Supporting Information


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1. Experimental Section

Melting points were taken on Veego (VMP-DS) using a Mel-Temp apparatus. The FT-IR spectra were recorded as KBr pellet on Bruker TENSOR-27 in the range of 4000-400 cm⁻¹. ¹H NMR spectra was scanned on 500 MHz FT-NMR Bruker Avance-400 in the range of 0.5 ppm -15 ppm and ¹³C NMR spectra was recorded on a Bruker DPX-300 spectrometer using internal standard tetramethysilane (TMS) and deuterated DMSO as a solvent in the range of 0.5 ppm to 250 ppm. ESI Mass spectra were taken on a Shimadzu GCMS-QP 2000A. Decomposition temperatures were determined using a Shimadzu DSC 60 differential scanning calorimeter with a heating rate of 10.0 °C min⁻¹ in air and it was calibrated with indium (156.6 °C, 28.45 Jg⁻¹). The texture of the mesophases were studied on a Leica DMLP polarising microscope equipped with a hot stage, a Mavotherm 32 temperature display unit and a Leica MPS 32 Data back display and also on hot stage polarizing microscopy using a Nikon 50i Pol microscope equipped with a Linkam THMS600 hot stage. X-ray diffraction (XRD) experiments were performed on a SEIFERT–FPM (XRD7), using Cu Kα X-ray lines at 1.5406 Å as the radiation source at 40 kV and 30 mA power and also Make -Philips X'PERT MPD. Powder X-ray diffractometer. The XRD patterns were recorded at transition temperature of compounds. An Agilent 4980 A Precision LCR meter with a four-terminal liquid dielectric test fixture (Agilent 16542 A) was used to measure dielectric permittivity over the frequency range 20 Hz to 2 MHz. All the dielectric measurements were carried out at temperatures within the range 50–110°C. The temperature of the sample was controlled using a hot stage (Instecmodel Hs–1) to an accuracy of ±0.5°C. The temperature near the sample was registered on a Mavotherm 32 temperature unit.
2. Synthetic procedure of intermediates and calix[4]arene derivatives:


A mixture of p-tert-butyl phenol (4.0 g, 0.33 mM), sodium hydroxide (NaOH) (1 g) and formaldehyde(1.8 ml,0.18 mM) solution was taken in an open vessel and was irradiated with 50 W power in a microwave synthesizer Discover(CEM)by stirring for 3 min. After cooling for 10 min, resulted yellow solid mass. Next, 4 ml of toluene and 30 ml of diphenyl ether was added in this yellow solid, again irradiated with microwave power of 100 W for 5 min with stirring and obtained a dark brown solution. Further, this solution was added in to 75 ml of ethyl acetate and kept for 2 h. Finally, white precipitate was obtained which was filtered and washed with ethyl acetate and finally dried. Yield, 3.5 g (96%). Elemental analysis for C_{44}H_{56}O_{4} :Calcd.;C;81.44%,H;8.70%,O;9.80%,Found.;C;80.11%,H;8.261%,O;9.90%.

\[\delta_H (DMSO, 400 MHz): 1.18(36H, \text{t-butyl, s}), 3.81 (8H, \text{ArCH}_2\text{Ar, s}), 7.12 (8H, \text{Ar-H, s}), 9.71(4H, \text{Ar-OH, s}).\]

\[\delta_{13C} \text{ NMR (DMSO) 149.3, 126.6, 126.4 (Ar-C), 34.5 (C(CH}_3)_3), 31.3(C(CH}_3)_3), 32.3(Ar-CH}_2\text{-Ar).}\]

ESI-MASS (m/z) 648 (M+1).

Synthesis of 4'-hydroxy-3, 4, 5-trimethoxy azobenzene (B1):

A solution of 3,4,5 trimethoxydiazonium chloride, which was prepared from (4.5 g, 0.02 mol), sodium nitrite (1.69 g, 0.02 mol) was added dropwise to 3,4,5-trimethoxy aniline in con. HCl (10 ml) with water (10 ml), was added gradually to a cold (0-5°C) solution of phenol (1.88 g, 0.02 mol) and sodium hydroxide (0.8 g, 0.02 mol) in water (5 ml) to give dark orange suspension. This was filtered and washed with water:MeOH (9:1) to afford the dark orange solid. The crude product was crystalized with methanol. The reaction progress was examined by tlc in hexane: ethyl acetate (7:3) mixture. Yield, 88%, mp 165-168°C. Anal.calc. C_{15}H_{16}N_2O_4 : C, 62.49; H, 5.59; N, 9.72; O, 22.20%. Found: C, 62.18; H, 5.50; N, 9.42; O, 22.10%. FT-IR (KBr) \nu :3200
cm⁻¹ (-OH), 1480 cm⁻¹ (-N=N-), 2890 cm⁻¹ (Ar-CH), \(^1\)H NMR (DMSO) 6.81 (s, OH, 1H), 3.90 (s, -OCH₃, 9H), 7.04 (d, Ar-H, 2H), 7.61 (d, Ar-H, 2H), 6.84 (d, Ar-H, 2H), \(^1^3\)C NMR (DMSO) 165, 152, 142 (Ar-C) 126, 105 (Ar-CH) 61, 60, 55 (-OCH₃ ). ESI-MASS: (m/z) 289(M+1).

