Reversibly photoswitchable alkoxy azobenzenes connected benzenetricarboxamide discotic liquid crystals with perpetual long range columnar assembly

Sudha Devi,[a,b] Indu Bala,[a,b] Santosh Prasad Gupta,[c] Pravesh Kumar,[a] Santanu Kumar Pal*[a] & Sugumar Venkataramani*[a]

[a]Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER), Mohali Sector-81, Knowledge city, Manauli-140306, India.
E-mail: skpal@iisermohali.ac.in and sugumarv@iisermohali.ac.in
[b]Equally contributed
[c]Department of Physics, Patna University, Patna- 800005

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1. General methods:

All the reactions have been carried out under argon or nitrogen atmosphere and the glass wares are dried in oven as well as under vacuum by heating. The reagents (AR grade or LR grade) and solvents were purchased from commercially available sources such as Sigma Aldrich, Merck and TCI etc. Anhydrous solvents for the reactions and for column chromatography have been distilled before use. All the intermediate products have been synthesised by following literature procedure starting from 4-aminoacetanilide and phenol. The NMR spectra have been recorded in Bruker Avance-III 400 MHz spectrometer. ^{1}H and ^{13}C NMR were recorded at operation frequencies 400 MHz and 100 MHz, respectively. For recording the samples, $CDCl_3$ and DMSO-d_6 have been used as the solvents. The chemical shift (δ) values are reported in parts per million (ppm) and the coupling constants (*J*) are reported in Hz. In all the cases the signals due to residual solvents in $CDCl_3$ (7.26 ppm) and DMSO-d_6 (2.50 ppm) have been used for internal calibration. High resolution mass spectra have been recorded using Waters Synapt G2-Si Q-TOF mass spectrometer. HRMS were obtained from a TOF mass analyser using electrospray ionization (ESI) in both positive and negative modes. Melting points were recorded on SMP20 melting point apparatus, which are uncorrected. FT-IR spectra were recorded on a Perkin-Elmer ATR spectrometer. Column chromatography was performed over silica gel (100–200 mesh) using EtOAc/hexane as an eluent. Thin layer chromatography was performed on Merck Silica gel 60 F_{254} TLC plates and visualized using UV (λ = 254 nm) chamber or iodine stain. UV-Vis photoswitching and kinetics studies have been performed either using a Cary 5000 spectrophotometer. For forward photoswitching (*E-Z* isomerization) samples were irradiated at 365 nm using a LED light source either from Applied Photophysics, SX/LED/360 with bandwidth 20 nm or a commercial 3W/9W LED light sources. The reverse isomerization has been induced by using either a 35 W CFL lamp. The PSS has been established by irradiating the sample for prolonged time such that no further spectral change is observed.

Polarised Optical Microscopy (POM): Textural observations of the mesophase were performed with Nikon Eclipse LV100POL polarising microscope provided with a Linkam heating stage (LTS 420). All images were captured using a Q-imaging camera.

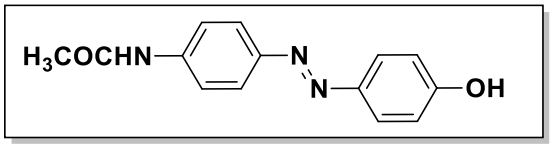
DSC Studies: The transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter (Perkin Elmer DSC 8000 coupled to a controlled liquid nitrogen accessory (CLN 2)) which was operated at a scanning rate of 10 °C min^{-1} both on heating and cooling.

X-ray diffraction studies: X-ray diffraction (XRD) was carried out using Cu Kα (λ=1.54 Å) radiation from a source (GeniX 3D, Xenocs) operating at 50 kV and 0.6 mA. The diffraction patterns were collected on a two module Pilatus detector.

Atomic Force Microscopy: Atomic force microscopy (AFM) was performed using Nano wizard 3, JPK Instruments, Germany. The images were acquired by Olympus, OMCL-TR400PSA-1. All AFM output files were analysed in JPK data processing software.

2. Synthesis of 7a-c/8a target compounds:

(a) **Synthesis of (*E*)-*N*-(4-((4-hydroxyphenyl)diazenyl)phenyl)acetamide (2)**



A mixture of *p*-aminoacetanilide (3.3 g, 22 mM) and deionized water in a two neck round bottom flask was cooled to 0 ºC. To this 37% conc. HCl (6.5 mL) was added and stirred to get a clear solution. Then a cold aqueous solution of sodium nitrite (1.52 g, 22 mM in 20 mL of water) was added dropwise into the reaction mixture. After the addition, the diazonium salt started forming. The reaction mixture was allowed to stir for half an hour for completion. After half an hour, at 0 ºC a cold aqueous solution of sodium acetate (5.9 g, 70 mM) and phenol (2.16 g, 23 mM in 100 mL of water) was added. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered off and to obtain a orange solid product, which was dried under vacuum to yield the desired product. Dark orange Solid, 2h, Yield = 91%, M.P = 157-161 ºC.

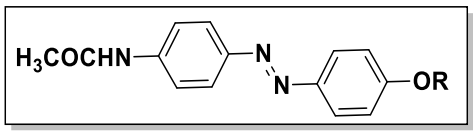
^{1}H NMR (400 MHz, DMSO-d$_6$), δ (ppm) = 2.10 (s, 3H, -$COCH_3$), 6.92-6.94 (d, *J* = 8.4 Hz, 2H), 7.74-7.78 (m, 2H), 10.30 (s, 1H, -OH).

^{13}C NMR (100 MHz, DMSO-d$_6$): δ(ppm) = 24.59,116.43, 119.58, 123.45, 124.97, 141.87, 145.52, 148.02, 161.42, 169.19.

HRMS (ESI): m/z [M+H]$^+$- calcd for **$C_{14}H_{14}N_3O_2$** : 255.1008, found 256.1086.

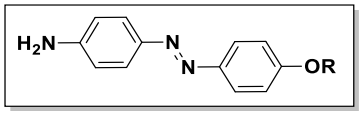
IR (ATR, cm^{-1}): 640, 675, 834, 965, 1142, 1226, 1264, 1322, 1369, 1401, 1500, 1529, 1587, 1651, 2586, 2660, 2789, 2920, 2998, 3043, 3341.

(b) General procedure for synthesis of (*E*)-*N*-(4-((4-alkoxyphenyl)diazenyl)phenyl)acetamide (3a-c)



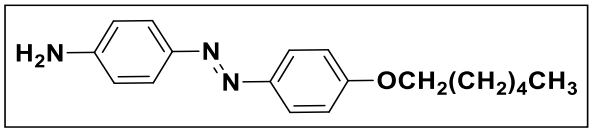
To a dry DMF (35 mL) solution of compound **1** (3.7 g, 14.5 mM), potassium carbonate (20.04 g, 14.5 mM) and pinch of potassium iodide have been charged and stirred at RT. After ten minutes alkyl bromide (2.4 g, 14.5 mM) was added slowly and then the reaction mixture was heated to 100 ºC. The reaction was monitored by TLC and after the completion, the DMF was evaporated under vacuum. The crude compound was used for the hydrolysis step without further purification. (5 h)

(c) General procedure for synthesis of (*E*)-4-((4-alkoxyphenyl)diazenyl)aniline (4a-c)



To the crude p-alkyloxyazoacetanilide derivatives (**3a-c**) (1.75 g, 5.16 mM) in ethanol (150 mL), 37% con. HCl (4 mL) was addded and let it refluxed. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was neutralised by adding aqueous sodium bicarbonate solution. The extraction of the reaction mixture was done in ethyl acetate. The extracted organic layer was washed with brine solution and evoprated to dryness and was subjected to purification by column chromatography. (Eluent: ethylacetate:n-hexane 20:80); **4a**-Orange Solid, 8 h, Yield = 82%, M.P = 96-99 ^{o}C; **4b**- Orange Solid, 8 h, Yield = 84%, M.P = 105-108 ^{o}C; **4c**- Orange Solid, 8 h, Yield = 84%, M.P = 111-113 ^{o}C.

(*E*)-4-((4-(hexyloxy)phenyl)diazenyl)aniline: **(4a)**



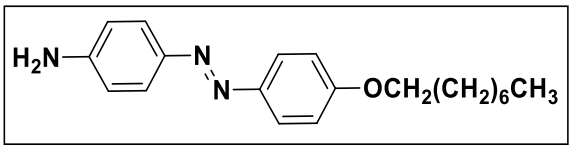
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 0.92-0.96 (t, *J* = 7.0 Hz, 3H), 1.36-1.40 (m, 4H), 1.48-1.50 (m, 2H), 1.82-1.85 (quin., 2H), 4.02 (br, 2H, -NH_2), 4.03-4.06 (t, *J* = 6.6 Hz, 2H), 6.75-6.77 (d, *J* = 8.7 Hz, 2H), 6.99-7.01 (d, *J* = 8.9 Hz 2H), 7.78-7.80 (d, *J* = 8.7 Hz, 2H), 7.84-7.87 (d, *J* = 8.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 14.07, 22.63, 25.73, 29.21, 31.61, 68.30, 114.63, 114.74, 124.04, 124.64, 145.66, 147.05, 148.93, 160.81.

HRMS (ESI): m/z $[M+H]^+$ calcd for **$C_{18}H_{24}N_3O$**: 298.1919, found 298.1906.

IR (ATR, cm^{-1}): 633, 717, 825, 1008, 1112, 1130, 1240, 1299, 1384, 1498, 1580, 2000, 2854, 2923, 3037, 3379, 3481.

(*E*)-4-((4-(octyloxy)phenyl)diazenyl)aniline: (4b)



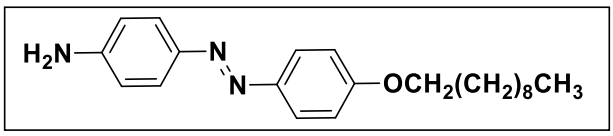
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 0.91-0.94 (t, ***J* = 6.8 Hz**, 3H), 1.32-1.37 (m, 8H), 1.46-1.54 (m, 2H), 1.81-1.85 (quin., 2H), 4.01 (br, 2H, -NH_2), 4.02-4.05 (t, ***J* = 6.5 Hz,** 2H), 6.74-6.76 (d, ***J* = 8.6 Hz,** 2H), 6.99-7.02 (d, ***J* = 8.9 Hz** 2H), 7.79-7.81 (d, ***J* = 8.6 Hz,** 2H), 7.86-7.88 (d, ***J* = 8.8 Hz,** 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 14.17, 22.71, 26.07, 29.27, 29.29, 29.41, 31.86, 68.32, 114.66, 114.74, 124.06, 124.66, 145.63, 147.06, 149.00, 160.82.

HRMS (ESI): m/z [M+H]$^+$ calcd for **$C_{20}H_{28}N_3O$** : 326.2232, found 326.2247.

IR(ATR, cm^{-1}): 632, 716, 826, 1010, 1132, 1239, 1297, 1387, 1460, 1494, 1582, 2548, 2853, 2922, 3037, 3192, 3380, 3480.

(*E*)-4-((4-(decyloxy)phenyl)diazenyl)aniline: **(4c)**

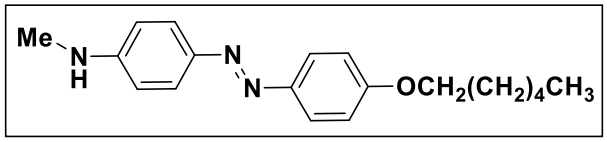


^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 0.92-0.93 (t, *J* = 6.7 Hz, 3H), 1.31-1.36 (m, 12H), 1.48-1.52 (m, 2H), 1.82-1.85 (quin., 2H), 4.01 (br s, 2H, -NH_2), 4.03-4.06 (t, *J* = 6.5 Hz, 2H), 6.75-6.77 (d, *J* = 8.1 Hz, 2H), 6.99-7.01 (d, *J* = 8.2 Hz, 2H), 7.78-7.80 (d, *J* = 7.8 Hz, 2H), 7.85-7.87 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 14.15, 22.70, 26.04, 29.25, 29.34, 29.42, 29.58, 29.59, 31.91, 68.31, 114.63, 114.72, 124.03, 124.63, 145.66, 147.05, 148.92, 160.80.

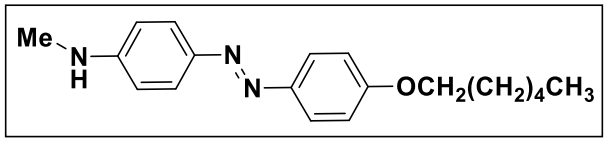
HRMS (ESI): m/z [M+H]$^+$- calcd for **$C_{22}H_{32}N_3O$**, theoretical: 354.2545; found 354.2545. **IR(ATR, cm^{-1}):** 634, 714, 829, 1014, 1057, 1139, 1238, 1303, 1392, 1462, 1499, 1584, 2642, 2851, 2914, 3040, 3205, 3346, 3476.

(d) Procedure for synthesis of (*E*)-4-((4-alkoxyphenyl)diazenyl)aniline (4a-NMe)



To the compound **4a** (100 mg, 0.32 mmol) dissolved in 15 ml methanol in 50 ml round bottom flask, formaldehyde solution (37 %) (0.4 mmol) was added. At 0 °C, the solution was stirred for 30 minutes and $NaCNBH_3$ (0.51 mmol) is added portion wise over 1 hour. The reaction completion was checked by TLC. The solvent was evaporated under vacuum and the product was extracted by using ethylacetate. The extracted organic layer was washed with brine solution, dried with anhydrous sodium sulphate and evaporated to dryness and was subjected to purification by column chromatography. (Eluent: ethylacetate:n-hexane, 1:19); Orange Solid, 2 h, Yield = 32 %, M.P = 76-78 ^{o}C.

(*E*)-4-((4-(hexyloxy)phenyl)diazenyl)-*N*-methylaniline: **(4a-NMe)**



^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 0.90-0.93 (t, *J* = 6.2 Hz, 3H), 1.35-1.37 (m, 4H), 1.44-1.51 (m, 2H), 1.77-1.84 (m, 2H), 2.91 (s. 3H), 4.00-4.03 (t, *J* = 6.6 Hz, 2H), 4.16 (br s, 1H, -NH-CH_3), 6.64-6.66 (d, *J* = 8.8 Hz, 2H), 6.96-6.98 (d, *J* = 8.9 Hz, 2H), 7.80-7.84 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 14.11, 22.74, 25.84, 29.34, 30.56, 31.72, 68.40, 112.01, 114.73, 123.98, 124.85, 144.81, 147.30, 151.47, 160.67.

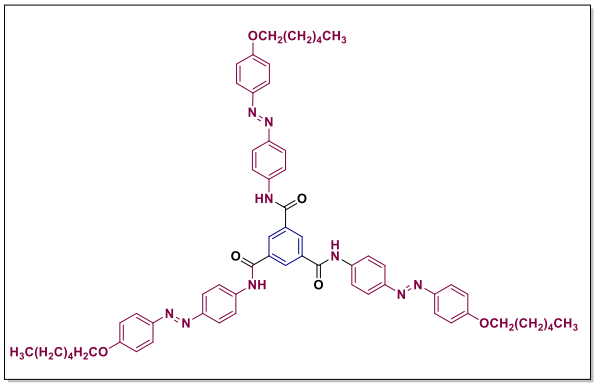
HRMS (ESI): m/z [M+H]$^+$- calcd for **$C_{19}H_{25}N_3O$**, theoretical: 312.2076; found: 312.2064.

IR (ATR, cm^{-1}): 3364, 2956, 2935, 2923, 2907, 2868, 2851, 2821, 1599, 1578, 1521, 1498, 1464, 1430, 1394, 1338, 1320, 1275, 1239, 1156, 1142, 1109, 1057, 1026, 988, 825, 800, 63, 724, 640, 619, 541, 506.

