Chapter III

Methodology

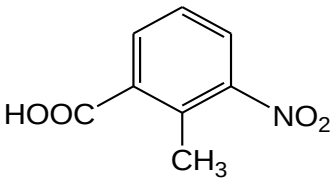
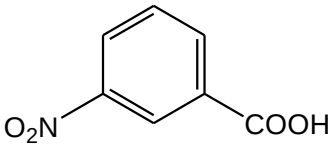
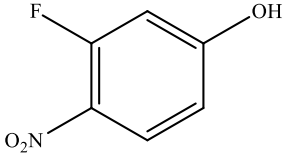
Describes the synthetic procedure towards the target compounds.

3. Experimental: Synthetic strategy and Methodology

The intermediate and target compounds are designed and synthesized following the procedures well documented in literature [1-3]. The synthesis was carried out on a trial basis and then the trial procedure was followed to get the maximum yield of the desired compounds in pure form. The compounds were recrystallized from suitable solvents or purified by column chromatography. The synthetic procedures for the intermediate as well as target compounds are described below. All the solvents are purified following standard procedures well depicted in the literature [4-6]. Silica gel (60-120 mesh) from Acme synthetic chemicals was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for Thin Layer Chromatography for reaction monitoring. Benzene, Chloroform, Ethyl acetate and Petroleum ether were used as eluents for chromatographic separation.

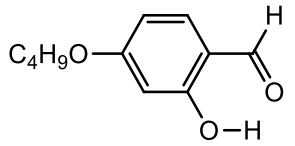
Table 3.1. Commercially available compounds

The following commercial compounds were procured from Frinton Chemicals, (U. S. A.), Tokyo Kasei Chemicals (Japan), Lancaster synthesis (U.K.), Aldrich chemicals (India) and Avocado chemicals (U.K.).

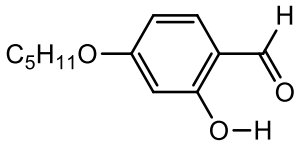
 1. 2-methyl-3-nitro benzoic acid	 2. 3-nitrobenzoicacid
 3. 3-fluoro-4-nitrophenol	

The following intermediate compounds and final products had been synthesized in the laboratory and characterized by complementary studies and are furnished below.

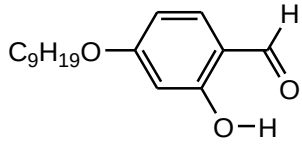
Table3.2. Intermediate compounds:

1) 

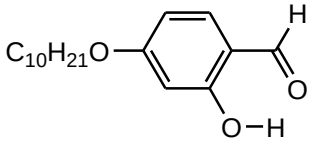
4-n-butyloxysalicylaldehyde

2) 

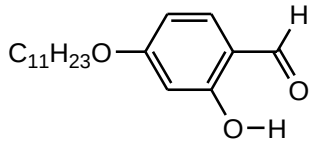
4-n-pentyloxysalicylaldehyde

3) 

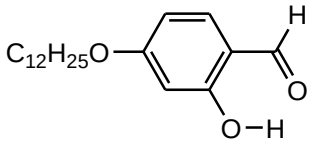
4-n-nonyloxysalicylaldehyde

4) 

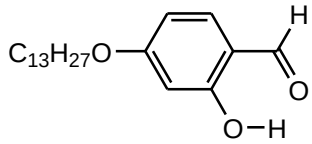
4-n-decyloxysalicylaldehyde

5) 

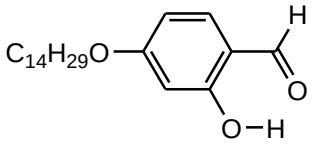
4-n-undecyloxysalicylaldehyde

6) 

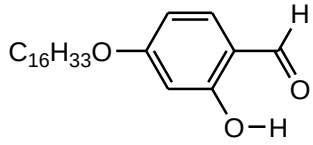
4-n-dodecyloxysalicylaldehyde

7) 