**Synthesis of 4'-hydroxy-4- benzonitrile azobenzene (B2):**

A solution of 4-benzonitrilediazonium chloride, which was prepared from (4.5 g, 0.03 mol), sodium nitrite (2.35 g, 0.03 mol) was added to 4-aminobenzonitrile with con. HCl (10 ml) in water (10 ml), was added gradually to a cold (0-5°C) solution of phenol (3.17 g, 0.033 mol) and sodium hydroxide (1.36 g, 0.034 mol) in water (5 ml) to get dark red suspension. The reaction mixture then filtered and washed with water:MeOH (9:1) to afford dark reddish solid. The crude product was crystalized with methanol. The reaction progress was monitored by tlc in hexane:ethyl acetate (7:3) mixture. Yield, 82% , mp 157-159°C. Anal.calc. C₁₄H₁₁N₃O: C, 70.87; H, 4.87; N, 17.71; O, 6.74% Found: C, 70.50; H, 4.65; N, 17.53; O, 6.64% FT-IR (KBr) \(\nu\):3340 cm⁻¹ (-OH), 1560 cm⁻¹ (-N=N-), \(^1\)H NMR (DMSO) 6.81 (s, OH, 1H), 4.90 (s, -CH₂CN, 2H), 7.11 (d, Ar-H, 2H), 7.52 (d, Ar-H, 2H), 7.82 (d, Ar-H, 2H), 8.51 (d, Ar-H, 2H), \(^1^3\)C NMR (DMSO) 162,146,157,138,115 (Ar-C), 130,126,125,118(Ar-CH) and 23.1 (–CH₂). ESI-MASS: (m/z) 239(M+2).

**Synthesis of 12-bromo-1((4-((3,4,5-trimethoxyphenyl)azo)phenyl)oxy)dodecane (C1):**

B1 (2.0 g, 0.007 mol), 1,12- dibromododecane (4.56 g, 0.014 mol), K₂CO₃ (1.93 g, 0.014 mol), KI (1.27 g, 0.014 mol) and anhydrous acetone (75 ml) were heated at reflux temperature for 24 h. The reaction progress was monitored by tlc hexane: ethyl acetate (6:4) mixture. After the completion of the reaction, the solvent was removed by vacumm and reaction mixture was extracted with dichloromethane:water (70:30). Petroleum ether was added to remove the
stickiness from the product. The crude product was subjected to column chromatography [ethyl acetate/hexane (30:70)] to get light orange solid. Yield, 89% mp 130-134°C.

Anal. calc. C$_{27}$H$_{39}$BrN$_2$O$_4$: C, 60.56; H, 7.34; Br, 14.92; N, 5.23; O, 11.95%. Found: C, 60.41; H, 7.23; Br, 14.88; N, 5.12; O, 11.79%. FT-IR (KBr) $\nu$: 1540 cm$^{-1}$ (-N=N-), 2970 cm$^{-1}$ (Ar-CH).

$^1$H NMR (DMSO) 1.85 (m, (CH$_2$)$_{11}$CH$_2$Br, 22H), 4.21 (t, -OCH$_2$, 2H), 3.91 (s, -OCH$_3$, 9H), 7.10 (d, Ar-H, 2H), 7.32 (d, Ar-H, 2H), 8.01 (d, Ar-H, 2H), $^{13}$C NMR (DMSO) 164, 153, 150, 147 (Ar-C), 125, 116, 104, 102 (Ar-CH), 36.2, 68.8 (-CH$_2$), 61.2 (-OCH$_3$) ESI-MASS: (m/z) 536 (M+1)

**Synthesis of 12-bromo-1-((4-((4-benzonitrilephenyl)azo)phenyl)oxy)dodecane (C2) :**

B$_2$ (2.0 g, 0.008 mol), 1,12-dibromododecane (5.26 g, 0.016 mol), K$_2$CO$_3$ (1.16 g, 0.016 mol), KI (1.47 g, 0.016 mol) and anhydrous acetone (75 ml) were heated at reflux temperature for 24 h, and the product was isolated as described above in C-1. Yield 87%, mp 123-126°C.