(e) General procedure for the synthesis of long chain triamide (7a-c/8a)

To the trimesic acid (0.05 g, 0.24 mM) in a two neck round bottom flask dry toluene (25 mL) was added under the argon atmosphere. To the insoluble reaction mixture, PCl_5 (0.25 gm, 1.2 mmol) was added in portions. After the complete addition of PCl_5, the reaction mixture was refluxed upto the formation of a transparent reaction mixture. (Note: The trimesylchloride is highly sensitive to moisture) A mixture of **4a-c/4a-NMe** (0.354 g, 1.2 mM), pyridine (0.19 g, 2.4 mM) and dry toluene (50 mL) have been taken in a two neck round bottom flask and stirred for ten minutes under argon atmosphere and cooled to 0 ^{o}C. Now trimesyl chloride solution in toluene from the previous stage of the reaction was carefully transferred into this reaction mixture. The reaction mixture was then allowed to stir at room temperature and the reaction was monitored by TLC. After the completion of the reaction, the toluene was evaporated in rotavap. Then the crude product was purified by column chromatography on silica gel (EtOAc:n-hexanes = 40:60) to obtain a pure product as dark orange colour solids. **7a**- Dark orange solid, 8 h, Yield = 76%, M. P.= 238 °C ; **7b**- Orange Solid, 10 h, Yield = 72%, M. P.= 190 °C; **7c**- Orange Solid, 10 h, Yield = 75%, M. P.= 175 °C; **8a**- orange solid, 10 h, Yield = 40%, M. P.= 173-174 °C.

***N*^{1},*N*^{3},*N*^{5}-tris(4-((*E*)-(4-(hexyloxy)phenyl)diazenyl)phenyl)benzene-1,3,5-tricarboxamide (7a):**



^{1}H NMR (400 MHz, DMSO), δ (ppm) = 0.87-0.90 (t, *J* = 6.9 Hz, 9H), 1.23-1.32 (m, 12H), 1.40-1.43 (m, 6H), 1.73-1.76 (m, 6H), 4.05-4.08 (t, *J* = 6.4 Hz, 6H), 7.12- 7.13 (d, *J* = 9.0 Hz, 6H), 7.86-7.88 (d, *J* = 8.8 Hz, 6H), 7.92-7.94 (d, *J* = 8.8 Hz, 6H), 8.07-8.09 (d, *J* = 8.8 Hz, 6H), 8.81 (s, 3H), 10.94 (s, 3H). **Note**: The compound shows proper splitting in DMSO-d_6 solvent as compared to $CDCl_3$.

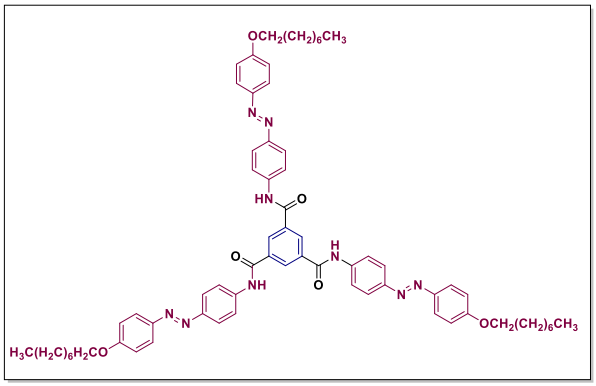
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 0.94 (t, *J* = 5.3 Hz, 9H), 1.36 (br, 12H), 1.47 (t, *J* = 5.7 Hz, 6H), 1.79 (t, *J* = 5.7 Hz, 6H), 3.92 (t, *J* = 6.6 Hz, 6H), 6.81-6.84 (d, *J* = 8.0 Hz, 6H), 7.74 (br, 21H), 9.87 (br, 3H, N-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 14.09, 22.64, 25.74, 29.26, 31.68, 68.20, 114.42, 120.43, 123.57, 124.78, 128.71, 135.70, 139.47, 146.74, 149.47, 161.32, 165.61.

HRMS (MALDI): m/z [M+H]$^+$ calcd for **$C_{63}H_{69}N_9O_6$** : 1048.5449; found 1048.5369.

IR (ATR, cm^{-1}): 624, 719, 839, 935, 1011, 1104, 1138, 1150, 1241, 1301, 1315, 1402, 1417, 1454, 1469, 1496, 1522, 1582, 1593, 1651, 1660, 2859, 2927, 3296, 3418.

***N*^{1},*N*^{3},*N*^{5}-tris(4-((*E*)-(4-(octyloxy)phenyl)diazenyl)phenyl)benzene-1,3,5-tricarboxamide (7b):**



^{1}H NMR (400 MHz, DMSO), δ (ppm) = 0.86 (t, *J* = 6.7 Hz, 9H), 1.22-1.29 (m, 24H), 1.40-1.43 (m, 6H), 1.72-1.75 (m, 6H), 4.04-4,07 (t, *J* = 5.8 Hz, 6H), 7.10-7.12 (d, *J* = 8.6 Hz, 6H), 7.85-7.87 (d, *J* = 8.4 Hz, 6H), 7.91-7.93 (d, *J* = 8.4 Hz, 6H), 8.06-8.08 (d, *J* = 8.5 Hz, 6H), 8.81 (s, 3H), 10.92 (s, 3H). **Note**: The compound shows proper splitting in DMSO-d_6 solvent as compared to $CDCl_3$.

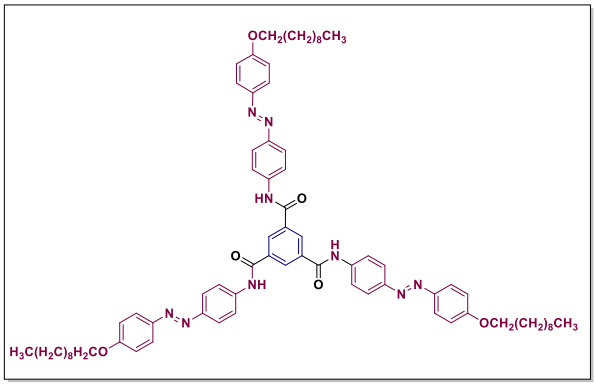
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 0.92 (t, *J* = 6.7 Hz, 9H), 1.32 (br, 24H), 1.47 (t, *J* = 6.8 Hz, 6H), 1.80 (t, *J* = 5.5 Hz, 6H), 3.94 (t, *J* = 4.3 Hz, 6H), 6.83-6.85 (d, *J* = 8.3 Hz, 6H), 7.76 (br, 21H), 9.91 (br, 3H, N-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 14.16, 22.72, 26.10, 29.32, 29.50, 31.90, 68.23, 114.42, 120.45, 123.63, 124.80, 128.73, 135.81, 139.47, 146.76, 149.54, 161.33, 165.79;

HRMS (ESI): m/z [M+H]$^+$- calcd for **$C_{69}H_{81}N_9O_6$** : 1132.6388, found 1132.6343;

IR (ATR, cm^{-1}): 623, 719, 789, 833, 910, 962, 1020, 1104, 1138, 1238, 1301, 1402, 1417, 1454, 1468, 1496, 1520, 1581, 1594, 1658, 2853, 2922, 3018, 3306.

***N*^{1},*N*^{3},*N*^{5}-tris(4-((*E*)-(4-(decyloxy)phenyl)diazenyl)phenyl)benzene-1,3,5-tricarboxamide (7c):**



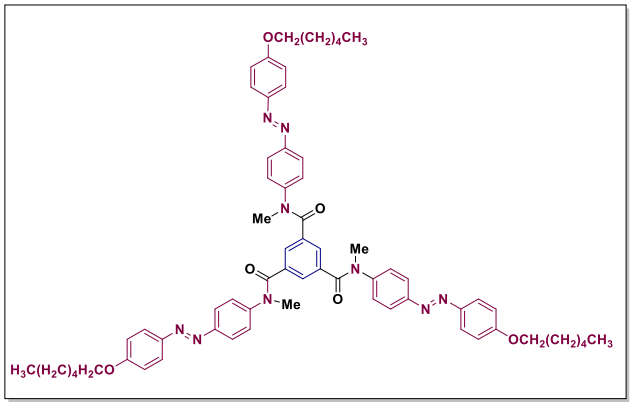
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 0.92 (t, *J* = 6.9 Hz, 9H), 1.31 (br, 28H), 1.47 (br, 6H), 1.80 (t, *J* = 6.5 Hz, 6H), 3.93 (t, *J* = 6.3 Hz, 6H), 6.83-6.85 (d, *J* = 7.7 Hz, 6H), 7.76 (br, 21H), 9.89 (br, 3H, N-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 14.17, 22.74, 26.11, 29.36, 29.42, 29.59, 29.69, 31.97, 68.23, 114.43, 120.52, 123.52, 124.77, 128.86, 135.45, 139.39, 146.69, 149.40, 161.36, 165.27.

HRMS (ESI): m/z $[M+H]^+$- calcd for **$C_{69}H_{81}N_9O_6$** : 1216.7327, found 1216.7275.

IR (ATR, cm^{-1}): 624, 719, 835, 943, 1013, 1104, 1139, 1240, 1302, 1402, 1417, 1454, 1468, 1497, 1524, 1582, 1595, 1659, 2852, 2921, 3047, 3307.

***N*^{1},*N*^{3},*N*^{5}-tris(4-((*E*)-(4-(hexyloxy)phenyl)diazenyl)phenyl)-*N*^{1},*N*^{3},*N*^{5}-trimethylbenzene-1,3,5-tricarboxamide (8a):**



^{1}H NMR (400 MHz, DMSO), δ (ppm) = 0.83-0.87 (t, *J* = 6.7 Hz, 9H), 1.25-1.28 (m, 12H), 1.34-1.39 (m, 6H), 1.65-1.70 (m, 6H), 3.28 (s, 9H), 3.97-4.00 (t, *J* = 6.5 Hz, 6H), 6.72-6.74 (d, *J* = 8.4 Hz, 6H), 6.95-6.97 (d, *J* = 9.0 Hz, 6H), 7.07 (s, 3H), 7.72-7.74 (d, *J* = 8.6 Hz, 6H), 7.83-7.85 (d, *J* = 8.9 Hz, 6H).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 0.89 (t, *J* = 6.9 Hz, 9H), 1.32-1.34 (m, 12H), 1.42-1.45 (m, 6H), 1.73-1.80 (m, 6H), 3.37 (s, 9H), 3.94-3.97 (t, *J* = 6.5 Hz, 6H), 6.54-6.56 (d, *J* =

8.2 Hz, 6H), 6.84-6.86 (d, *J* = 8.9 Hz, 6H), 7.12 (s, 3H), 7.85-7.88 (d, *J* = 8.6 Hz, 6H), 7.94-7.97 (d, *J* = 8.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 169.24, 161.13, 150.69, 146.81, 145.94, 136.38, 130.00, 127.72, 125.11, 123.86, 114.84, 68.50, 37.79, 31.66, 29.22, 25.78, 22.70, 14.14.

HRMS (ESI): m/z $[M+H]^+$ calcd for **$C_{66}H_{75}N_9O_6$** : 1090.5919, found 1090.5968.

IR (ATR, cm^{-1}): 2953, 2925, 2856, 1649, 1595, 1574, 1495, 1468, 1455, 1379, 1347, 1300, 1251, 1138, 1105, 1009, 935,897, 839, 769, 732, 703, 682, 581, 561, 516, 505.

3. Photoswitching studies:

(a) Analysis of photoswitching behaviour of 7a-c ($CHCl_3$) by UV-Vis spectroscopy

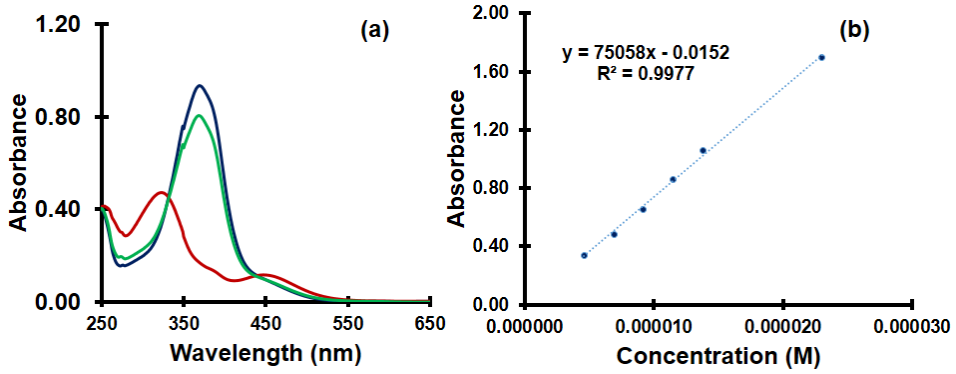


Figure S1. (a) Photoswitching studies of **7a** in $CHCl_3$; The blue spectrum is corresponding to (***E***)-**7a**, and red one is recorded after irradiation at 365 nm. The green one is recorded after irradiation using a CFL bulb (white light)) (b) Molar extinction coefficient in $CHCl_3$.

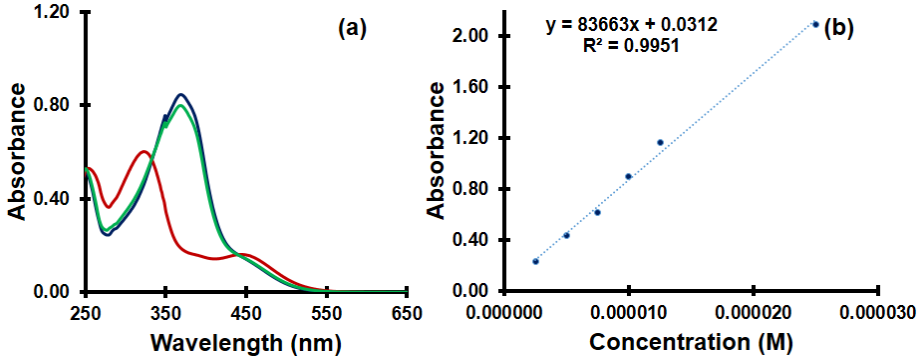


Figure S2. (a) Photoswitching studies of **7b** in $CHCl_3$; The blue spectrum is corresponding to (***E***)-**7a**, and red one is recorded after irradiation at 365 nm. The green one is recorded after irradiation using a CFL bulb (white light)) (b) Molar extinction coefficient in $CHCl_3$.

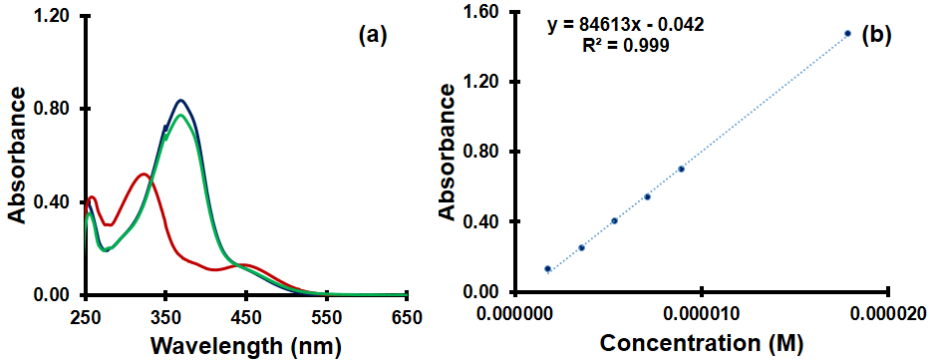


Figure S3. (a) Photoswitching studies of **7c** in $CHCl_3$; The blue spectrum is corresponding to (***E***)-**7c**, and red one is recorded after irradiation at 365 nm. The green one is recorded after irradiation using a CFL bulb (white light). (b) Molar extinction coefficient in $CHCl_3$.