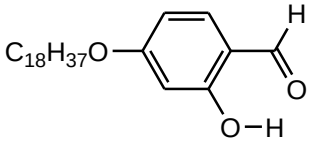
4-n-tridecyloxysalicylaldehyde

8) 

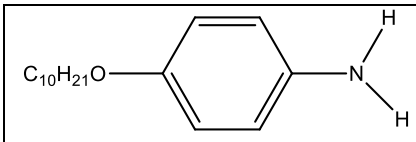
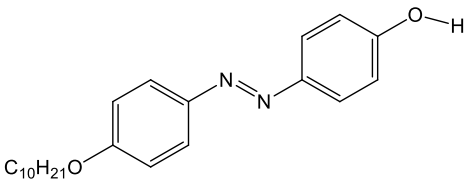
4-n-tetradecyloxysalicylaldehyde

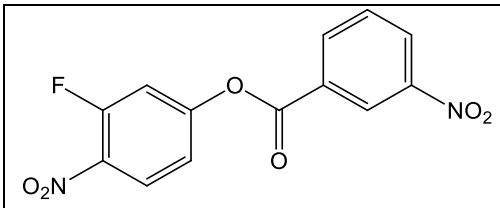
9) 

4-n-hexadecyloxysalicylaldehyde

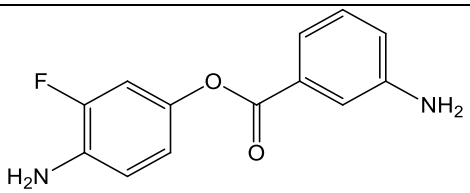
10) 

4-n-octadecyloxysalicylaldehyde ,

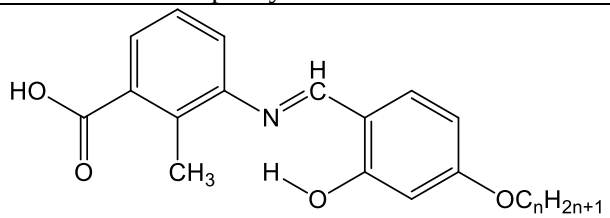
 11) 4-n-decyloxy aniline	 12) (E)-((4-decyloxy)phenyl)diazenyl)phenol



13) 3-fluoro-4-nitrophenyl 3-nitrobenzoate

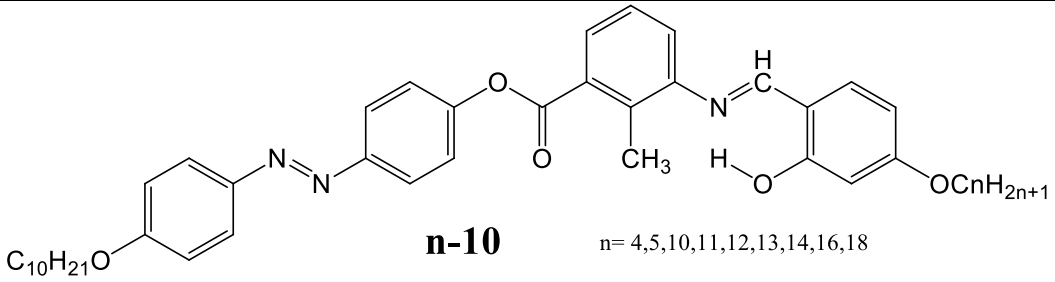


14) 4-amino-3-fluorophenyl 3-aminobenzoate



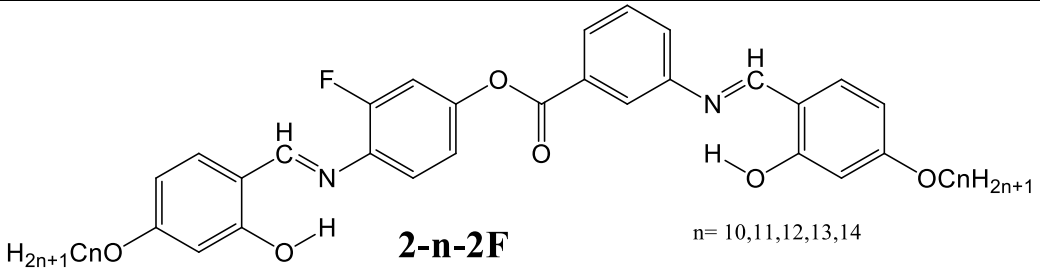
(15) 3-[N-(4/-n-alkyloxysalicylideneamino)]-2-methyl-benzoicacid