Anal. calc. C$_{26}$H$_{34}$BrN$_3$O: C, 64.46; H, 7.07; Br, 16.49; N, 8.67; O, 3.30%. Found: C, 64.34; H, 6.99; Br, 16.32; N, 8.44; O, 3.24%. FT-IR (KBr) $\nu$: 1550 cm$^{-1}$ (-N=N-), 2950 cm$^{-1}$ (Ar-CH).

$^1$H NMR (DMSO) 1.35 (m, (CH$_2$)$_{11}$CH$_2$Br, 22H), 4.1 (t, -OCH$_2$, 2H), 4.5 (s, -CH$_2$CN, 2H), 7.2 (d, Ar-H, 2H), 7.6 (d, Ar-H, 2H), 7.8 (d, Ar-H, 2H), 8.6 (d, Ar-H, 2H), $^{13}$C NMR (DMSO) 162, 153, 147, 136 (Ar-C) 129.5, 123.6, 121.8, 118.7, 113.4 (-CH) 69.1, 34.1, 30.1, 26.1, 25.8 (-CH$_2$), 117 (-CN). ESI-MASS: (m/z) 485 (M-1).

**Synthesis of 10-bromo-1-((4-((3,4,5-trimethoxyphenyl)azo)phenyl)oxy)decane compound (C3) :**

B$_1$ (2.0 g, 0.007 mol), 1,10-dibromodecane (1.56 g, 0.007 mol), K$_2$CO$_3$ (1.93 g, 0.014 mol), KI (1.27 g, 0.014 mol) and anhydrous acetone (75 ml) were heated at reflux temperature for 24 h, and the product was isolated as described above in C-1. Yield 78%, mp 124-126°C. Anal. calc.
C$_{25}$H$_{35}$BrN$_2$O$_4$: C, 59.17; H, 6.95; Br, 15.75; N, 5.52; O, 12.61%. Found: C, 58.97; H, 6.45; Br, 15.12; N, 5.43; O, 11.9%. FT-IR (KBr) $\nu$: 1550 cm$^{-1}$ (-N=N-), 2900 cm$^{-1}$ (Ar-CH).

$^1$H NMR (DMSO) 1.31 (m, (CH$_2$)$_9$CH$_2$Br, 18H), 4.12 (t, -OCH$_2$, 2H), 3.80 (s, -OCH$_3$, 9H), 7.11 (d, Ar-H, 2H), 7.81 (d, Ar-H, 2H), 6.82 (d, Ar-H, 2H). $^{13}$C NMR (DMSO) 162, 152, 147, 141 (Ar-C), 123, 114, 102, 101 (Ar-CH), 68.8, 34.1 (-CH$_2$), 60.8 (-OCH$_3$). ESI-MASS: (m/z) 508 (M+1).

**Synthesis of 10-bromo-1-((4-((4-benzonitrilephenyl)azo)phenyl)oxy)decane (C4):**

B2 (2.0 g, 0.008 mol), 1,10- dibromodecane (1.23g, 0.008mol), K$_2$CO$_3$ (1.16 g,0.016 mol), KI (1.47g, 0.016 mol) and anhydrous acetone ( 75 ml) were heated at reflux temperature for 24 h, and the product was isolated as described above in C-1. Yield. 82% mp 117-120$^\circ$C. Anal.calc. C$_{24}$H$_{30}$BrN$_3$O: C, 63.16; H, 6.63; Br, 17.51; N, 9.21; O, 3.51%. Found: C, 63.11; H, 6.56; Br, 17.32; N, 9.16; O, 3.31%. FT-IR (KBr) $\nu$: 1580 cm$^{-1}$ (-N=N-), 3100 cm$^{-1}$ (Ar-CH). $^1$H NMR (DMSO) 1.33 (m, (CH$_2$)$_9$CH$_2$Br, 18H), 4.10 (t, -OCH$_2$, 2H), 4.31 (s, -CH$_2$CN, 2H), 7.35 (d, Ar-H, 2H), 7.44 (d, Ar-H, 2H), 8.08 (d, Ar-H, 2H), 8.61 (d, Ar-H, 2H). $^{13}$C NMR (DMSO) 161, 154, 145, 135 (Ar-C) 128.8, 124.6, 121.8, 113.4 (-CH) 68.8, 34.1 (-CH$_2$), 117.6 (-CN). ESI-MASS: (m/z) 458 (M+2).