(b) Analysis of photoswitching behaviour of 7a-c (DMSO) by UV-Vis spectroscopy

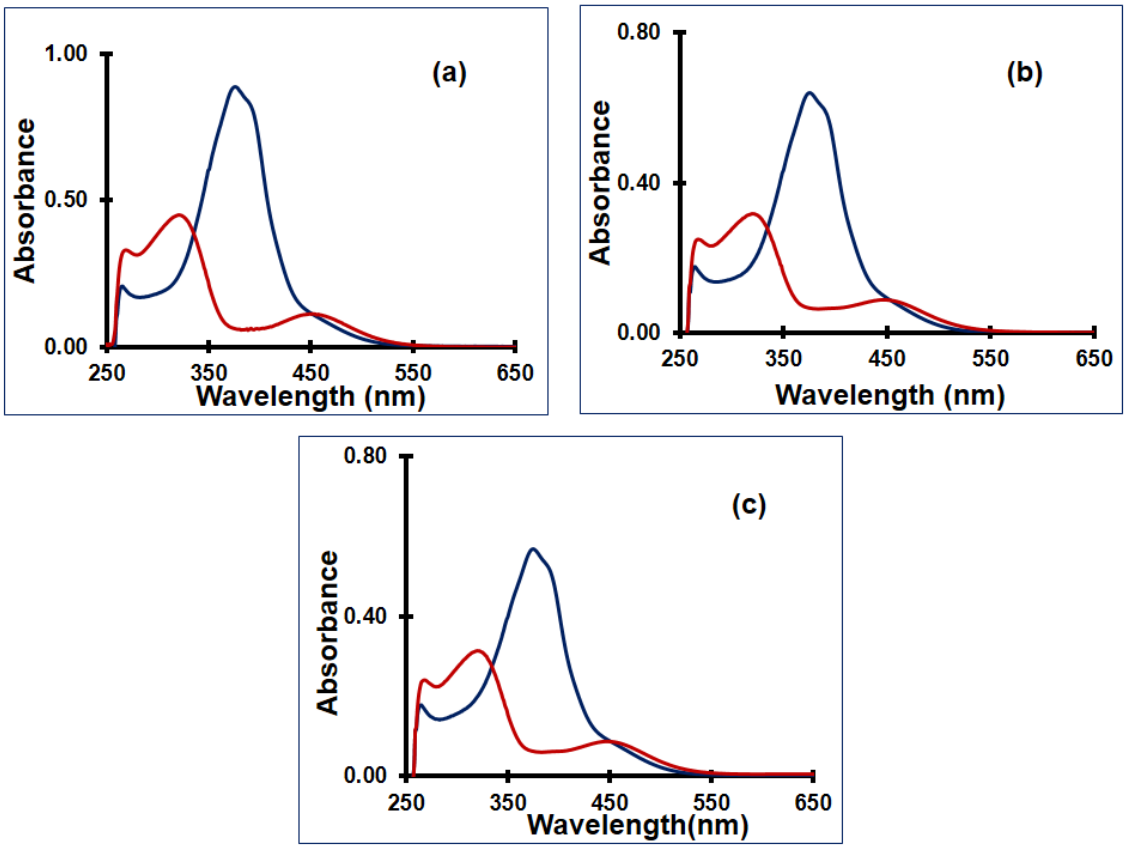


Figure S4. (a) Photoswitching studies in DMSO of (a) **7a** (b) **7b** and (c) **7c.** (The blue spectrum is corresponding to (***E***)-, and red one is recorded after irradiation at 365 nm.

(c) Analysis of photoswitching behaviour of 8a ($CHCl_3$/DMSO) by UV-Vis spectroscopy

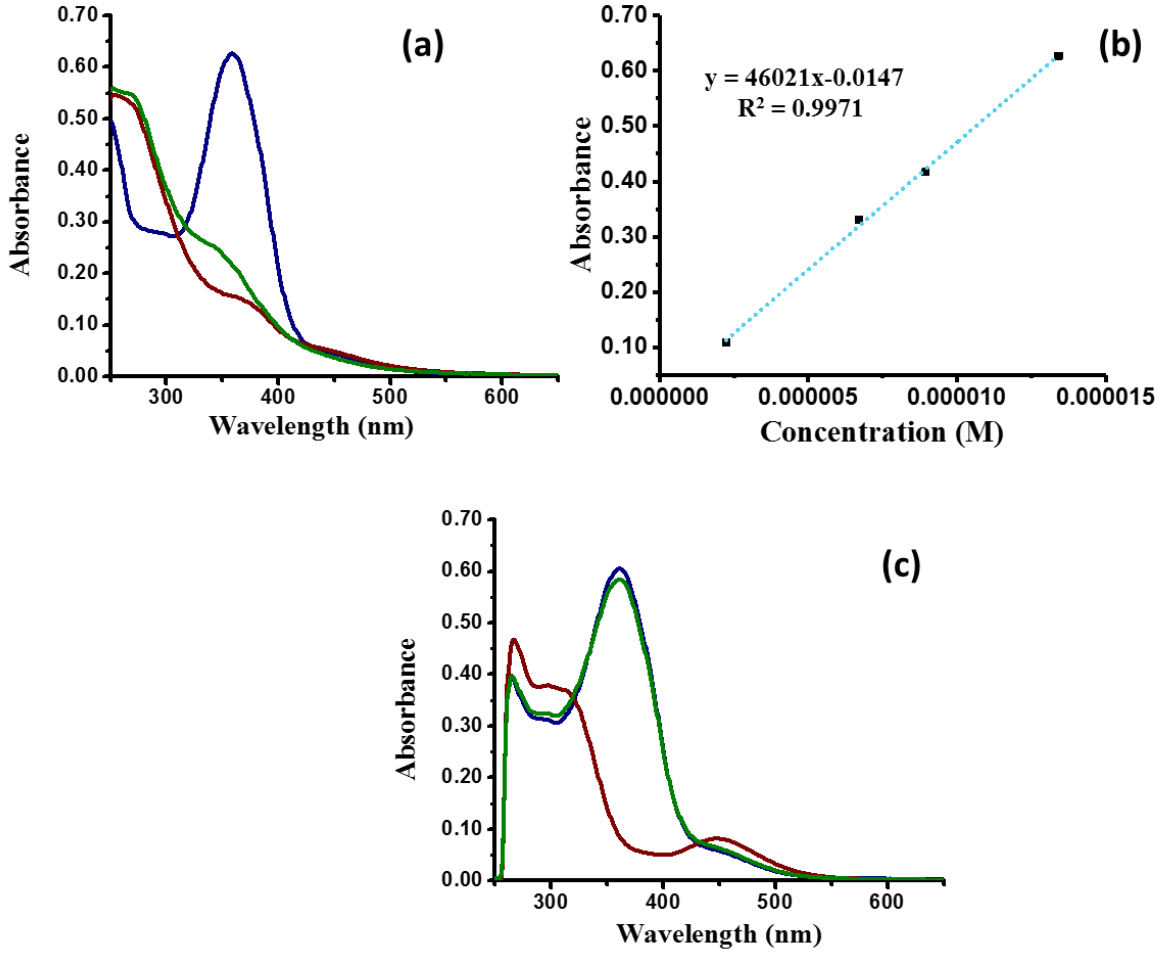


Figure S5. (a) Analysis of photoswitching behaviour of **8a** in $CHCl_3$ (13.4 μM); (b) Estimation of Molar extinction coefficient at 359 nm (π– π∗ absorption) of **8a**-*EEE* in $CHCl_3$; (c) Analysis of photoswitching behaviour of **8a** in DMSO (13.6 μM). The blue spectrum corresponds to **8a**-*EEE*, and red one is recorded after irradiation at 365 nm. The green one is recorded after irradiation using a 505 nm light.

(d) Analysis of photoswitching behaviour of 8a in solid state by UV-Vis spectroscopy

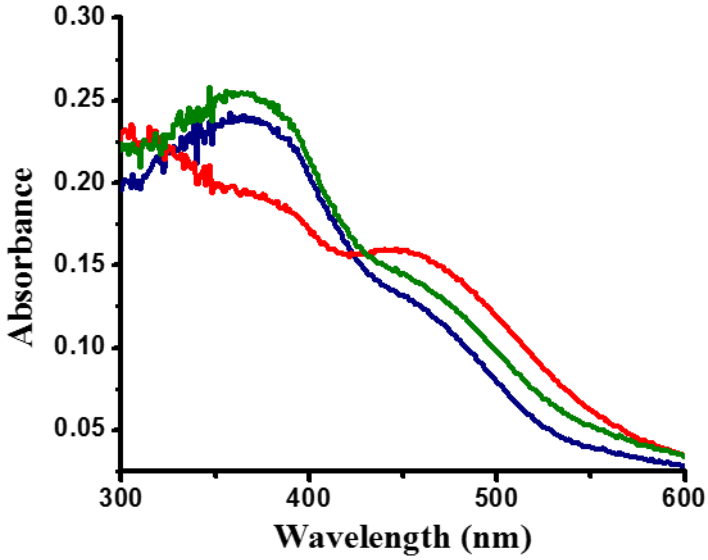


Figure S6. Analysis of photoswitching behaviour in solid state for **8a** in KBr medium. The blue coloured spectrum is due to the **8a**-*EEE* (before irradiation), whereas the red one indicates the changes after irradiation at 365 nm. The spectra appearing in green was observed after reverse switching on illuminating with 505 nm light.

(e) Analysis of photoswitching behaviour of 7a by using NMR spectroscopy

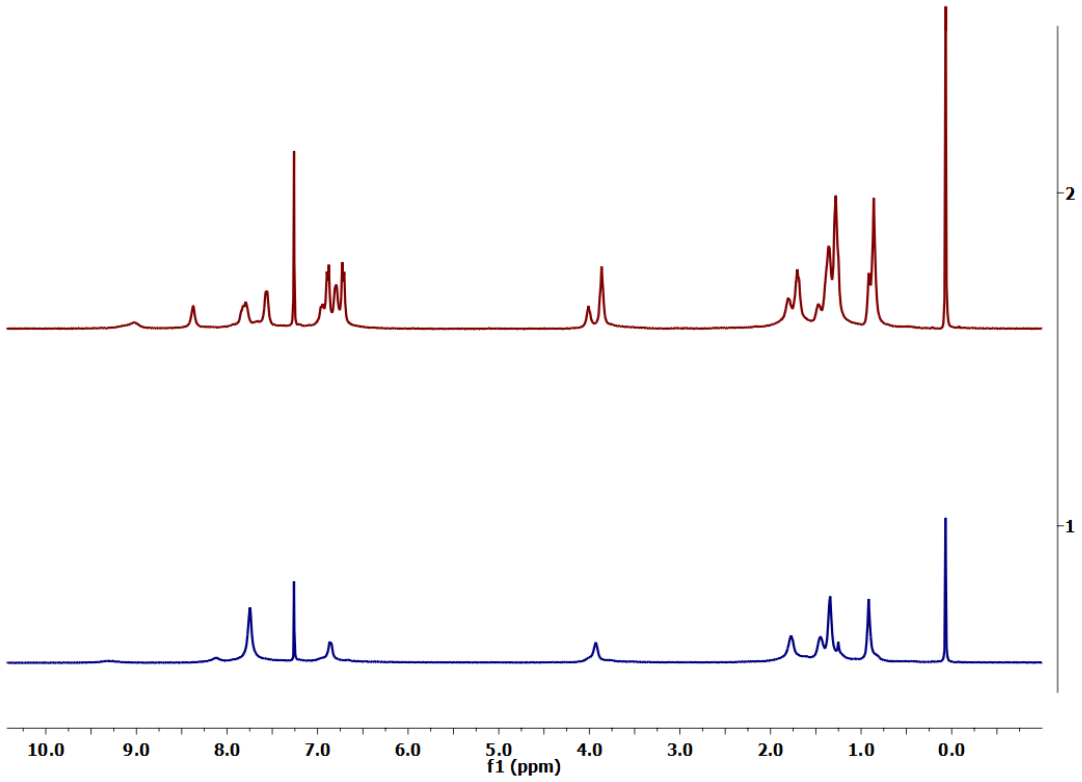


Figure S7. ^{1}H NMR spectra of (a) The spectrum (shown in blue colour) corresponds to **7a**-*EEE* (4.8 mM concentration in $CDCl_3$); (b) The spectrum (shown in red colour) corresponds to the same solution subjected to irradiation at 365 nm for 1 h.

(f) Analysis of photoswitching behaviour of 8a by using NMR spectroscopy

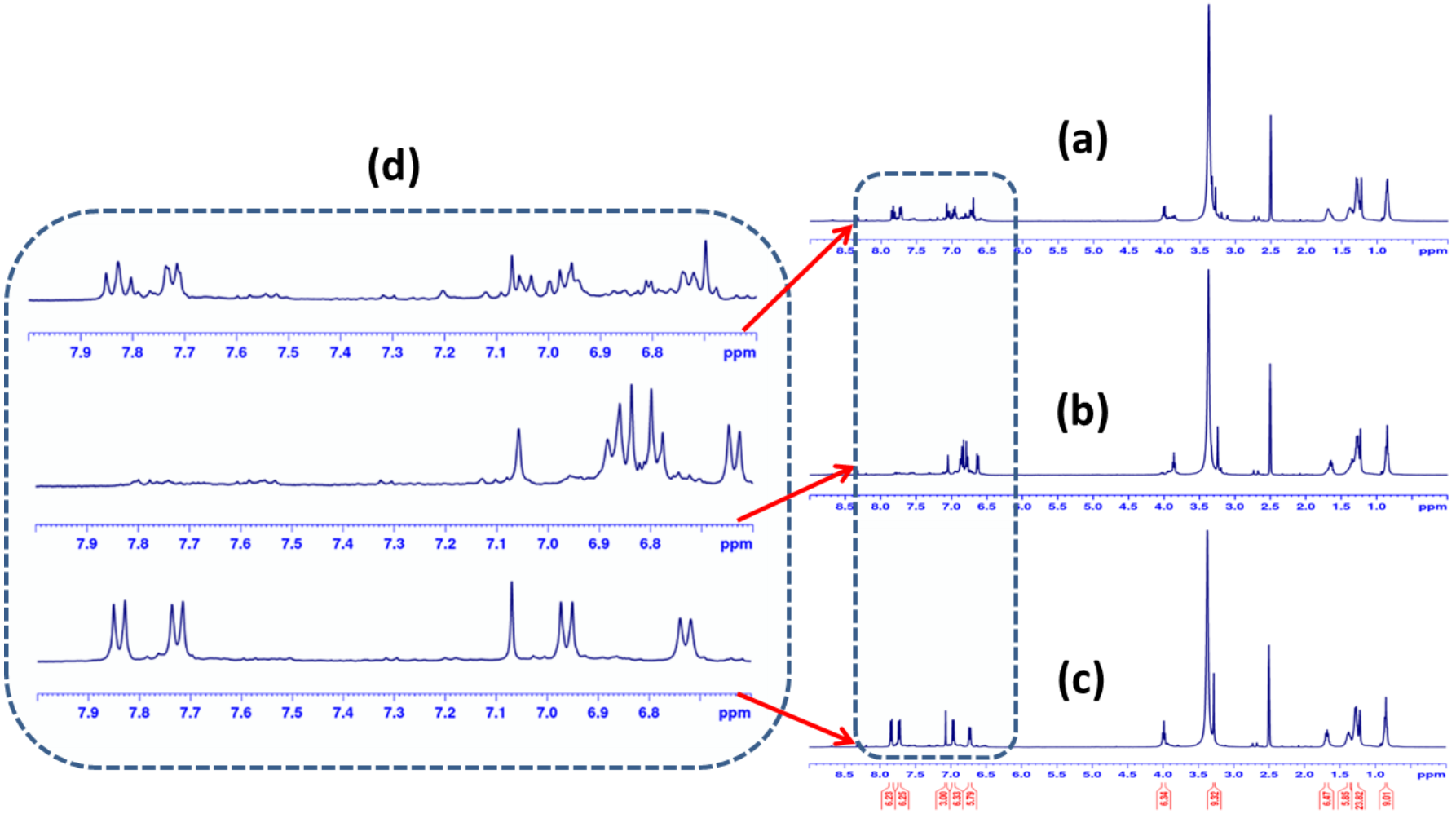


Figure S8. ^{1}H NMR spectra of **8a**-*EEE* (8.4 mM in DMSO-d_6) (a) before irradiation; (b) after irradiating with 365 nm UV light for 90 minutes; (c) after irradiating with the 505 nm light corresponding to the reverse isomerisation step; (d) Zoomed region corresponds to the aromatic protons (as insert).

