Supplementary Information:

Tri-*s*-triazine (*s*-heptazine), a novel electron-deficient core for soft self-assembled supramolecular structures

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All the chemicals and reagents are AR-grade quality and purchased from Sigma-Aldrich. The solvents were dried and distilled using standard protocols. The intermediate and final compounds were purified by column chromatography using silica gel (100–200) mesh and recrystallization from the suitable solvent. Spectral and elemental analysis confirmed the structure and purity of all compounds. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using Shimadzu – 8400 spectrometer; only major peaks are reported in cm^{-1}. ^{1}H Nuclear magnetic resonance spectroscopy (NMR) and ^{13}C NMR were recorded on Bruker 500 MHz machine using deuterated chloroform ($CDCl_3$) as a solvent, and chemical shifts are recorded in ppm from tetramethylsilane as internal standard ($CDCl_3$: ^{1}H NMR: $\delta = 7.23$; ^{13}C NMR = 77.0). Data were reported as: s = singlet, d = doublet, t = triplet m = multiplet, bd = broad doublet. Elemental analysis was carried out using Elementar Vario MICRO Select instrument. The microscopic textures were recorded on a sample placed between ordinary glass slides using Olympus BX51 polarising optical microscope (Olympus, Tokyo, Japan) in conjunction with Mettler FP82HT hot stage and Mettler FP90 central processor. The phase transition temperature and associated enthalpies of the liquid crystalline samples were determined by Mettler Toledo DSC instrument using 2–4 mg samples and a scan rate of 10°C min^{-1}. Further detailed examination of liquid crystalline mesophase structure is done by X-ray diffraction using Panalytical (Empyrean) Cu-Kα (1.54 Å) X-ray diffractometer. Thermal stability was established by Perkin Elmer TGA4000 analyser. UV-Vis Spectra was measured by Thermo Scientific™ NanoDrop 2000c. Emission spectra were recorded by Cary eclipse fluorescence spectrophotometer. Mass spectra were recorded on Bruker Daltonics flexAnalysis.

Synthesis of 3: Fallowed by reference.[1]

Synthesis of 4:

Compound **3** (5.00 g) was transferred to a round bottom flask. 2.5 M aqueous KOH solution (100 ml) was added to the flask. The reaction mixture was refluxed at 110 ºC for 8h with vigorous stirring. After 8h a clear solution was observed; the reaction mixture was cooled to the room temperature and the solution was kept it in the freezer for 2h. Needle like colorless crystals appeared which were filtered and washed two times with cold ethanol. Obtained crystals were dried at 60 ºC for 2h under reduced pressure to provide color less needle like crystals (3.2 g) which were taken as such for the next step.

Synthesis of 5:

Compound **4** (5g, 18.18 mmol) was taken in the round bottom flask and dried well under high vacuum. PCl_5 (11.35g, 54.54 mmol, 3eq) and $POCl_3$ (90ml, 963.54 mmol, 53eq) were added to the flask. The reaction mixture was refluxed at 100 ºC under nitrogen for 6h to get a yellow color solution which was cooled to the room temperature and concentrated under reduced pressure. To that 20 ml ice cold water was added and stirred for about 1 minute and filtered through filter paper using a Buchner funnel and washed with ice cold water. The compound was immediately scraped off from the filter paper and taken into a round bottom flask and dried by using rotavapor at 70 °C for 2h. Brilliant yellow color solid of 2,5,8-trichloro-s-heptazine was obtained which was dried under high vacuum for 6h. Yield: 62%. Note: Exposure to the water during the above procedure must be avoided in order to minimize the hydrolysis of chloride to hydroxide). IR (film) υ_{max}: 1641, 1604, 1502, 1465, 1377, 1307, 1203, 1087, 941, 823, 639 cm^{-1}; ^{13}C NMR (125 MHz, Benzene-d_6): δ ppm =157.92, 175.86.

General procedure for the synthesis of 7a, 7b, 7c:

A solution of **5** (1eq) and **6** (3.4 eq) in dry toluene (40ml) was refluxed for 24h under nitrogen. After 24h, mixture was filtered to remove the suspended particles and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether: ethyl acetate (9:1) as eluent to get desired product which was precipitated by using cold methanol and dried under the high vacuum.

Compound 7a: **5** (0.100g, 0.361mmol, 1eq), **6a** (0.690g, 1.23mmol, 3.4eq), toluene 20ml, yield: 52%, IR (film) υ_{max}: 3377, 2953, 2924, 2852, 2727, 2681, 1656, 1649, 1599, 1502, 1444, 1377, 1298, 1232, 1116,1043 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.23 – 8.04 (bd, 1H), 7.92 – 7.82 (bd 2H), 6.88 - 6.80 (m, 6H), 3.96 - 3.88 (m, 18H), 1.76 - 1.71 (m, 18H), 1.44 - 1.41 (m, 18H), 1.30 -1.25 (m, 98H), 0.89 - 0.86 (m, 27H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 162.60, 162.49, 162.39, 156.23, 155.56, 155.00, 153.74, 153.21, 153.17, 152.96, 136.00, 135.92, 132.24, 132.08, 102.45, 102.09, 101.28, 101.11, 73.58, 69.44, 69.34, 69.27, 69.18, 31.95, 30.39, 30.34, 29.71, 29.67, 29.54, 29.41, 26.23, 26.19, 22.71, 14.12; Mass (MALDI-TOF): *m/z* 1853.45; Elemental analysis: C, 73. 90; H, 10.77; N, 7.56 calculated (%): C, 73.6; H,10.93; N, 7.33 (expt. %).