Table3.3. Final compounds:



n-10 n= 4,5,10,11,12,13,14,16,18

(16) 4-((E)-(4-(decyloxy)phenyl)diazenyl)phenyl3-((E)-(4-(alkyloxy)-2 hydroxybenzylidene)amino)-2-methylbenzoate



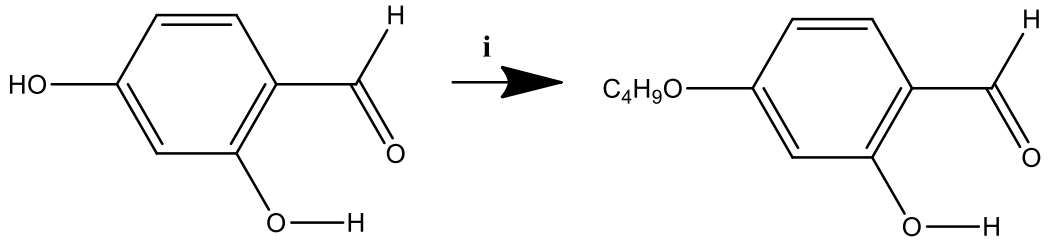
2-n-2F n= 10,11,12,13,14

(17). 3-fluoro-4-((E)-(2-hydroxy-4-(alkyloxy)benzylidene)amino)phenyl-3-((E)-(2-hydroxy-4-(alkyloxy)benzylidene)amino)benzoate

3.4. Synthesis of intermediates:

3.4.1. Synthesis of alkoxysalicylaldehyde:

4-n-butyloxysalicylaldehyde:



Scheme 1: i. acetone(dry), $NaHCO_3$, C_4H_9Br , KI, reflux,12 h

The synthesis of 4-alkoxy-salicylaldehyde viz., mono alkylation was performed by using a modified literature[14] procedure to improve the product yield. 2,4-dihydroxybenzaldehyde (10g, 72.4 mmol), 1-bromobutane (75 mmol, 10.1 ml), $NaHCO_3$ (6.30g, 75 mmol) and KI (catalytic amount) were mixed in dry acetone (250ml) and then the mixture was refluxed for 12 hours. It was then filtered hot to remove the insoluble solid. To neutralize the warm solution dilute HCl was added, which was then extracted twice with $CHCl_3$ (100ml). The combined extracts were concentrated to give a purple solid. The product was purified by column chromatography using silica gel (60-120 mesh) eluting with a mixture of chloroform and hexane (V/V; 1/1) followed by evaporation of solvent gave the product as a white liquid.

4-n-butyloxysalicylaldehyde Yield: 8.43 gm, 60%.

IR ν_{max} in cm-1: 1665 (νC=O, aldehyde), 3440 (νO-H, H-bonded).

^{1}HNMR($CDCl_3$, 300 MHz) for : δ = 11.48 (s, 1H, -OH); 9.69 (s, 1H, -CH=O); 7.45 (d, 1H, J = 9.2 Hz, ArH); 6.50 (d, 1H, J = 8.8 Hz, ArH); 6.43 (d, 1H, J = 8.6 Hz, ArH); 4.00 (t,2H, J = 6.3 Hz, -O-CH_2-); 1.60 (q, 2H, J = 6.6 Hz, - CH_2-CH_2-); 0.90 (t, 3H, J = 6.3 Hz, -CH_3). Elemental analysis calculated for $C_{11}H_{14}O_3$: C = 68.02%; H = 7.27%; Found C = 68.01%; H = 7.26%.