4. Kinetics plots for the formation constants of 7a-*EEE* using UV-Vis spectroscopy:

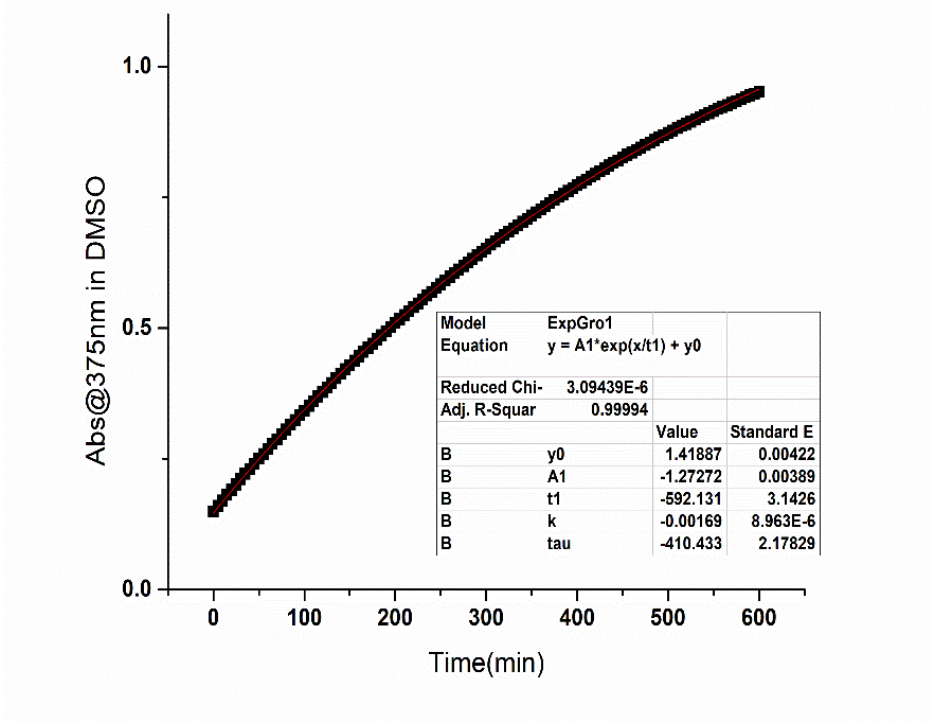


Figure S9. First order formation kinetics for the reverse switching in **7a** (10.8 mM solution in DMSO).

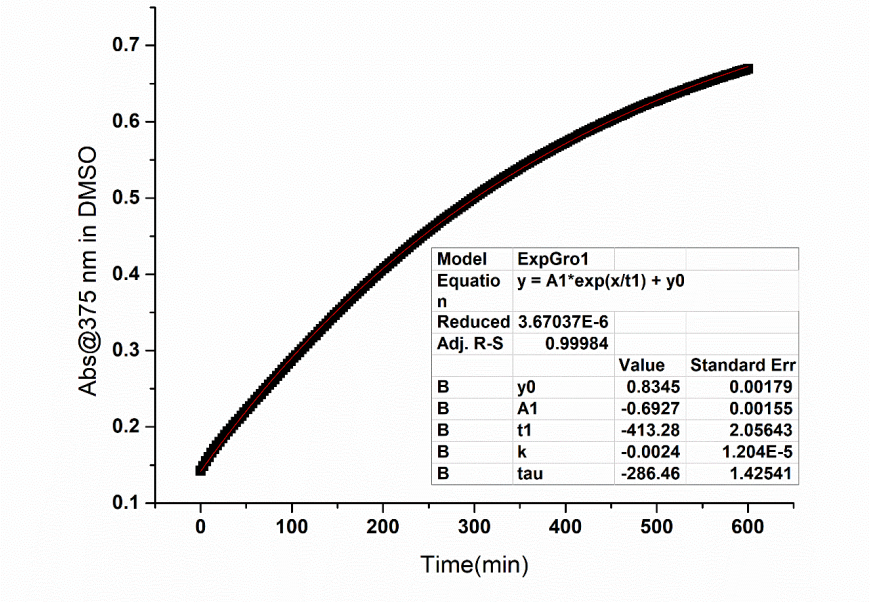


Figure S10. First order formation kinetics for the reverse switching in **7b** (8.0 mM solution in DMSO).

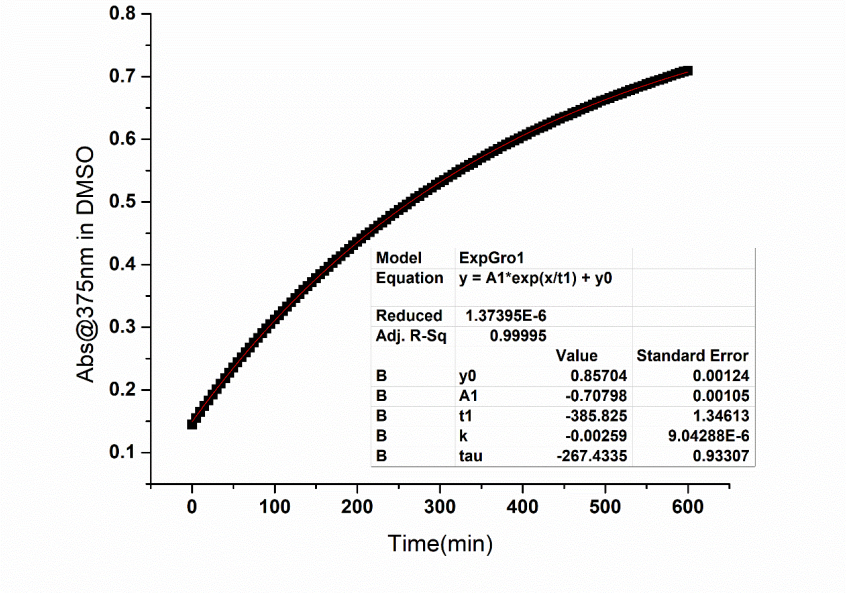


Figure S11. First order formation kinetics for the reverse switching in **7c** (7.5 mM solution in DMSO).

5. ^{1}H and ^{13}C-NMR spectral characterization data:

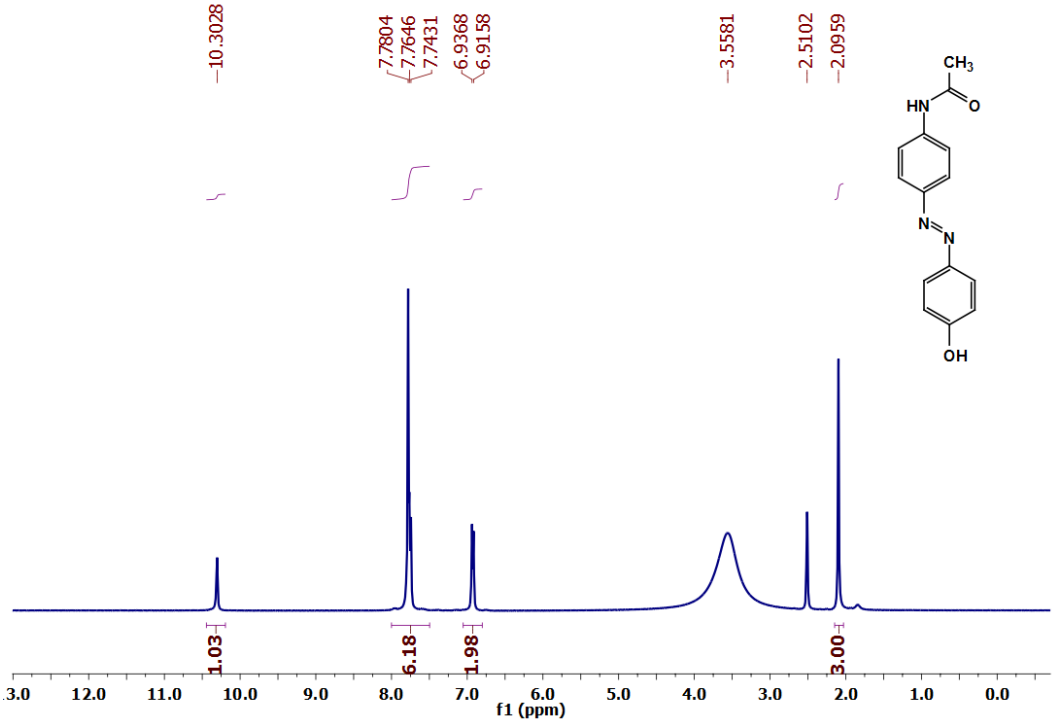


Figure S12. ^{1}H NMR spectrum of (*E*)-*N*-(4-((4-hydroxyphenyl)diazenyl)phenyl)acetamide **(2)** in $CDCl_3$.

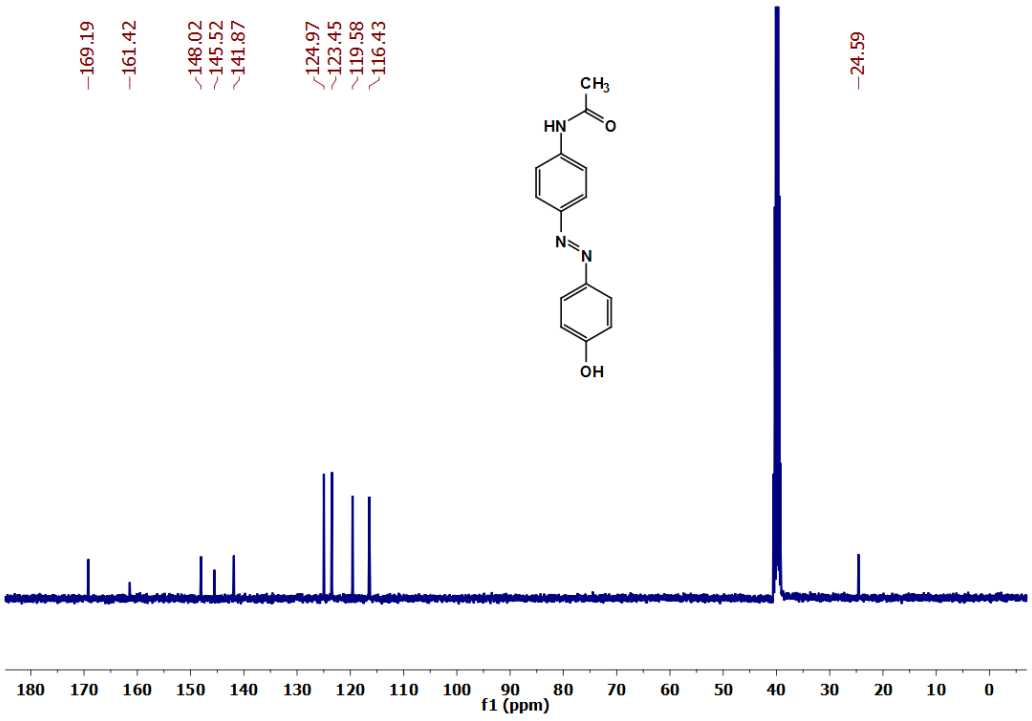


Figure S13. ^{13}C NMR spectrum of (*E*)-*N*-(4-((4-hydroxyphenyl)diazenyl)phenyl)acetamide **(2)** in $CDCl_3$.

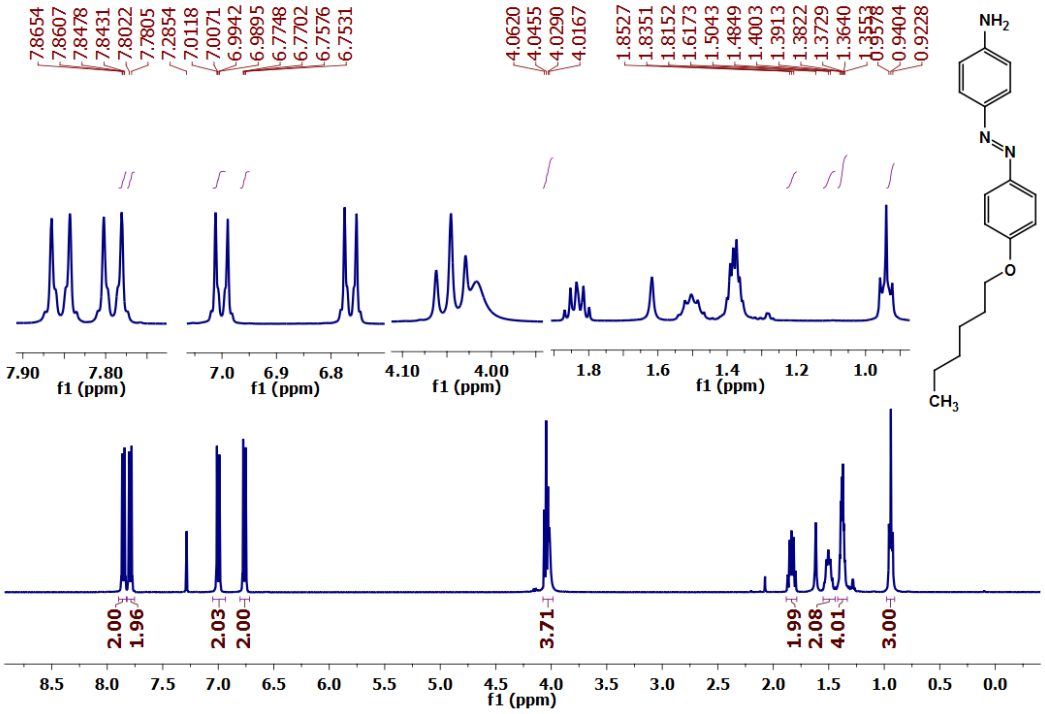


Figure S14. ^{1}H NMR spectrum of (*E*)-4-((4-(hexyloxy)phenyl)diazenyl)aniline **(4a)** in $CDCl_3$.

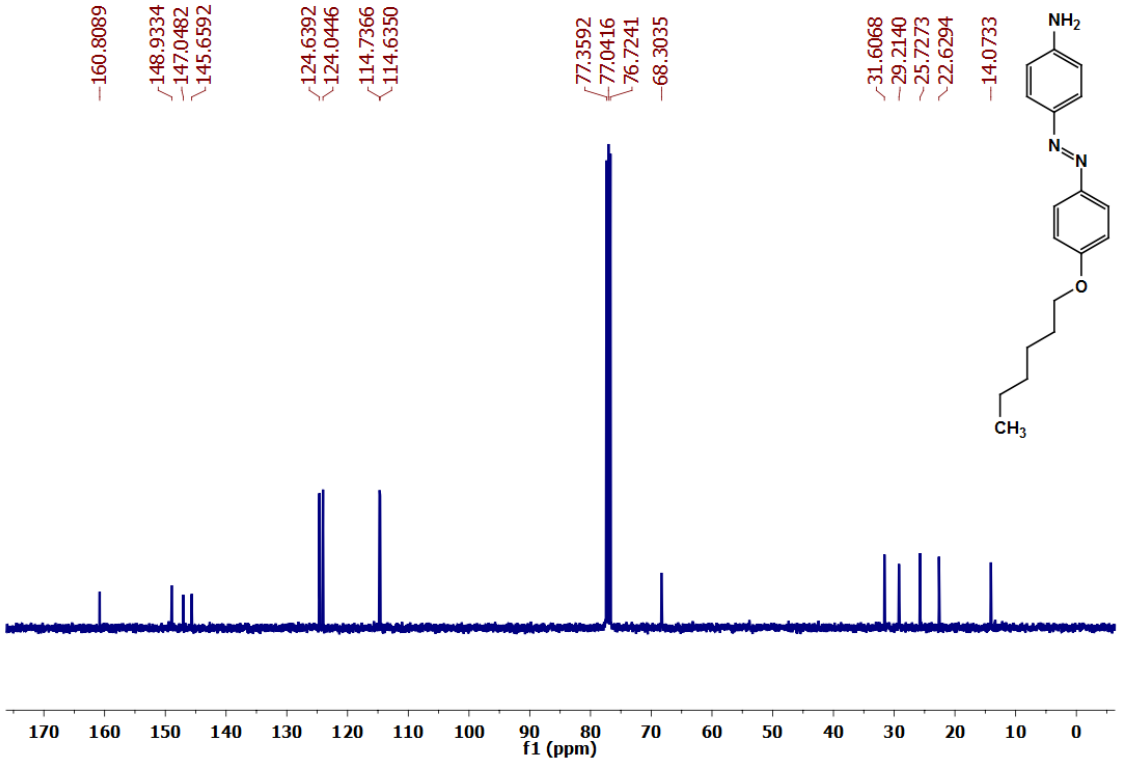


Figure S15. ^{13}C NMR spectrum of (*E*)-4-((4-(hexyloxy)phenyl)diazenyl)aniline **(4a)** in $CDCl_3$.