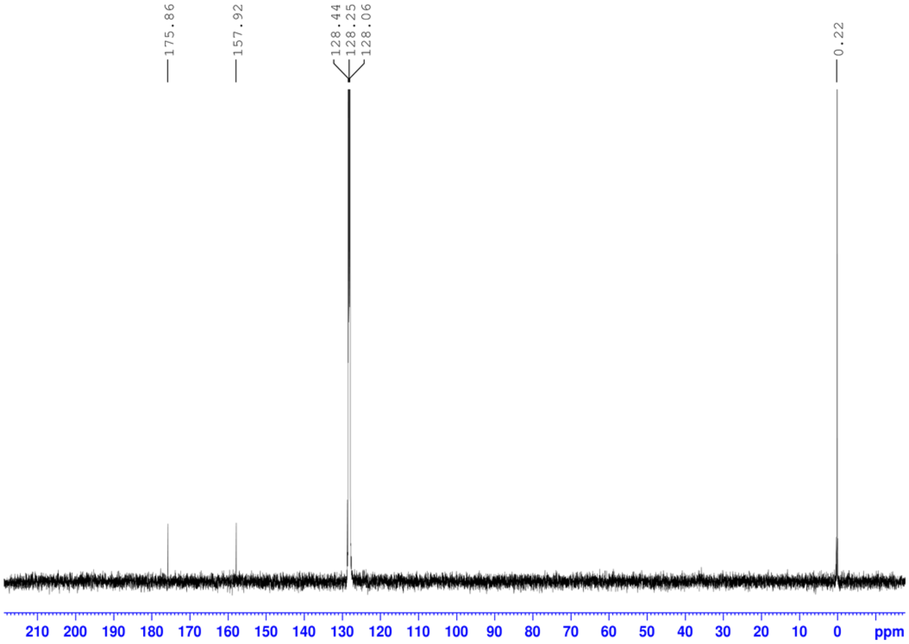
Compound 7b: **5** (0.100g, 0.361mmol, 1eq), **6b** (0.80g, 1.23mmol, 3.4eq), toluene 20ml, yield: 55%, IR (film) υmax: 3389, 2953, 2922, 2852, 2746, 2675, 1649, 1643, 1502, 1454, 1435, 1377, 1232, 1116, 721 cm−1; ^{1}H NMR (500 MHz, $CDCl_3$),): δ (ppm) = 7.96 -7.61 (b d , 1H), 7.49 – 7.45 (b d, 2H), 6.86 – 6.76 (m, 6H), 3.97 – 3.88 (m, 18H), 1.76 – 1.69 (m, 18H), 1.46 – 1.43 (m, 18H), 1.29 – 1.25 (m, 146H), 0.89 – 0.86 (m, 27H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 162.69, 162.52, 156.28, 155.64, 155.02, 153.20, 153.17, 152.91, 136.01, 135.91, 132.21, 132.04, 102.65, 102.17, 101.33, 101.10, 73.57, 69.44, 69.34, 69.28, 69.19, 31.95, 30.38, 30.34, 30.05, 29.71, 29.54, 29.41, 26.23, 26.19, 22.70, 14.11; Mass (MALDI-TOF): *m/z* 2105.73; Elemental analysis: C, 75.30; H, 11.20; N, 6.65 calculated (%): C, 75.21; H,11.81; N, 6.33 (expt. %).

Compound 7c: **5** (0.200g, 0.723mmol, 1eq), **6c** (2.00g, 2.459mmol, 3.4eq), toluene 40ml, yield: 52%, IR (film) υmax:3390, 2953, 2922, 2852, 1649, 1597, 1502, 1454, 1377, 1224, 1120, 771, 721 cm−1; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.70 – 7.56 (b d, 1H), 7.32 – 7.31 (b d, 2H), 6.84 – 6.73 (m,6H), 3.96 – 3.89 (m, 18H), 1.78 - 1.69 (m, 18H), 1.46 – 1.41(m, 19H), 1.30 -1.25 (m, 218H), 0.87 (t, 27H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 162.74, 162.61, 162.51, 156.32, 155.69, 155.59, 155.06, 153.20, 152.94, 135.97, 132.18, 131.98, 102.62, 102.06, 101.43, 101.09, 73.57, 69.35, 69.20, 31.95, 30.39, 29.77, 29.70, 29.56, 29.45, 29.40, 26.20, 22.70, 14.11; Mass (MALDI-TOF): *m/z* 2610.57; Elemental analysis: C, 77.30; H, 11.82; N, 5.37 calculated (%): C, 76.80; H, 12.25; N, 4.83 (expt. %).

