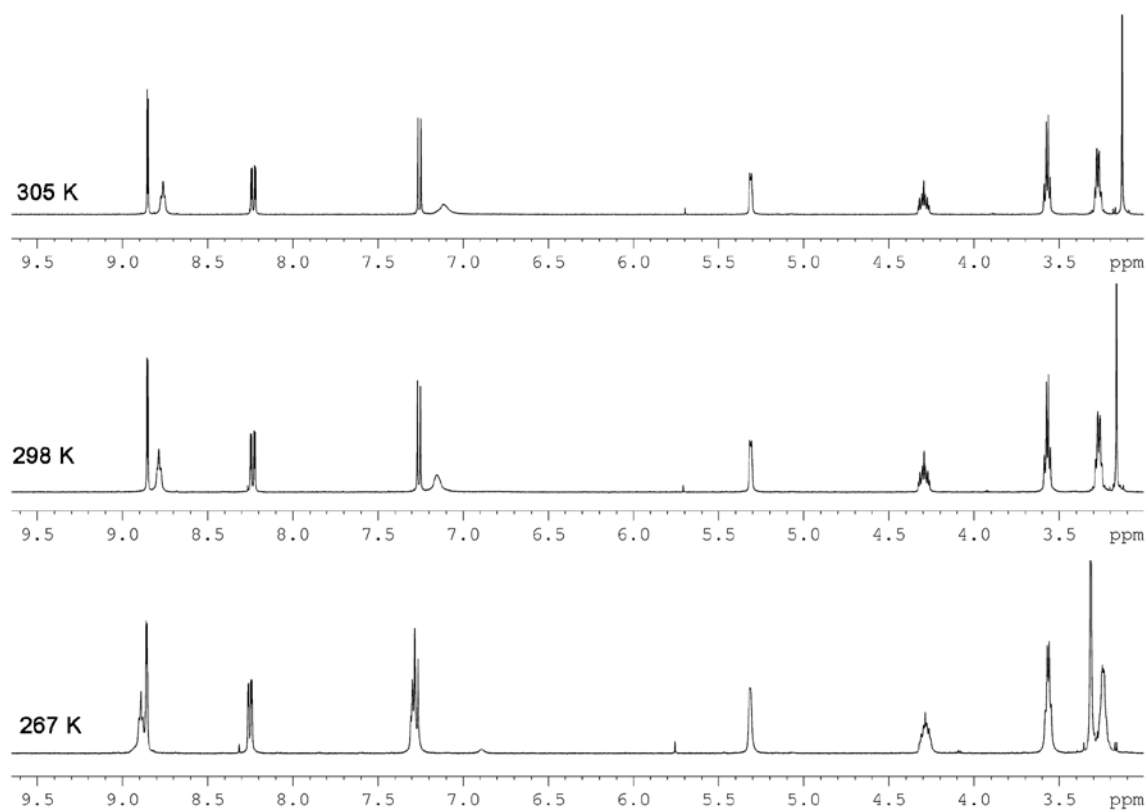
SI 17: 125 MHz ^{13}C , DEPT-135 and APT NMR Spectra of Compound 2 in $\text{DMSO}-d_6$

500 MHz ^1H NMR Spectrum of Compound 3:



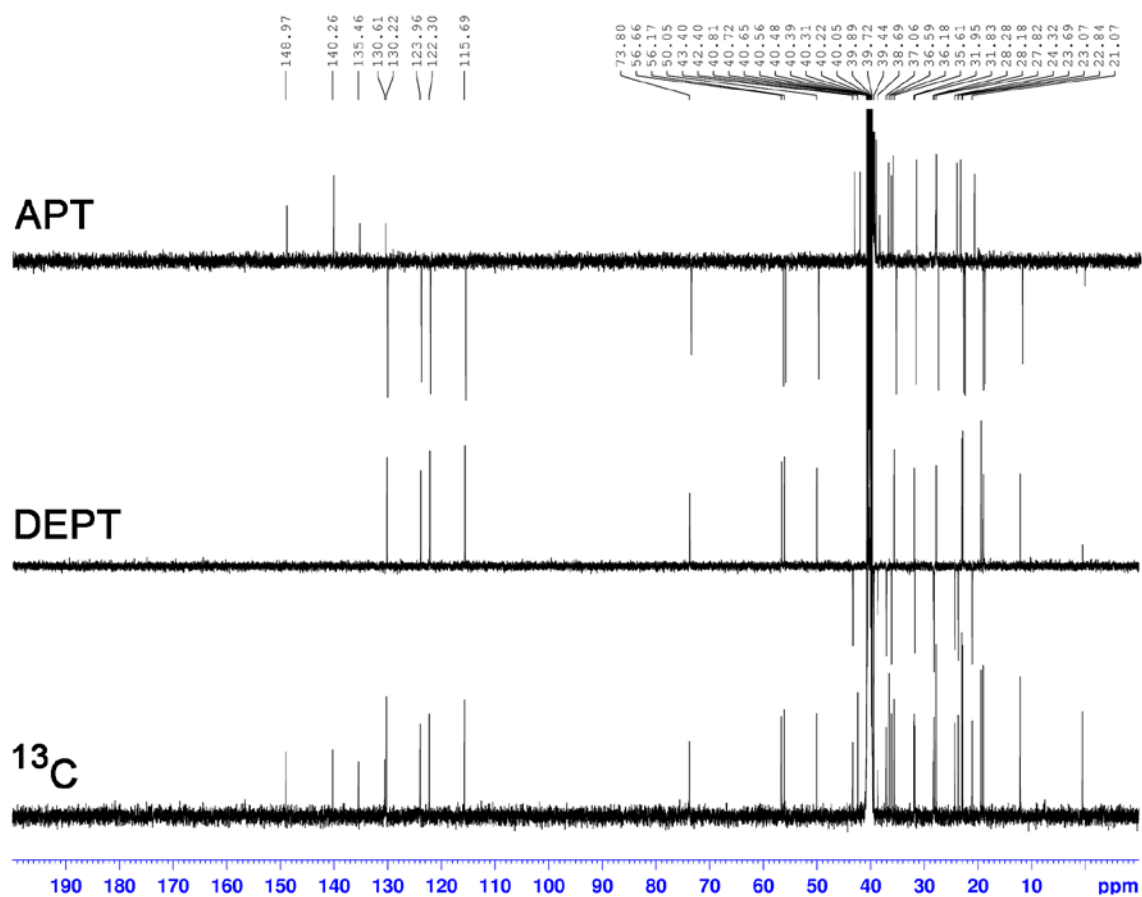
SI 18: 500 MHz ^1H NMR Spectrum of Compound 3 in $\text{DMSO}-d_6$, 267 K

VT 500 MHz ^1H NMR Spectra of Compound 3:



SI 19: 500 MHz ^1H NMR Spectra of Compound 3 ($\text{DMSO-}d_6$) at variable temperatures

125 MHz ^{13}C , DEPT-135 and APT NMR Spectra of Compound 3:



SI 20: 125 MHz ^{13}C , DEPT-135 and APT NMR Spectra of Compound 3 in $\text{DMSO}-d_6$