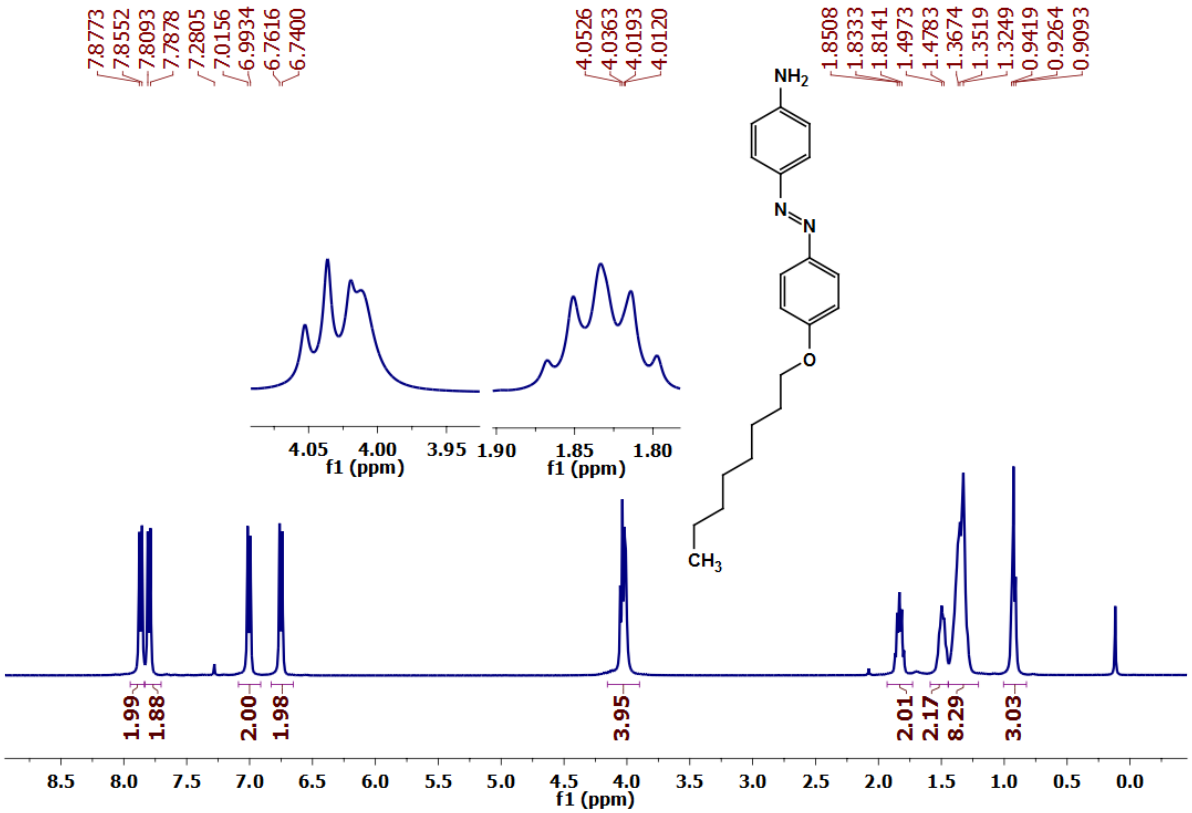


Figure S16. ^{1}H NMR spectrum of (*E*)-4-((4-(octyloxy)phenyl)diazenyl)aniline **(4b)** in $CDCl_3$.

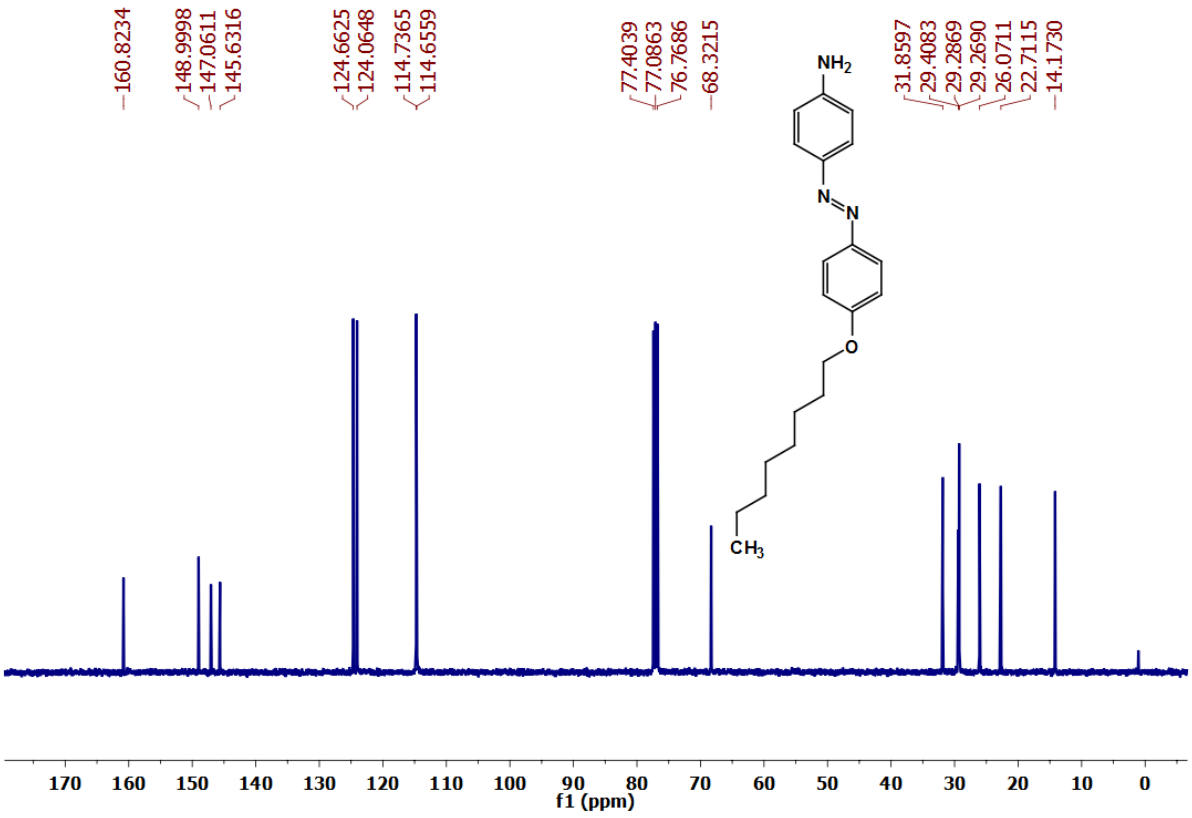


Figure S17. ^{13}C NMR spectrum of (*E*)-4-((4-(octyloxy)phenyl)diazenyl)aniline **(4b)** in $CDCl_3$.

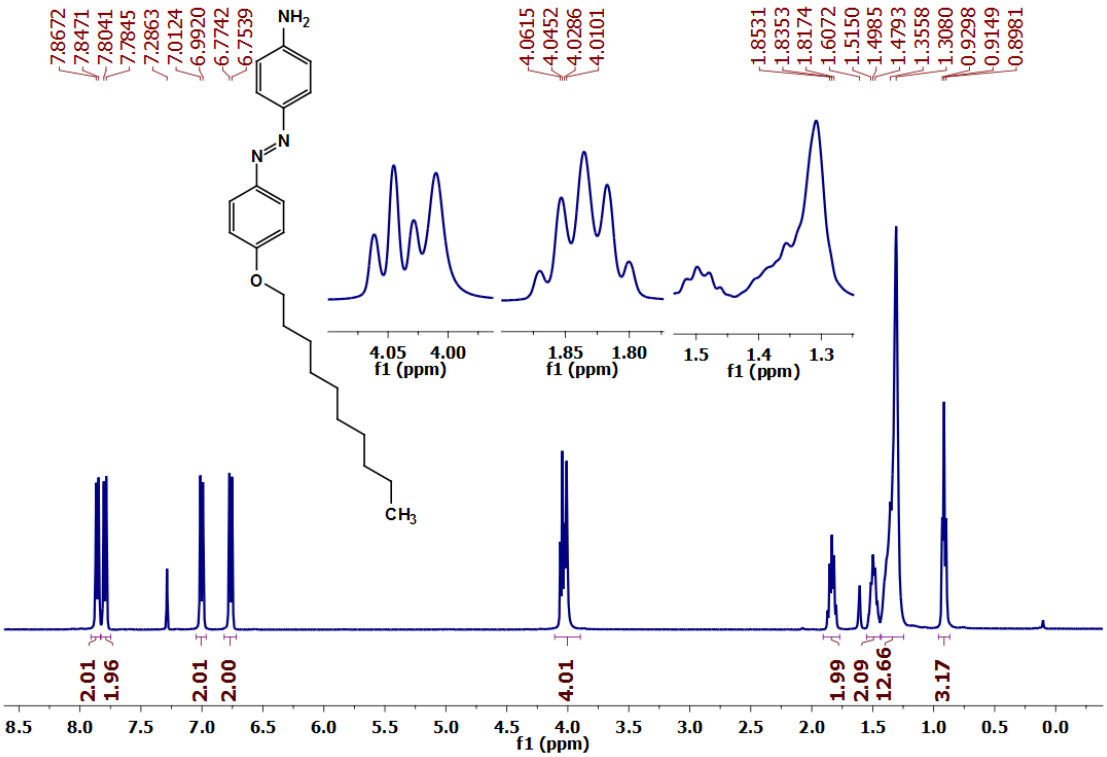


Figure S18. ^{1}H NMR spectrum of (*E*)-4-((4-(decyloxy)phenyl)diazenyl)aniline **(4c))** in $CDCl_3$.

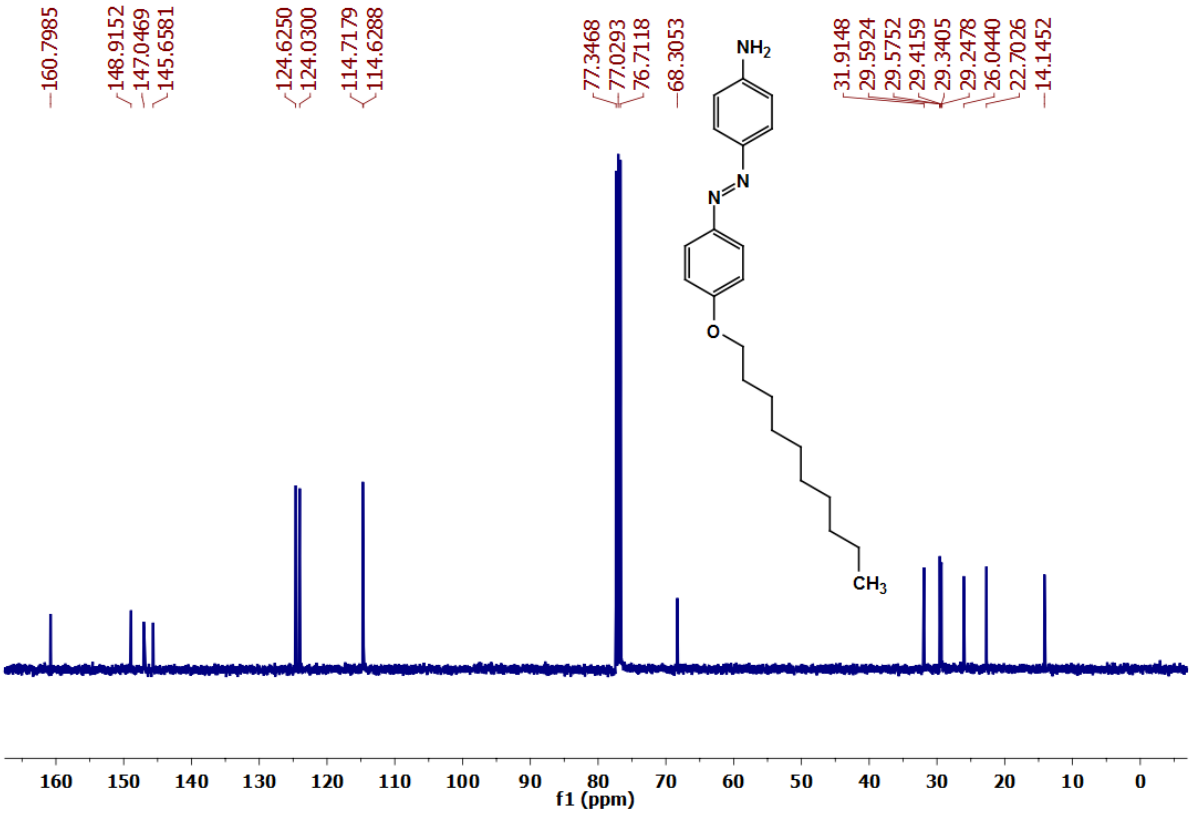


Figure S19. ^{13}C NMR spectrum of (*E*)-4-((4-(decyloxy)phenyl)diazenyl)aniline **(4c)** in $CDCl_3$.

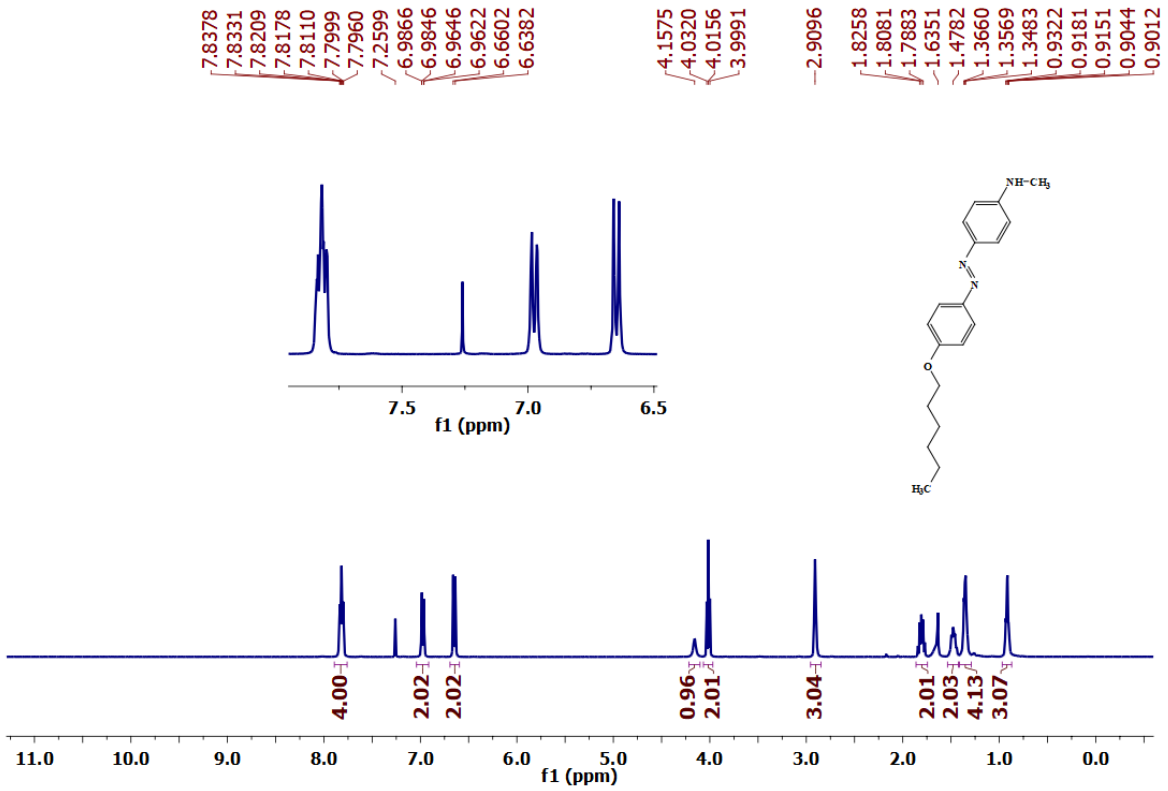


Figure S20. ^{1}H NMR spectrum of (*E*)-4-((4-(hexyloxy)phenyl)diazenyl)-*N*-methylaniline **(4a-NMe)** in $CDCl_3$.