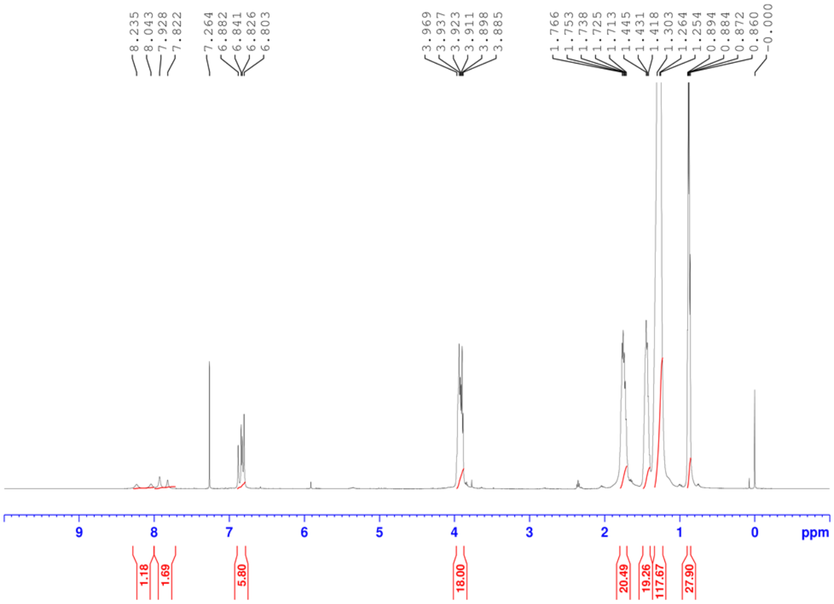
Note:

In ^{1}H NMR and ^{13}C NMR, splitting of the (N-H) protons, aromatic protons and carbon peaks was observed. This could be because the peripheral nitrogen atoms are co-planar with heptazine core indicating an SP_2 hybridization and strong delocalization of the lone pair electrons of nitrogen on to the hetazine [2-4]