The other required 4-n-alkyloxysalicyladehydes were prepared **(n = 5, 10, 11, 12, 13, 14, 16 and 18)** following above procedure with appropriate amount of alkyl

bromides. The required 1-bromoalkanes, respective yields of the aldehydes, spectroscopic and analytical data are presented below.

4-n-pentyloxysalicylaldehyde: 1-bromopentane (11.2 ml, 75 mmol). 15.07 g of light brown liquid was obtained which was subjected to column chromatography to obtain in pure form. Yield = 11.0g, (73%).

IR ν_{max} in cm^{-1}: 1666 ($\nu_{C=O}$, aldehyde), 3438 (ν_{O-H}, H-bonded);

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.42 (s, 1H, -**OH**); 9.56 (s, 1H, -**CH**=O); 7.40 (d, 1H, J = 8.4 Hz, Ar**H**); 6.78 (d, 1H, J = 8.9 Hz, Ar**H**); 6.61 (d, 1H, J = 8.7 Hz, Ar**H**); 4.15 (t, 2H, J = 6.8 Hz, -O-**CH_2**-); 1.68 (q, 2H, J = 6.6 Hz, - OCH_2-**CH_2**-); 1.38-1.23 (m, 12H, -(**CH_2)$_2$**-); 0.86 (t, 3H, J = 6.6 Hz, -**CH_3**). Elemental analysis calculated for $C_{12}H_{16}O_3$: C = 69.21%; H = 7.74%; Found C = 69.2%; H = 7.73%.

4-n-decyloxysalicylaldehyde:

1-bromodecane (17.7 ml, 75 mmol). 13.5 g of white solid was obtained which was subjected to column chromatography to obtain in pure form. Yield = 13.5g, (73%).

IR ν_{max} in cm^{-1}: 1668 ($\nu_{C=O}$, aldehyde), 3443 (ν_{O-H}, H-bonded);

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.39 (s, 1H, -**OH**); 9.71 (s, 1H, -**CH**=O); 7.44 (d, 1H, J = 8.9 Hz, Ar**H**); 6.51 (d, 1H, J = 8.8 Hz, Ar**H**); 6.41 (d, 1H, J = 8.7 Hz, Ar**H**); 4.05 (t, 2H, J = 6.3 Hz, -O-**CH_2**-); 1.66 (q, 2H, J = 6.6 Hz, - CH_2-**CH_2**-); 1.41-1.25 (m, 14H, -(**CH_2)$_7$**-); 0.86 (t, 3H, J = 6.6 Hz, -**CH_3**). Elemental analysis calculated for $C_{17}H_{26}O_3$: C = 73.34%; H = 9.41%; Found C = 73.39%; H = 9.40%.

4-n-undecyloxysalicylaldehyde:

1-bromoundecane (17.5 ml, 75 mmol). 15.5 g of white solid was obtained which was subjected to column chromatography to obtain in pure form. Yield = 15g, (74%).

IR ν_{max} in cm^{-1}: 1660 ($\nu_{C=O}$, aldehyde), 3442 (ν_{O-H}, H-bonded);

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.41 (s, 1H, -**OH**); 9.71 (s, 1H, -**CH**=O); 7.44 (d, 1H, J = 8.7 Hz, Ar**H**); 6.55 (d, 1H, J = 8.8 Hz, Ar**H**); 6.31 (d, 1H, J = 8.9 Hz, Ar**H**); 3.99 (t, 2H, J = 6.3 Hz, -O-**CH_2**-); 1.63 (q, 2H, J = 6.6 Hz, - OCH_2-**CH_2**-); 1.51-1.25 (m, 16H, -(**CH_2**)$_8$-); 0.86 (t, 3H, J = 6.6 Hz, -**CH_3**). Elemental analysis calculated for $C_{18}H_{28}O_3$: C = 73.93%; H = 9.65%; Found C = 73.99%; H =9.72%.

4-n-dodecyloxysalicylaldehyde:

1-bromododecane (18.8 ml,75 mmol). 16.9 g of white solid was obtained which was subjected to column chromatography to obtain in pure form. Yield = 15.2g, (70%).