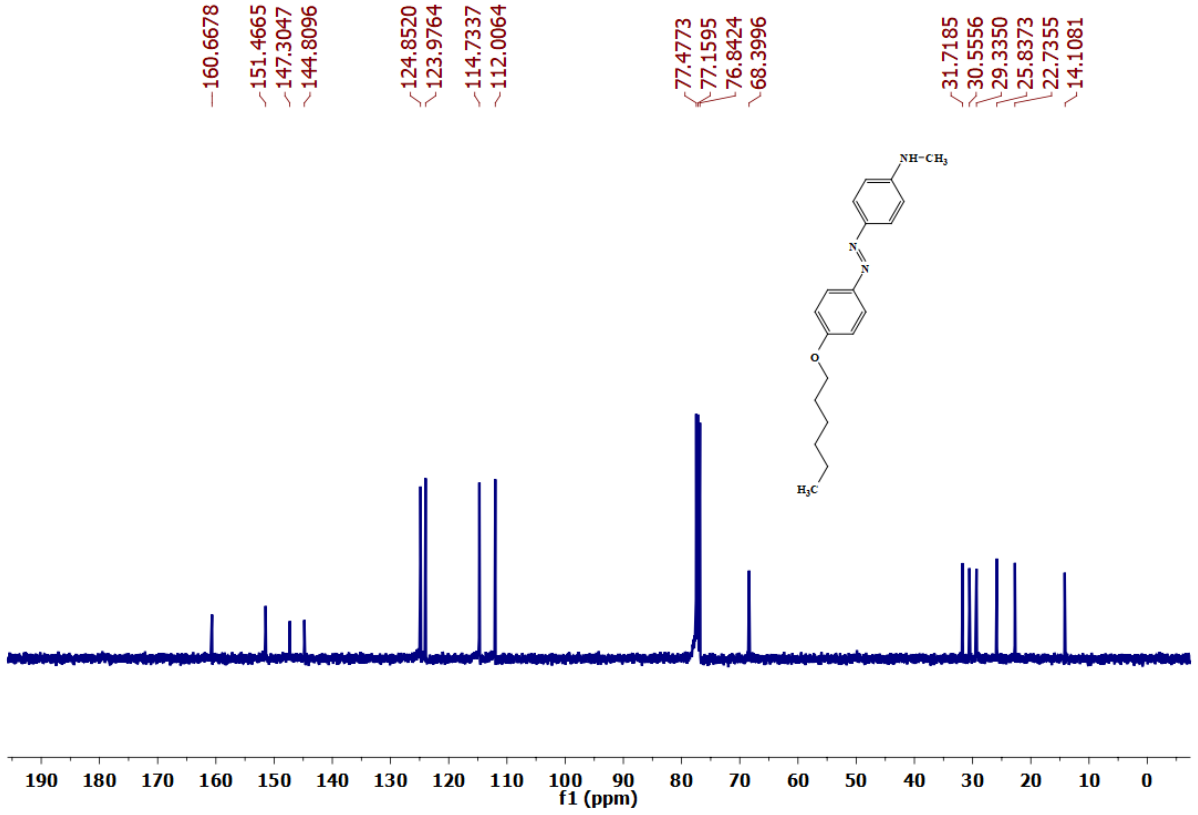


Figure S21. ^{13}C NMR spectrum of (*E*)-4-((4-(hexyloxy)phenyl)diazenyl)-*N*-methylaniline **(4a-NMe)** in $CDCl_3$.

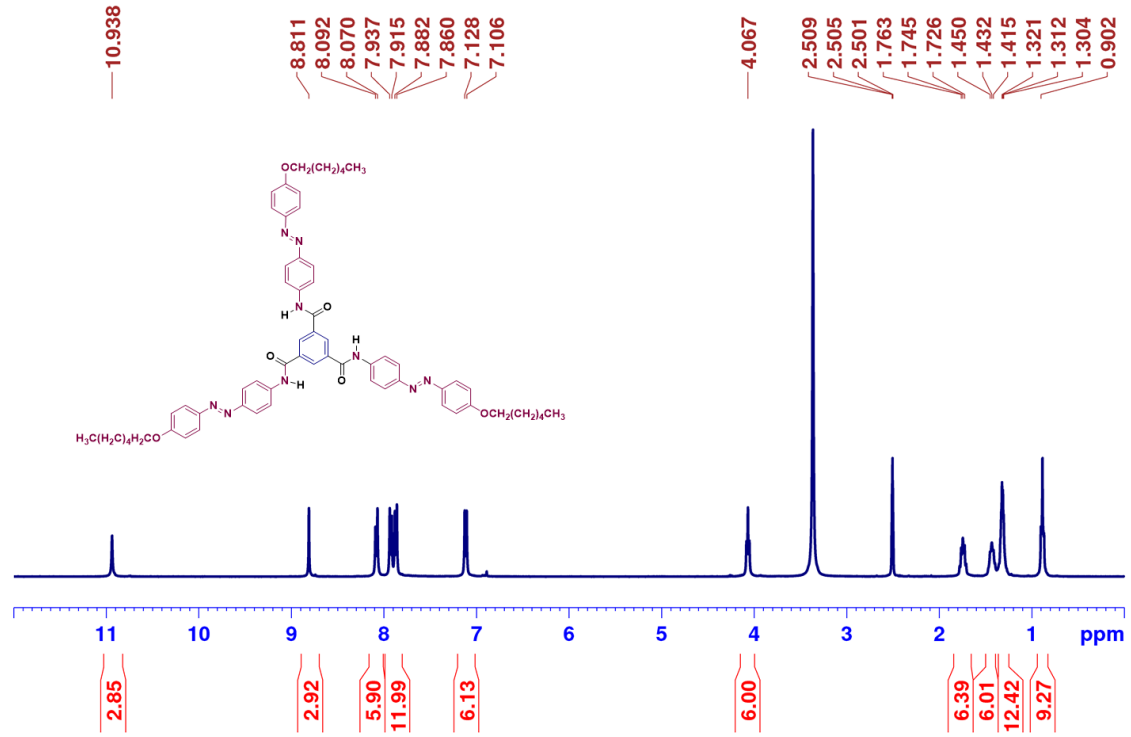


Figure S22. ^{1}H NMR spectrum of N^{1},N^{3}-bis(4-((*E*)-(4-(hexyloxy)phenyl)diazenyl)phenyl)-N^{5}-(4-((*E*)-(4-((pentyloxy)methyl)phenyl)diazenyl)phenyl)benzene-1,3,5-tricarboxamide (**7a**) in DMSO-d_6.

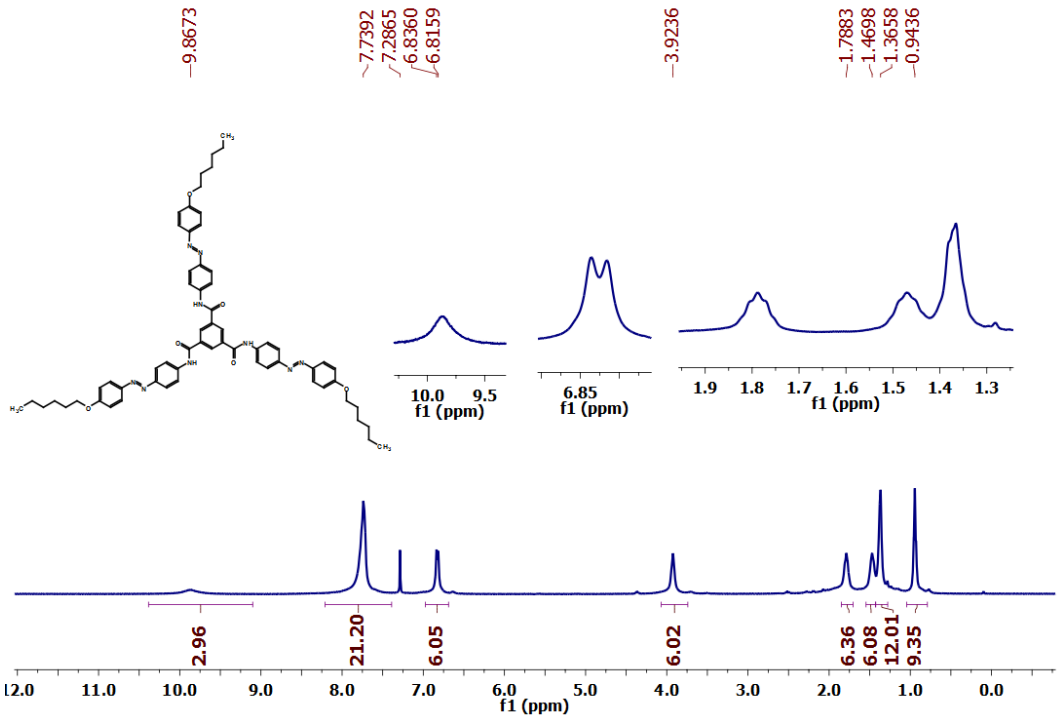


Figure S23. ^{1}H NMR spectrum of N^{1},N^{3}-bis(4-((*E*)-(4-(hexyloxy)phenyl)diazenyl)phenyl)-N^{5}-(4-((*E*)-(4-((pentyloxy)methyl)phenyl)diazenyl)phenyl)benzene-1,3,5-tricarboxamide (**7a**) in $CDCl_3$.

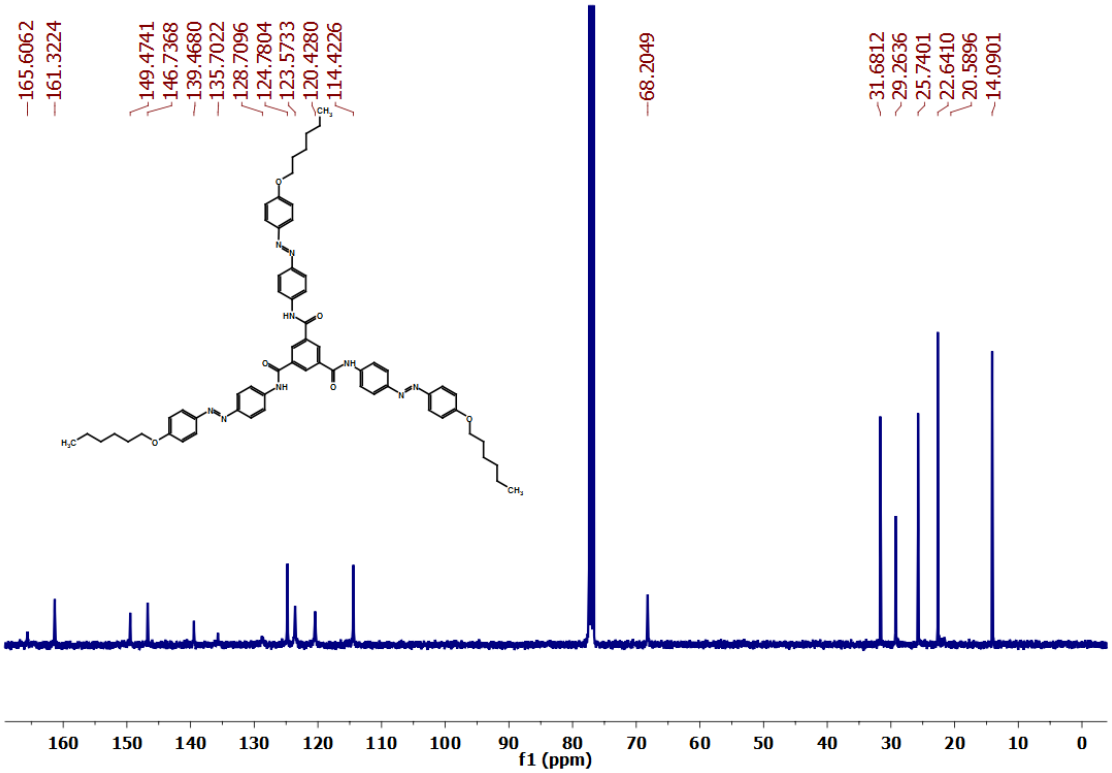


Figure S24. ^{13}C NMR spectrum of N^1,N^3-bis(4-((*E*)-(4-(hexyloxy)phenyl)diazenyl)phenyl)-N^5-(4-((*E*)-(4-((pentyloxy)methyl)phenyl)diazenyl)phenyl)benzene-1,3,5-tricarboxamide (**7a**) in $CDCl_3$.

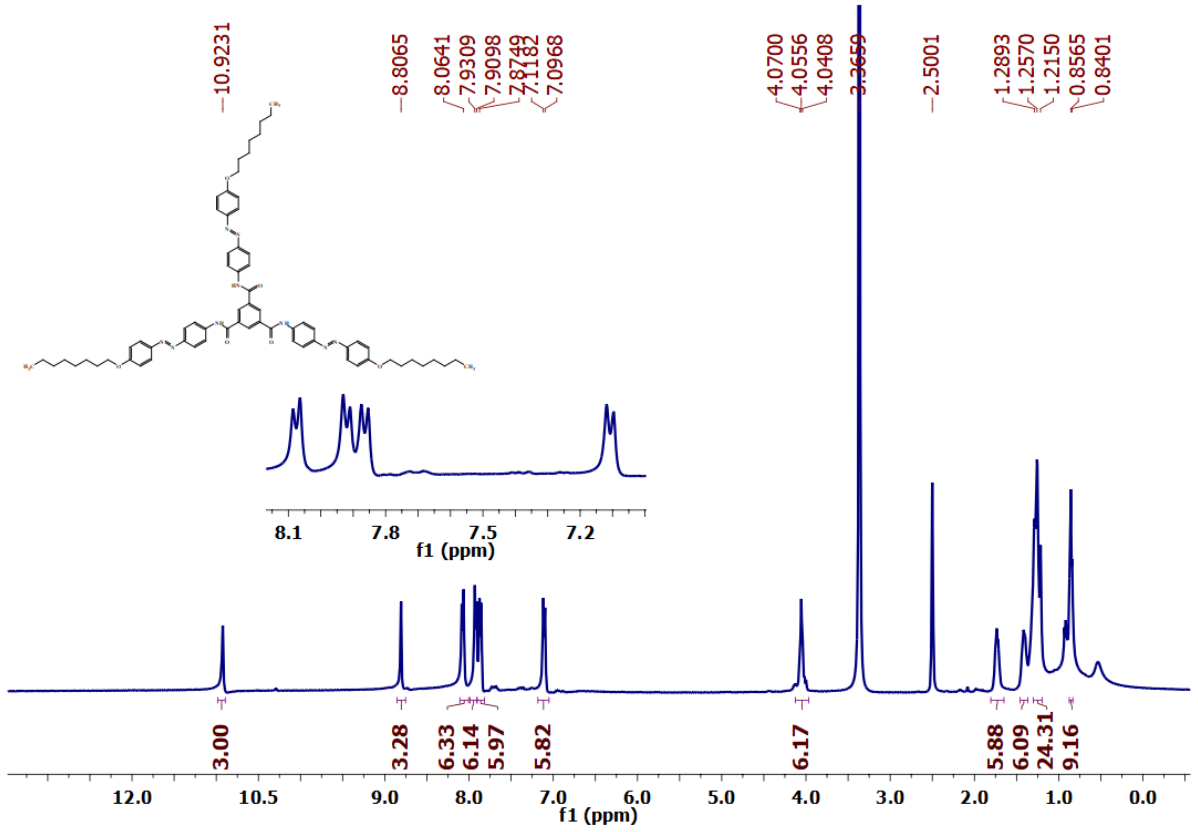


Figure S25. ^{1}H NMR spectrum of N^1,N^3-bis(4-((*E*)-(4-(octyloxy)phenyl)diazenyl)phenyl)-N^5-(4-((*E*)-(4-((pentyloxy)methyl)phenyl)diazenyl)phenyl)benzene-1,3,5-tricarboxamide (**7b**) in DMSO-d_6.