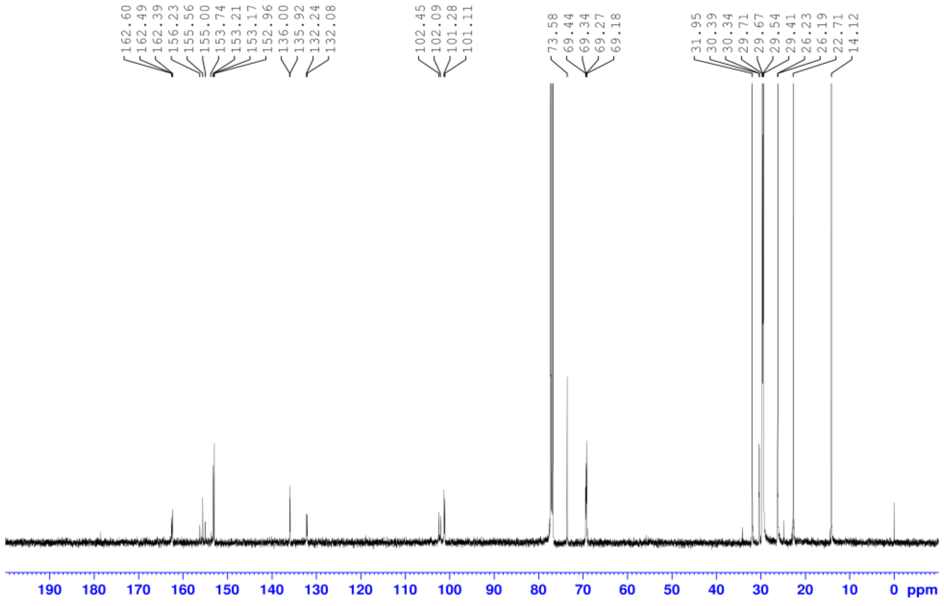
^{13}C NMR Spectra of 5



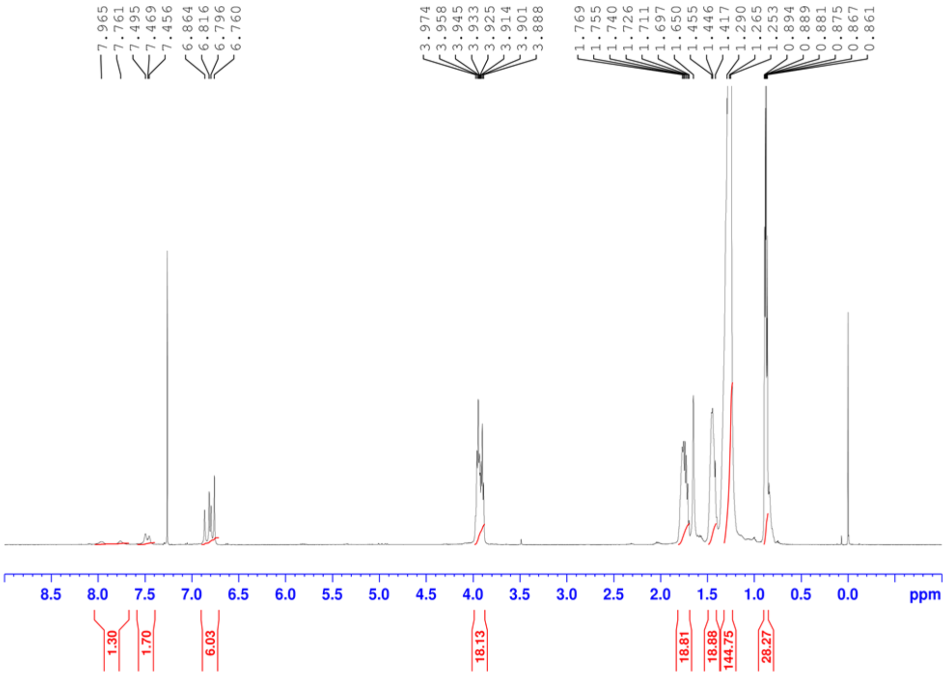
^{1}H NMR Spectra of 7a



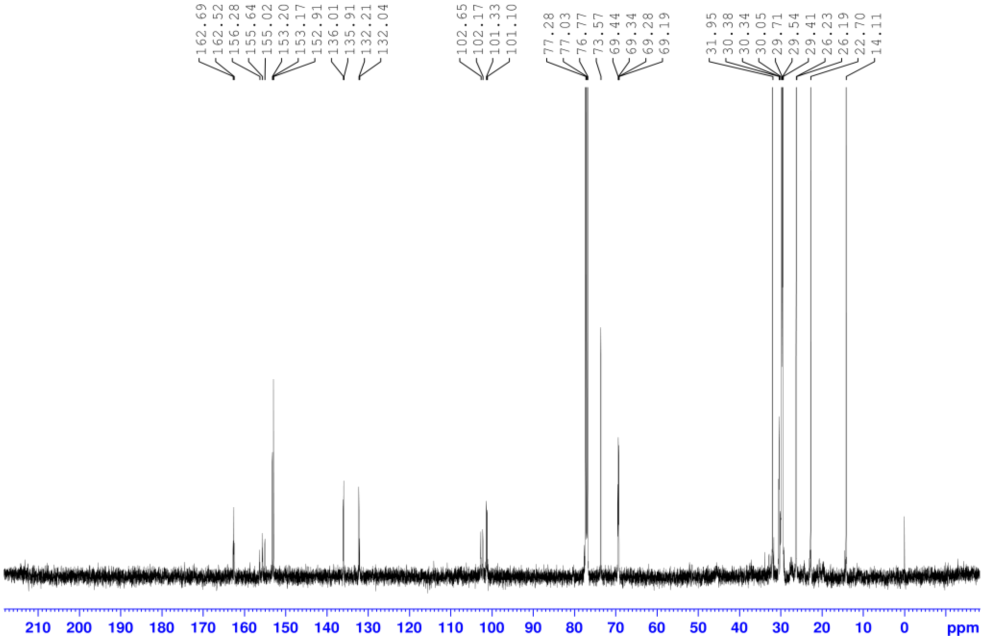
^{13}C NMR Spectra of 7a