4-n-dodecyloxysalicylaldehyde Yield: 13.8 gm, 60%.

IR ν_{max} in cm-1: 1666 (νC=O, aldehyde), 3449 (νO-H, H-bonded).

^{1}HNMR($CDCl_3$, 300 MHz): δ = 11.48 (s, 1H, -OH); 9.69 (s, 1H, -CH=O); 7.42 (d, 1H, J = 9.2 Hz, ArH); 6.52 (d, 1H, J = 8.8 Hz, ArH); 6.41 (d, 1H, J = 8.6 Hz, ArH); 4.00 (t,2H, J = 6.3 Hz, -O-CH_2-); 1.60 (q, 2H, J = 6.6 Hz, - CH_2-CH_2-); 1.44-1.26 (m, 18H, -$(CH_2)_9$-); 0.90 (t, 3H, J = 6.3 Hz, -CH_3). Elemental analysis calculated for $C_{19}H_{30}O_3$: C = 74.47%; H = 9.87%; Found C = 74.95%; H = 9.86%.

4-n-tridecyloxysalicylaldehyde:

1-bromotridecane (10 ml, 40 mmol), 9 g of white solid was obtained which was subjected to column chromatography to obtain in pure form. Yield = 8 g, (72%).

IR ν_{max} in cm^{-1}: 1661 ($\nu_{C=O}$, aldehyde), 3444 (ν_{O-H}, H-bonded);

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.39 (s, 1H, -**OH**); 9.71 (s, 1H, -**CH**=O); 7.44 (d, 1H, J = 8.7 Hz, Ar**H**); 6.54 (d, 1H, J = 8.6 Hz, Ar**H**); 6.33 (d, 1H, J = 8.7 Hz,

Ar**H**); 4.10 (t, 2H, J = 6.3 Hz, -O-**CH$_2$**-); 1.66 (m, 2H, - OCH$_2$-**CH$_2$**-); 1.45-1.27 (m, 20H, -(**CH$_2$)$_{10}$**-); 0.88 (t, 3H, J = 6.6 Hz, -**CH$_3$**). Elemental analysis calculated for $C_{20}H_{32}O_3$: C = 74.96%; H =10.06%; Found C = 75.00%; H =10.01%

4-n-tetradecyloxysalicylaldehyde:

1-bromotetradecane (20.7 ml, 75 mmol). 18 g of white solid was obtained which was subjected to column chromatography to obtain in pure form. Yield = 17.2g, (74%).

IR ν_{max} in cm^{-1}: 1663 ($\nu_{C=O}$, aldehyde), 3448 (ν_{O-H}, H-bonded);

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.30 (s, 1H, -**OH**); 9.71 (s, 1H, -**CH**=O); 7.55 (d, 1H, J = 8.7 Hz, Ar**H**); 6.50 (d, 1H, J = 8.7 Hz, Ar**H**); 6.33 (d, 1H, J = 8.9 Hz, Ar**H**); 4.11 (t, 2H, J = 6.8 Hz, -O-**CH$_2$**-); 1.63 (q, 2H, J = 6.7 Hz, - OCH$_2$-**CH$_2$**-); 1.34-1.27 (m, 22H, -(**CH$_2$)$_{11}$**-); 0.88 (t, 3H, J = 6.8 Hz, -**CH$_3$**). Elemental analysis calculated for $C_{21}H_{34}O_3$: C = 75.41%; H =10.25%; Found C = 75.34; H = 10.32%

4-n-hexadecyloxysalicylaldehyde:

1-bromohexadecane (22.8 ml,75 mmol). 21 g of white solid was obtained which was subjected to column chromatography to obtain in pure form. Yield=20.2g, (77%).