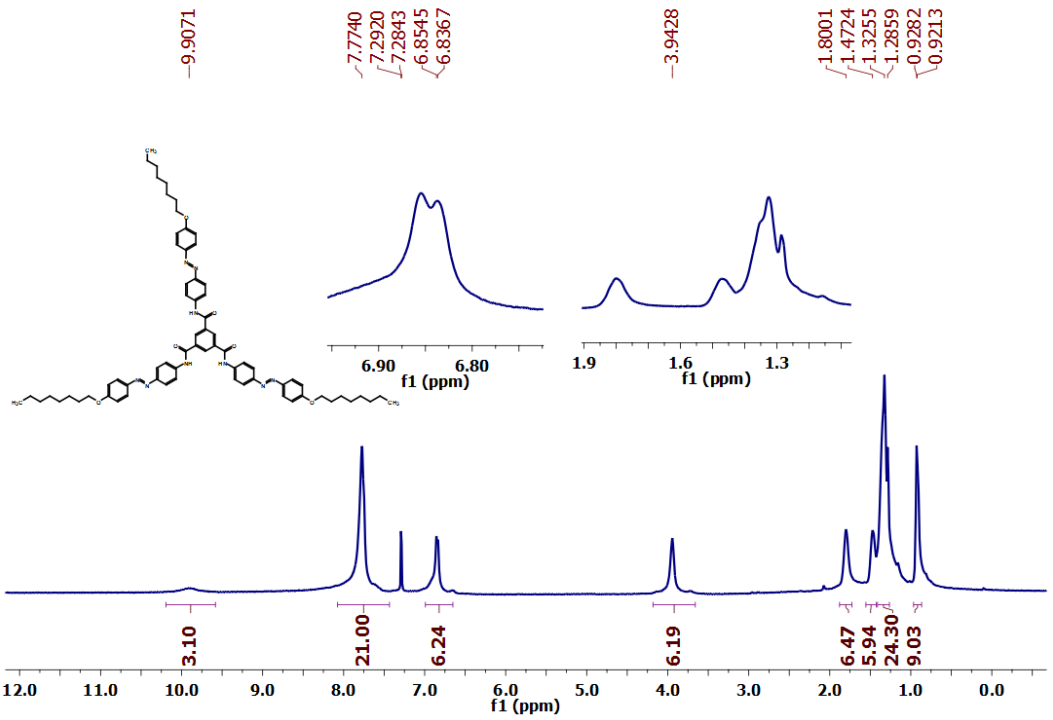


Figure S26. ^{1}H NMR spectrum of N^{1},N^{3}-bis(4-((*E*)-(4-(octyloxy)phenyl)diazenyl)phenyl)-N^{5}-(4-((*E*)-(4-((pentyloxy)methyl)phenyl)diazenyl)phenyl)benzene-1,3,5-tricarboxamide (**7b**) in $CDCl_3$.

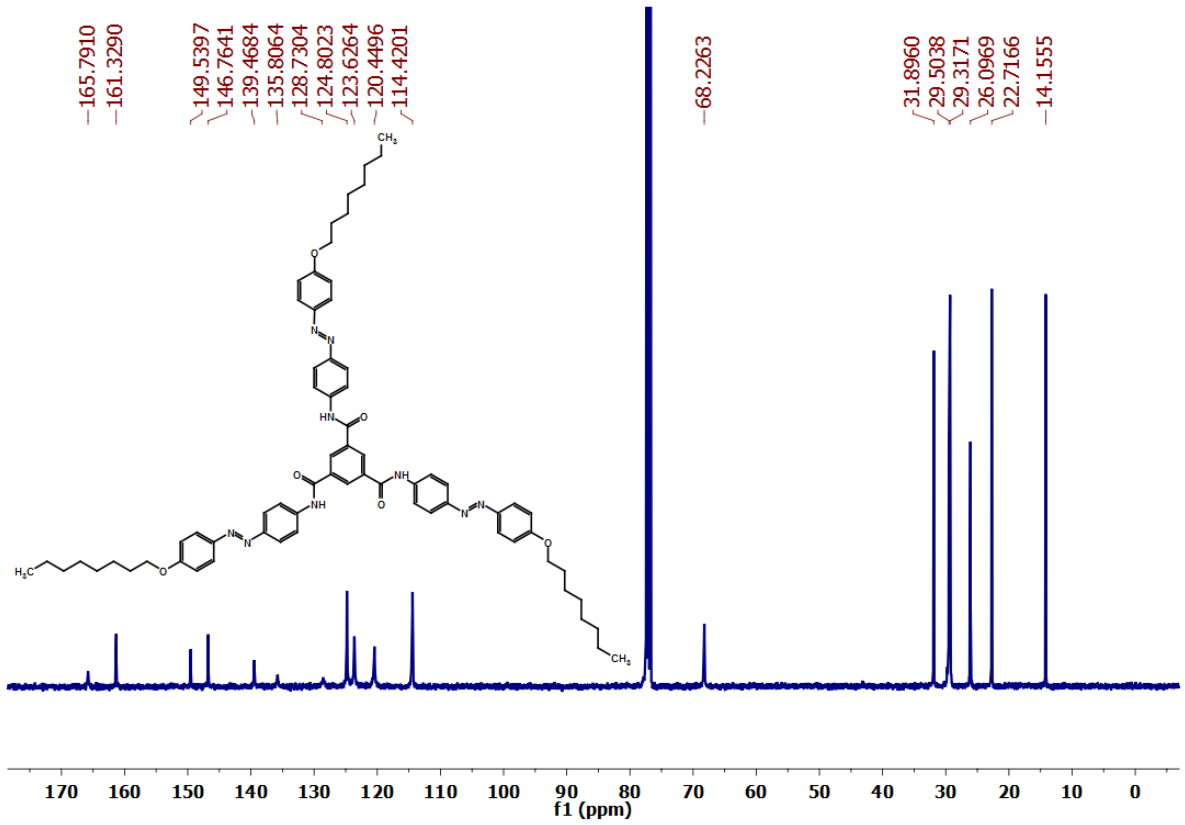


Figure S27. ^{13}C NMR spectrum of N^{1},N^{3}-bis(4-((*E*)-(4-(octyloxy)phenyl)diazenyl)phenyl)-N^{5}-(4-((*E*)-(4-((pentyloxy)methyl)phenyl)diazenyl)phenyl)benzene-1,3,5-tricarboxamide (**7b**) in $CDCl_3$.

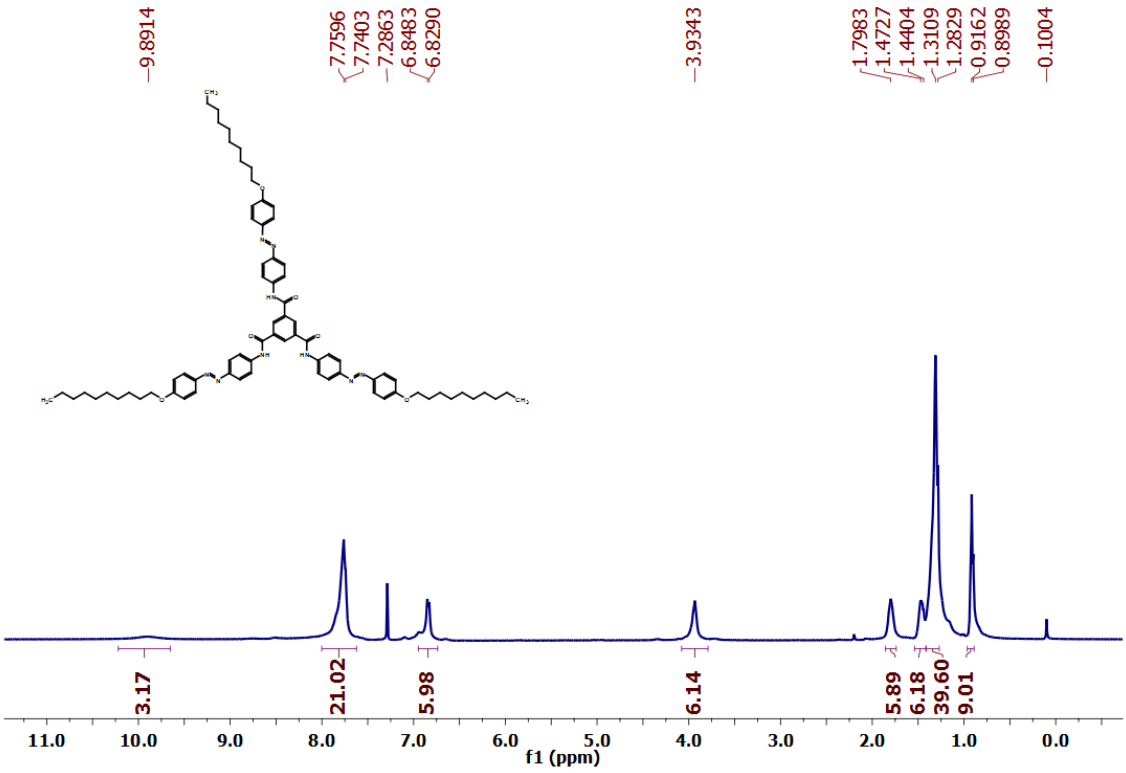


Figure S28. ^{1}H NMR spectrum of N^{1},N^{3}-bis(4-((*E*)-(4-(decyloxy)phenyl)diazenyl)phenyl)-N^{5}-(4-((*E*)-(4-((pentyloxy)methyl)phenyl)diazenyl)phenyl)benzene-1,3,5-tricarboxamide (**7c**) in $CDCl_3$.

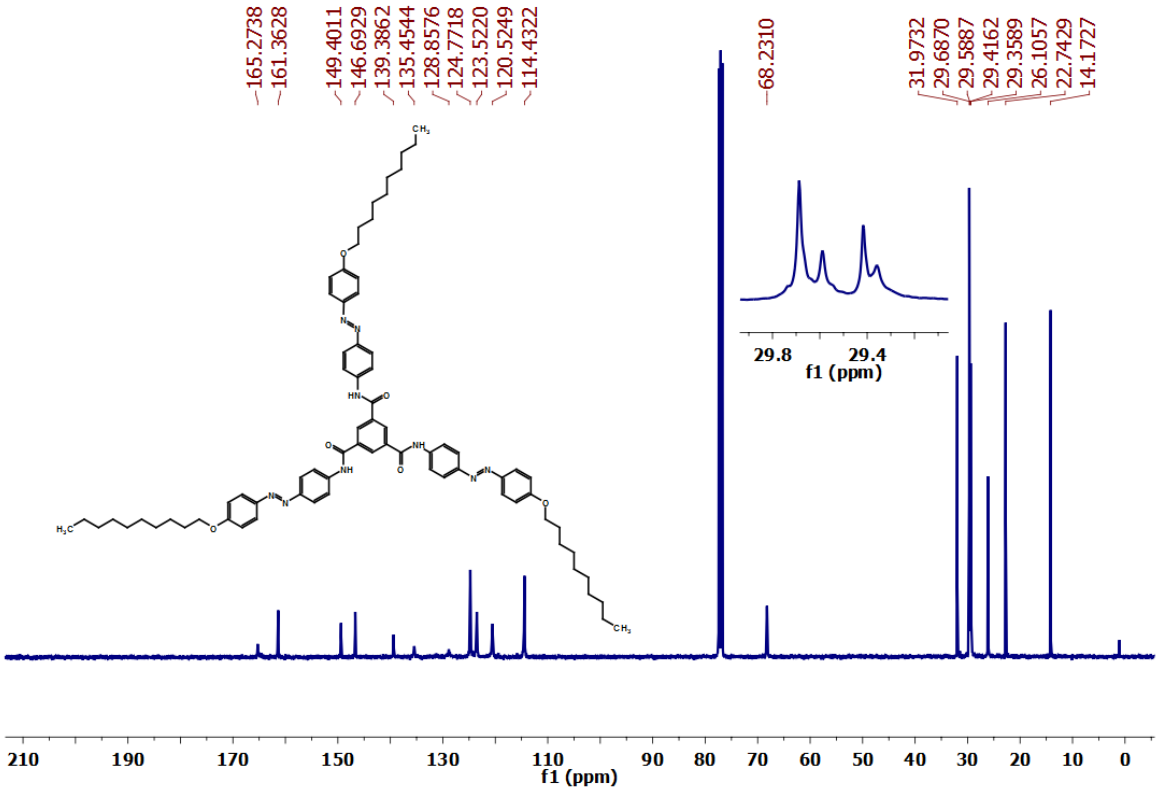


Figure S29. ^{13}C NMR spectrum of N^{1},N^{3}-bis(4-((*E*)-(4-(decyloxy)phenyl)diazenyl)phenyl)-N^{5}-(4-((*E*)-(4-((pentyloxy)methyl)phenyl)diazenyl)phenyl)benzene-1,3,5-tricarboxamide (**7c**) in $CDCl_3$.

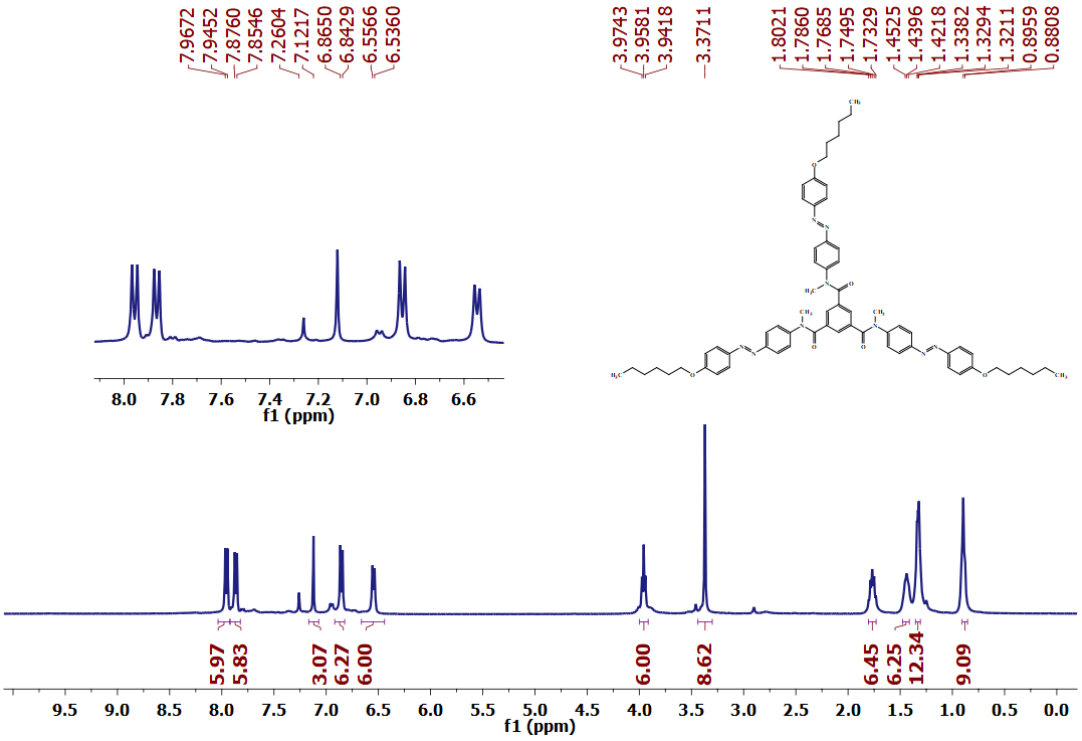


Figure S30. ^{1}H NMR spectrum of *N*^{1},*N*^{3},*N*^{5}-tris(4-((*E*)-(4-(hexyloxy)phenyl)diazenyl)phenyl)-*N*^{1},*N*^{3},*N*^{5}-trimethylbenzene-1,3,5-tricarboxamide (**8a**) in $CDCl_3$.