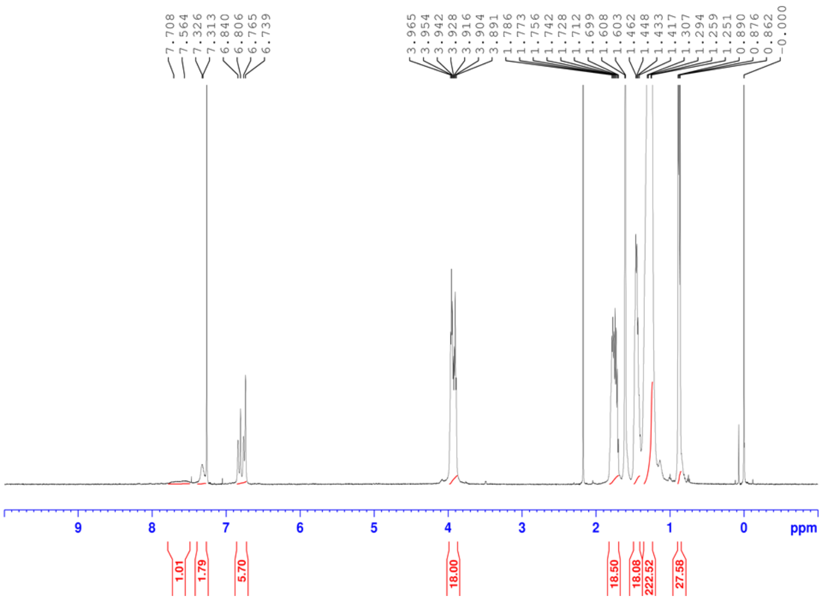
^{1}H NMR Spectra of 7b



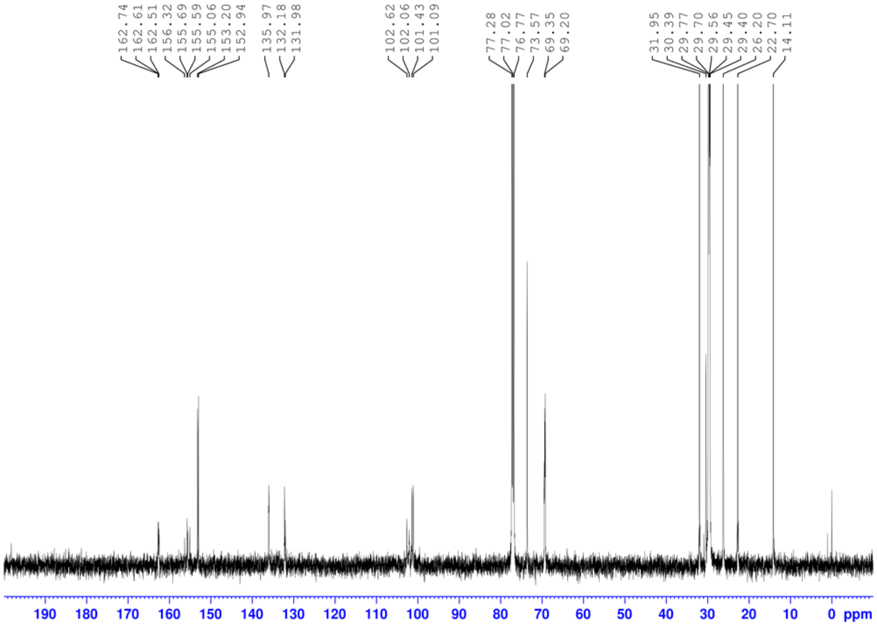
^{13}C NMR Spectra of 7b



^{1}H NMR Spectra of 7c



^{13}C NMR Spectra of 7c



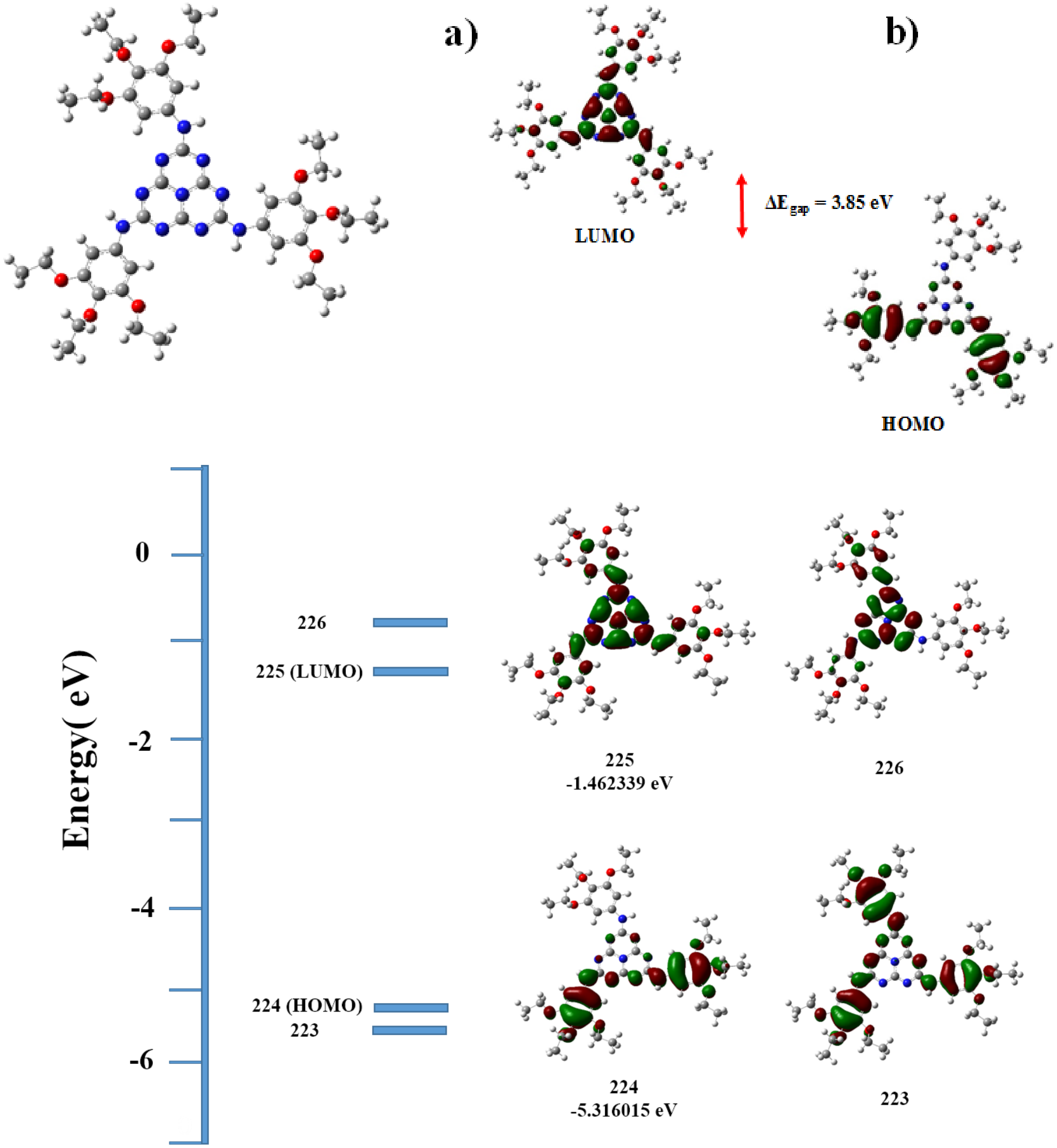


Figure S1. a) Energy-minimized structure; **b)** HOMO and LUMO Energy gap; **c)** energy level diagrams of heptazine derivative calculated by using **B3LYP** employing the **6-31G(d)** basis set.