p-tert-butylicalix[4]arene (1 g, 0.0015 mol), C1(1.60 g, 0.003 mol), K$_2$CO$_3$ (0.414 g, 0.003 mol), KI (0.276 g, 0.003 mol) in anhydrous acetone (50 ml) were reacted at refluxed temperature for 24 h. The actual reaction time consider by only taking tlc at regular interval of time [hexane: ethyl acetate (6:4)]. After the evaporation of acetone, the crude was extracted with dichloromethane:water (60:40) and then washed with HCl (50 ml, 10%), and dried over MgSO$_4$. The resulting mixture was concentrated to get light brown solid. The material was then subjected...
to column chromatography [hexane/ethyl acetate (60:40)]. The final compound was recrystallised with methanol. Yield 81%, mp 185-188°C. Anal. calc: C₉₈H₁₃₂N₄O₁₂ : C, 75.54; H, 8.54; N, 3.60; O, 12.32%. Found: C, 74.87; H, 8.32; N, 3.43; O, 12.21%. FT-IR (KBr) ν:
3250 cm⁻¹ (-OH), 1590 cm⁻¹ (-N=N-), 2980 cm⁻¹ (Ar-CH).

1H NMR (DMSO) 1.23 (s, C(CH₃)₆, 18H), 1.15 (s, C(CH₃)₆, 18H), 1.18 (m, (CH₂)₁₀, 40H), 3.81 (s, -OCH₃, 18H), 3.88 (d, ArCH₂Ar, 8H), 4.02 (t, -OCH₂, 8H), 7.11 (s, ArH, 4H), 6.95 (s, ArH, 4H), 6.93 (d, ArH, 4H), 7.76 (d, ArH, 4H).

13C NMR (DMSO) 153, 151, 148, 134, 127 (Ar-C), 126.1, 124.8, 116.1, 104.1 (-CH), 69.1, 34.1, 29.7, 26.1 (-CH₂), 62.1, 58.1, 31.8 (-OCH₃), 32.7 (bridge –CH₂), 31.3 (-CH₃), 34.4 (C(CH₃)₃) ESI-MASS: (m/z) 1557 (M+1).


p-tert-butylcalix[4]arene (1 g, 0.0015 mol), C2 (1.45 g, 0.003 mol), K₂CO₃ (0.425 g, 0.003 mol), KI (0.283 g, 0.003 mol) in anhydrous acetone (50 ml) were reacted at refluxed temperature for 24 h, and the product was isolated as described above in D-1. Yield 0.7g, mp 175-180°C. Anal. calc: C₉₈H₁₂₂N₆O₆: C, 79.19; H, 8.45; N, 5.77; O, 6.59%. Found: C, 79.08; H, 8.24; N, 5.58; O, 6.12% FT-IR (KBr) ν: 3350 cm⁻¹ (-OH), 1600 cm⁻¹ (-N=N-), 3050 cm⁻¹ (Ar-CH).

1H NMR (DMSO) 1.25 (s, C(CH₃)₆, 18H), 1.20 (s, C(CH₃)₆, 18H), 1.29 (m, (CH₂)₁₀, 40H), 4.4 (s, -CH₂CN, 4H), 3.82 (d, ArCH₂Ar, 8H), 4.14 (t, -OCH₂, 8H), 7.2 (s, ArH, 4H), 6.98 (s, ArH, 4H), 7.01 (d, ArH, 4H), 7.7 (d, ArH, 4H).

13C NMR (DMSO) 163.3, 153.4, 150.5, 146.2, 136.5, 129.1(Ar-C), 128.1, 125.6, 124.1, 116.3, 114.7 (-CH), 70.2, 68.3, 33.1, 30.1, 29.6, 23.1(-CH₂), 117.7(-CH₂CN), 32.5 (bridge –CH₂), 31.6 (-CH₃), 34.9 ((CH₃)₃). ESI-MASS: (m/z) 1456 (M+1).