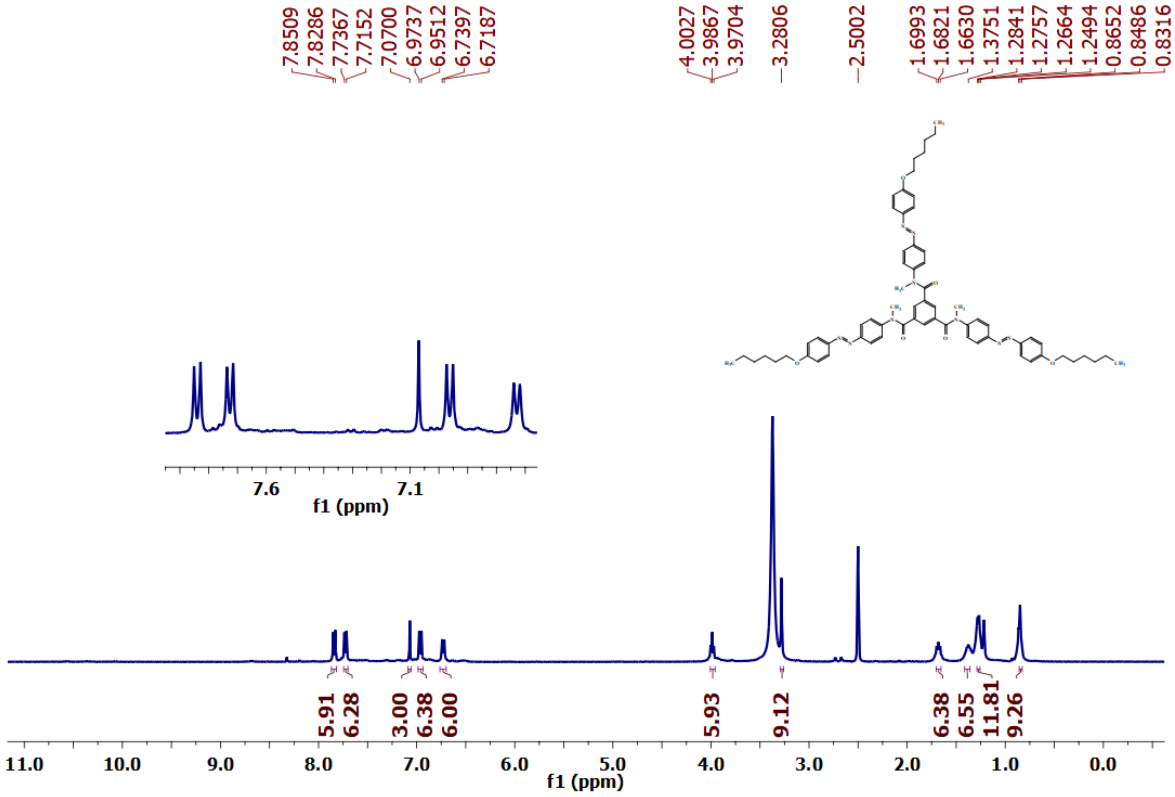


Figure S31. ^{1}H NMR spectrum of *N*^{1},*N*^{3},*N*^{5}-tris(4-((*E*)-(4-(hexyloxy)phenyl)diazenyl)phenyl)-*N*^{1},*N*^{3},*N*^{5}-trimethylbenzene-1,3,5-tricarboxamide (**8a**) in DMSO-d_6.

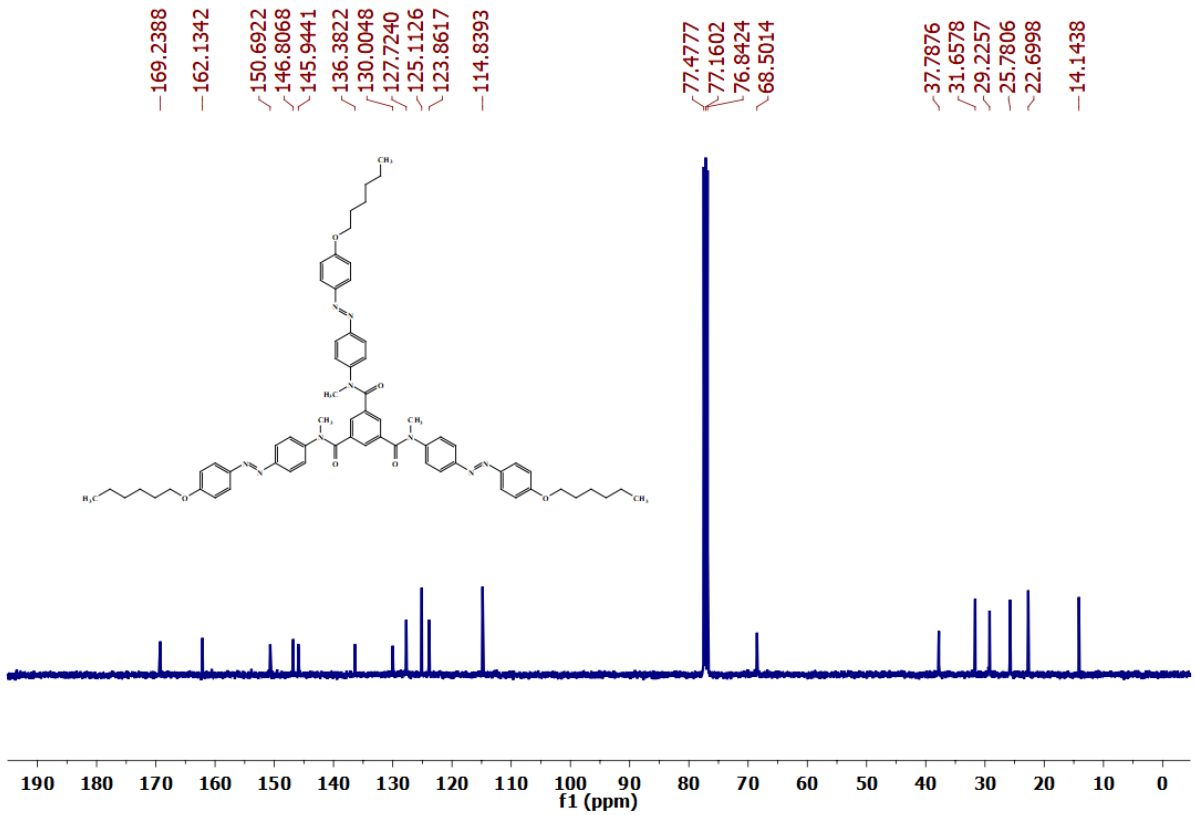


Figure S32. ^{13}C NMR spectrum of N^1,N^3,N^5-tris(4-((*E*)-(4-(hexyloxy)phenyl)diazenyl)phenyl)-N^1,N^3,N^5-trimethylbenzene-1,3,5-tricarboxamide (**8a**) in $CDCl_3$.

6. Analysis of solid state/LC photoswitching by UV-Vis, POM, AFM and GISAXS/GIWAXS XRD on thin film:

(a) Analysis of photoswitching behaviour in thin films by UV-Vis spectroscopy

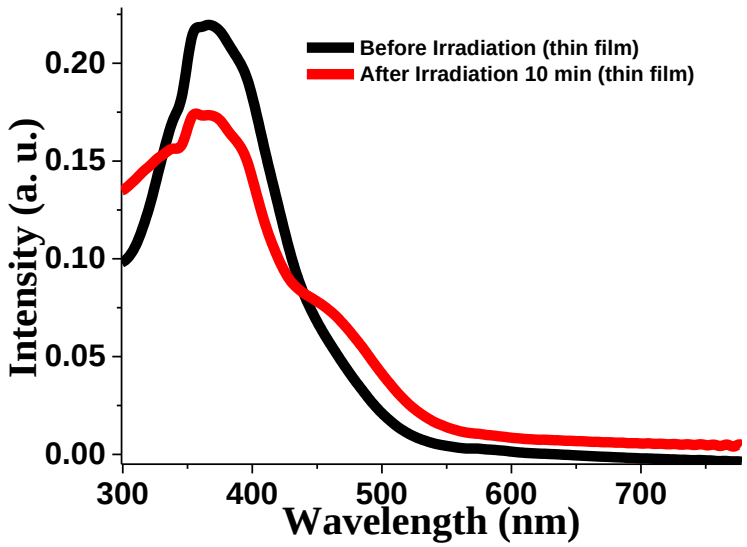


Figure S33. Photoswitching behaviour in solid state for **7a** in thin film. The black coloured spectrum is due to the **7a**-*EEE* spectra (before irradiation)**,** whereas the red one indicates the changes after irradiation at 365 nm.

(b) Analysis of photoswitching behaviour in thin film by GISAXS/GIWAXS XRD

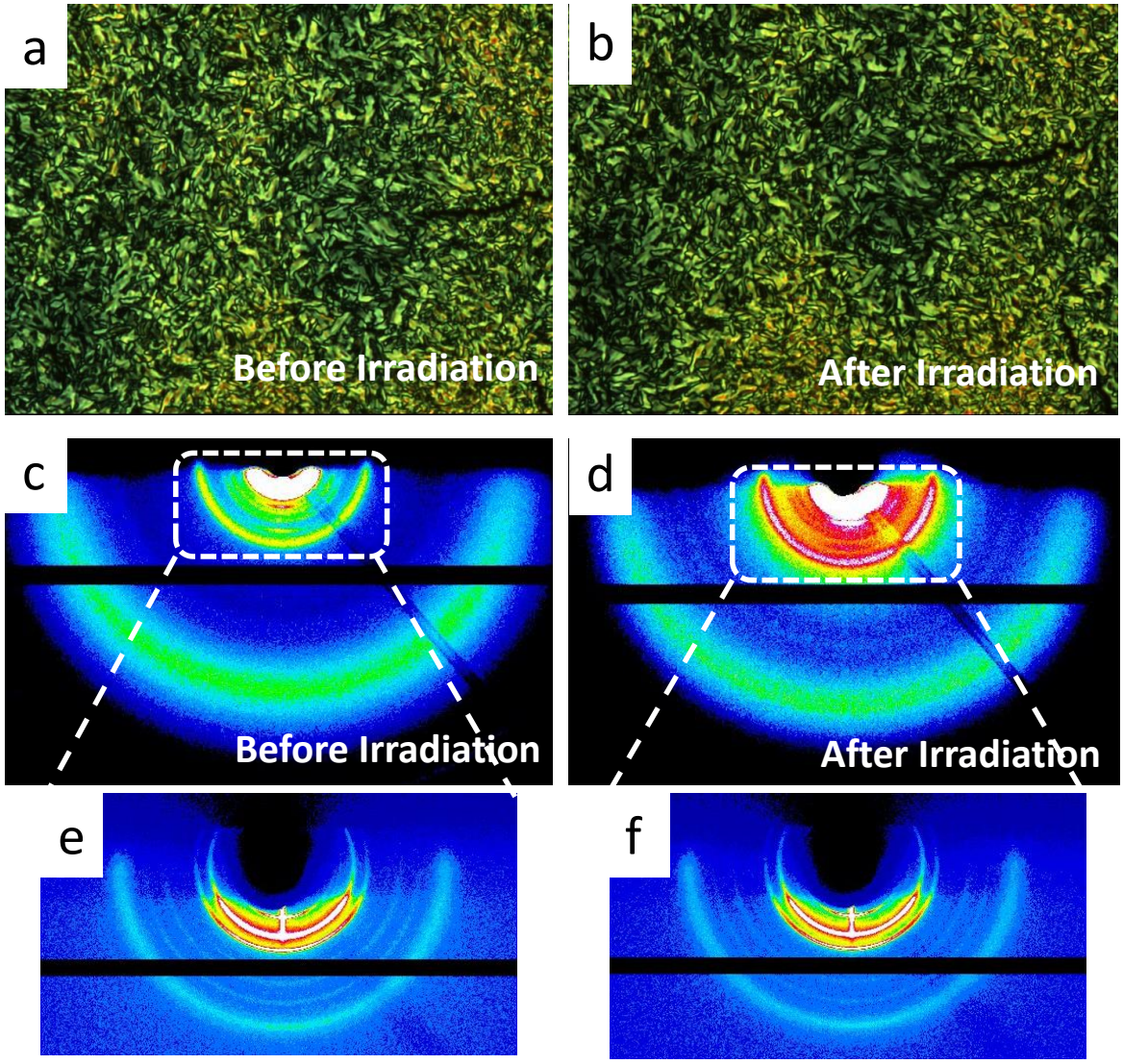


Figure S34. POM textures of **7a** at room temperature: (a) before irradiation; (b) after irradiation. GIWAXS pattern of compound **7a** thin film: (c) before irradiation; (d) after irradiation. GISAXS pattern of compound **7a** thin film: (e) before irradiation; (f) after irradiation.

(c) Analysis of photoswitching behaviour in thin film by AFM

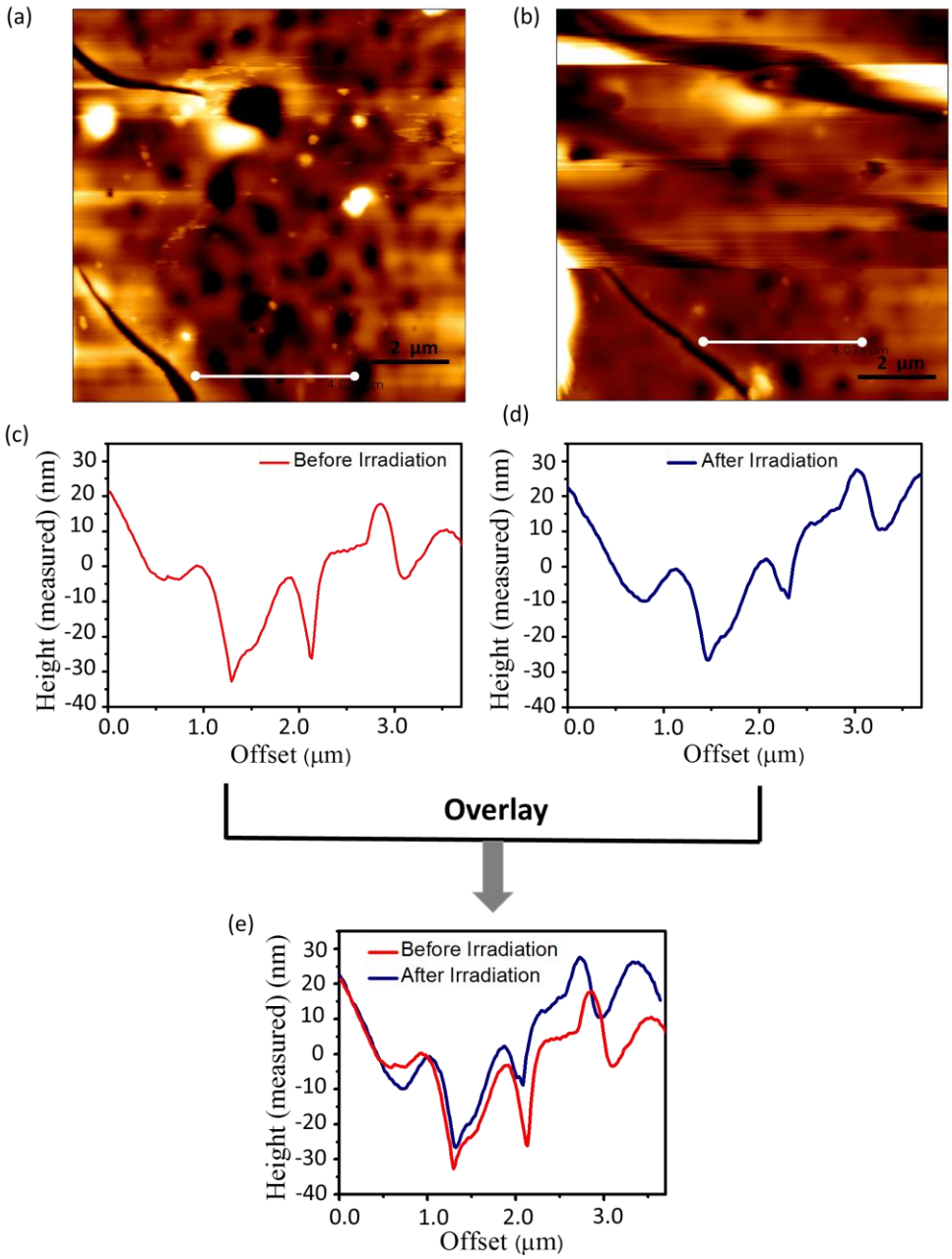


Figure S35. AFM Images of drop casted film of **7a** on glass substrate (a) before irradiation; (b) after irradiation with 365 nm UV light; (c) Height vs offset plots before irradiation corresponding to the area marked in white colored line in image "a"; (d) Height vs offset plots after irradiation corresponding to the area marked in white colored line in image "b"; (e) Overlay of "c" and "d".