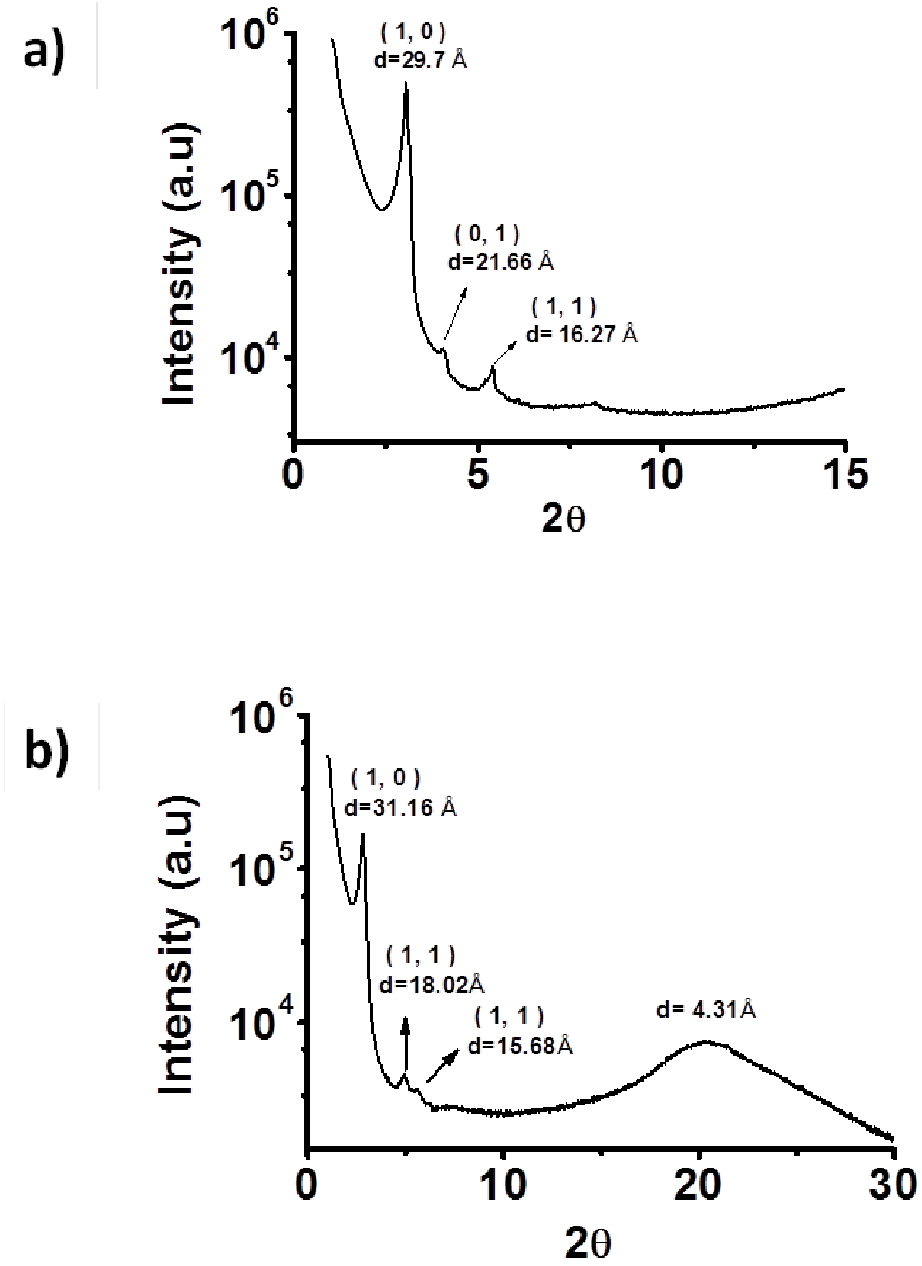


Figure S2. The one-dimensional intensity versus 2θ profile derived from X-ray diffraction. **a) 7a** at room temperature, **b) 7b** at room temperature **c) 7b** at 80 °C.

Compounds	**T (°C)**	**d-spacing(Å)**	**Phase type**	**Lattice parameter(Å)**
7a	RT	29.7 (10), 21.6 (01), 16.27 (11)	Col_{ob}	a = 30.10, b =21.95, γ = 99.44
	100	28.07(10), 16.51 (11), 4.33	Col_{h}	a = 32.41
7b	RT	31.16 (10), 18.02 (11), 15.68 (20) 4.31	Col_{h}	a = 35.98
	80	30.32 (10), 17.42 (11), 15.03 (20), 11.38 (21), 4.44	Col_{h}	a = 35.01
7c	60	35.77 (10), 20.51 (11), 17.78 (20), 13.39 (21), 4.50	Col_{h}	a = 41.30

Table S1: Layer spacing obtained from XRD for **7a, 7b, 7c**

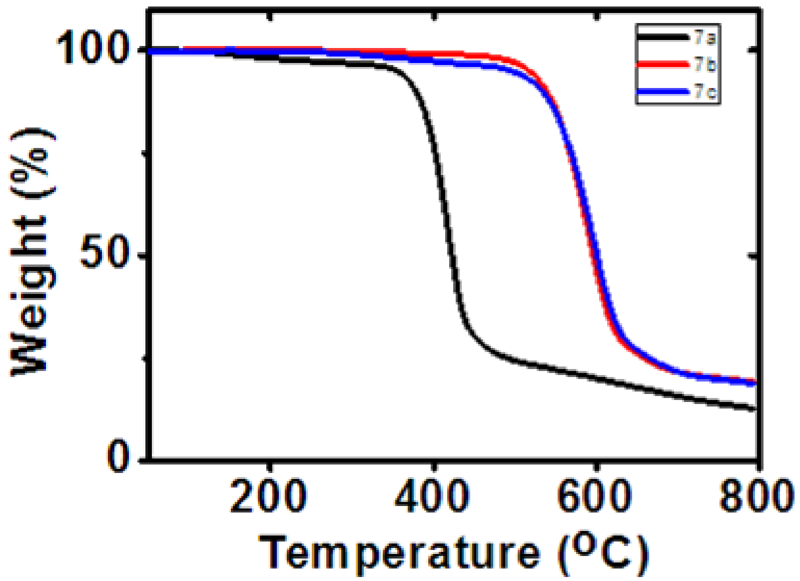


Figure S3. TGA spectra of **7a, 7b** and **7c** which show excellent thermal stability of the three compounds.