p-tert-butylcalix[4]arene (1 g, 0.0015 mol), C3 (1.60 g, 0.003 mol), K₂CO₃ (0.414 g, 0.003 mol), KI (0.276 g, 0.003 mol) in anhydrous acetone (50 ml) were reacted at refluxed temperature for 24 h, and the product was isolated as described above in D-1. Yield 85%, mp 178-180°C. Anal. calc.: C₉₄H₁₂₄N₄O₁₂: C, 75.17; H, 8.32; N, 3.73; O, 12.78%. Found: C, 75.12; H, 7.94; N, 3.6; O, 12.34%. FT-IR (KBr) ν: 3200 cm⁻¹ (-OH), 1540 cm⁻¹ (-N=N-), 2950 cm⁻¹ (Ar-CH). ¹H NMR (DMSO) 1.32 (s, C(CH₃)₆, 18H), 1.25 (s, C(CH₃)₆, 18H), 1.28 (m, (CH₂)₈, 32H), 3.84 (s, -OCH₃, 18H), 4.06 (d, ArCH₂Ar, 8H), 4.02 (t, -OCH₂, 8H), 7.31 (s, ArH, 4H), 6.95 (s, ArH, 4H), 6.98 (d, ArH, 4H), 7.42 (d, ArH, 4H). ¹³C NMR (DMSO) 155, 154, 150, 132, 125 (Ar-C), 125.8, 123.8, 117.1, 105.1 (-CH), 67.1, 32.1, 29.5, 26.7 (-CH₂), 62.5, 57.9, 34.8 (-OCH₃), 32.9 (bridge –CH₂), 31.9 (-CH₃), 34.6 (C (CH₃)₃). ESI-MASS: (m/z) 1501 (M+K⁺).


p-tert-butylcalix[4]arene (1 g, 0.0015 mol), C₄ (1.45 g, 0.003 mol), K₂CO₃ (0.425 g, 0.003 mol), KI (0.283 g, 0.003 mol) in anhydrous acetone (50 ml) were reacted at refluxed temperature for 24 h, and the product was isolated as described above in D-1. Yield 79% mp 172-175°C. Anal. calc.: C₉₂H₁₁₄N₆O₆: C, 78.93; H, 8.21; N, 6.0; O, 6.86%. Found: C, 78.69; H, 8.11; N, 5.85; O, 6.67%. FT-IR (KBr) ν: 3450 cm⁻¹ (-OH), 1560 cm⁻¹ (-N=N-), 2950 cm⁻¹ (Ar-CH). ¹H NMR (DMSO) 1.22 (s, C(CH₃)₆, 18H), 1.18 (s, C(CH₃)₆, 18H), 1.41 (m, (CH₂)₈, 32H), 4.07 (s, -CH₂CN, 4H), 3.86 (d, ArCH₂Ar, 8H), 4.3 (t, -OCH₂, 8H), 7.4 (s, ArH, 4H), 7.0 (s, ArH, 4H), 7.3 (d, ArH, 4H), 7.8 (d, ArH, 4H). ¹³C NMR (DMSO) 160, 152.4, 151.7, 146.2, 136.5 (Ar-C), 126.1, 124.8, 122.6, 115.3, 110.2, 69.3, 33.4, 30.7, 29.5 (-CH₂), 117.7 (-CH₂CN), 32.3 (bridge –CH₂), 31.9 (-CH₃), 34.3 (C (CH₃)₃). ESI-MASS: (m/z) 1400 (M+1⁺).
Figure S1: Variation of dielectric permittivity with log frequency for compound D-1 to D-4

Figure S2: Variation of dissipation factor (tan δ) with log frequency at different temperatures,(D-1 ,D-2)
Figure S3: Variation of dissipation factor (tan δ) with log frequency at different temperatures (D-3 and D-4).

Figure S4: UV/vis absorption spectra of sample D-1 (1 × 10^{-2}M) (a) fresh solution sample, (b) after exposure to 320–380 nm light, and (c) after keeping the exposed sample in darkness overnight.
**Figure S5:** UV/vis absorption spectra of sample D-2 \((1 \times 10^{-2} \text{M})\) (a) fresh solution sample, (b) after exposure to 320–380 nm light, and (c) after keeping the exposed sample in darkness overnight.

**Figure S6:** FT-IR spectra of compound D-1
Figure S7: FT-IR spectra of compound D-2

Figure S8: $^1$H NMR spectra of compound D-1 using DMSO as a solvent.
Figure S9: $^1$H NMR spectra of compound D-4 using DMSO as a solvent.

Figure S10: ESI-MASS spectra of compound D-1.
Figure S11: ESI-MASS spectra of compound D-2.

Figure S12: Proposed mechanism of trans-cis confirmation in calix[4]arene scaffolds
Table: Transition Temperatures (°C) and enthalpies of transitions (kJ/mol) for the compounds (D-1 to D-4)

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<th>Compound</th>
<th>Transition</th>
<th>Temperature(°C)</th>
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<th>$^{b}\Delta H$(Joule/Gram)</th>
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<td>D-1</td>
<td>Cr-SmC</td>
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<td></td>
<td>SmC- N</td>
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