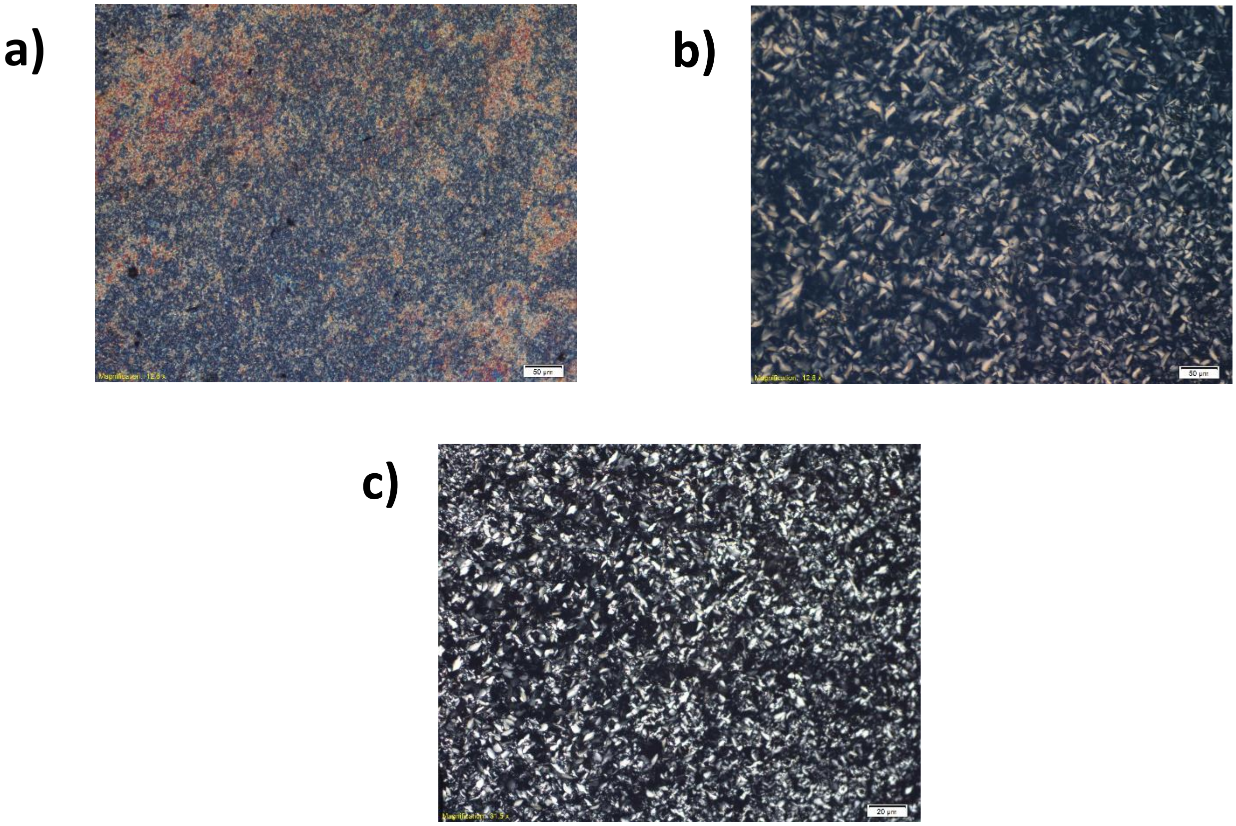


Figure S4. Birefringence texture observed under POM: a**)** compound **7b** at room temperature and **b)** compound **7b** mosaic texture observed on cooling from the isotropic phase at 103 °C. **c)** compound **7c,** mosaic texture observed on cooling from the isotropic phase at 60 °C.

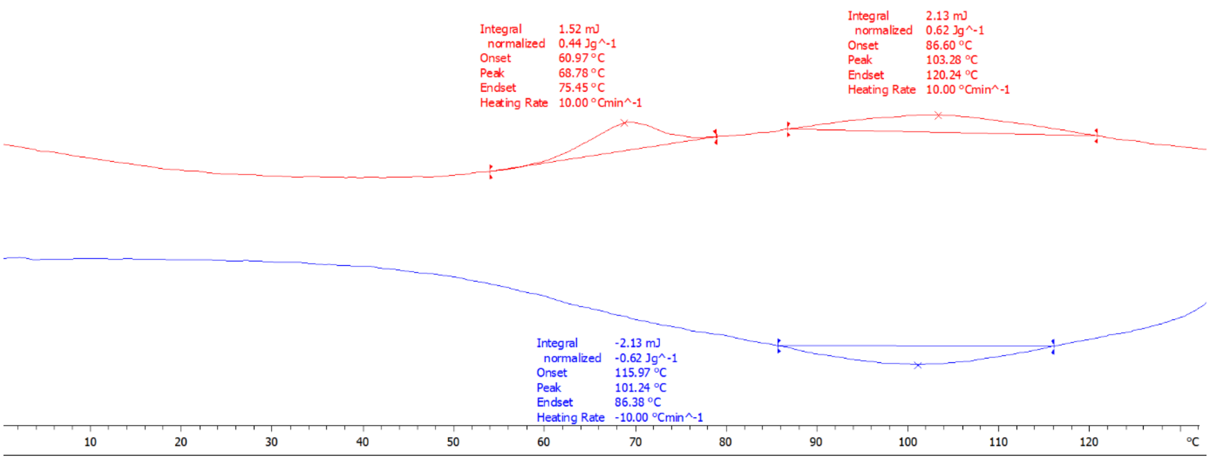


Figure S5. DSC thermograms obtained for **7a** on heating and cooling cycles at a scan rate of 10°C/min.

Compound 7b does not show any peak in the DSC. This could be because of the highly disordered nature of the mesophase or because of the limited amount of material (2-3 mg) taken for the DSC. Paucity of the material at this moment prevented more detailed studies which will be reported in future.

1. F. Weinrotter, K. Wegleitner, and W. Muller, US Patent 4008234, Feb. 15, 1977.
2. A. Zambon, J.-M. Mouesca, C. Gheorghiu, P. A. Bayle, J. Pécaut, M. Claeys-Bruno, S. Gambarelli and L. Dubois, *Chem. Sci.*, 2016, **7**, 945–950.
3. A. Schwarzer and E. Kroke, New J. Chem., 2011, **35**, 953.
4. B. Jurgens, E. Irran, J. Senker, P. Kroll, H. Muller and W. Schnick, *J. Am. Chem. Soc.*, 2003, **125,** 10288.