IR ν_{max} in cm^{-1}: 1665 ($\nu_{C=O}$, aldehyde), 3440 (ν_{O-H}, H-bonded);

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.25 (s, 1H, -**OH**); 9.55 (s, 1H, -**CH**=O); 7.70 (d, 1H, J = 8.7 Hz, Ar**H**); 6.55 (d, 1H, J = 8.8 Hz, Ar**H**); 6.41 (d, 1H, J = 8.8 Hz, Ar**H**); 4.11 (t, 2H, J = 6.8 Hz, -O-**CH$_2$**-); 1.58 (q, 2H, J = 6.7 Hz, - OCH$_2$-**CH$_2$**-); 1.36-1.28 (m, 26H, -(**CH$_2$)$_{13}$**-); 0.86 (t, 3H, J = 6.8 Hz, -**CH$_3$**). Elemental analysis calculated for $C_{23}H_{38}O_3$: C = 76.20%; H =10.56%; Found C = 76.08; H = 10.53%

4-n-octadecyloxysalicylaldehyde:

1-bromooctadecane (25ml,75 mmol). 23.5 g of white solid was obtained which was subjected to column chromatography to obtain in pure form.

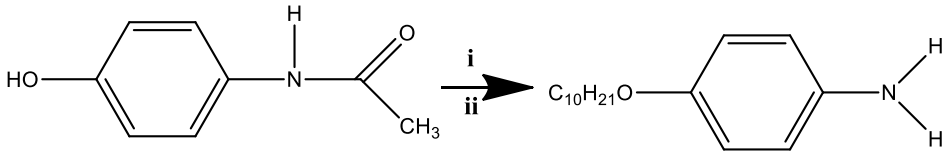
4-n-octadecyloxysalicylaldehyde: Yield: 20.5 gm, 70%.

IR νmax in cm-1: 1666 (νC=O, aldehyde), 3449 (νO-H, H-bonded).

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.30 (s, 1H, -**OH**); 9.54 (s, 1H, -**CH**=O); 7.65 (d, 1H, J = 8.8 Hz, Ar**H**); 6.50 (d, 1H, J = 8.7 Hz, Ar**H**); 6.26 (d, 1H, J = 8.6 Hz, Ar**H**); 4.00 (t, 2H, J = 6.8 Hz, -O-**CH_2**-); 1.66 (q, 2H, J = 6.6 Hz, - OCH_2-**CH_2**-); 1.33-1.25 (m, 24H, -(**CH_2)$_{15}$**-); 0.85 (t, 3H, J = 6.7 Hz, -**CH_3**). Elemental analysis calculated for $C_{25}H_{42}O_3$: C = 76.87%; H =10.84%; Found C = 76.78; H = 10.80%.

3.4.2. Synthesis of alkoxyaniline:

4-n-decyloxyaniline:



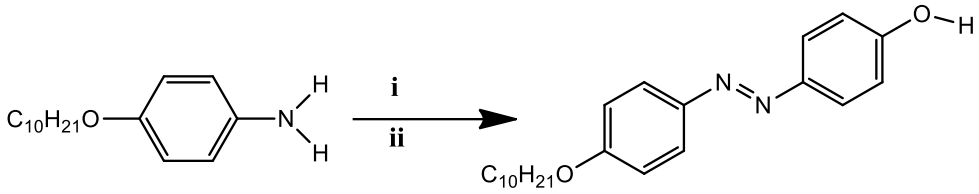
Scheme 2: i. acetone(dry), K_2CO_3, $C_{10}H_{21}Br$, KI, reflux,40 h
ii. ethanol,35%HCl, reflux 4h

A solution of 1-bromodecane (22.1g, 0.10mol) was added to a suspension of 4-acetamidophenol (15.17g, 0.10mol) and potassium carbonate (41.0g, 0.3mol) along with a catalytic amount of potassium iodide (0.25g) in dry acetone (200ml), the mixture was refluxed for 40 h and when it was hot the solution was filtered through Buchner funnel and the solvent acetone was evaporated from the filtrate to yield a colourless powder. The residues in the funnel were washed with ether several times and the washings were evaporated to give the solid. Both the solids were combined and dissolved in dichloromethane and the solution was washed with a solution of NaOH (2 x 100 cm^3, 2mol/dm^3) followed by a solution of NaCl (2 x 100cm^3, 2mol/dm^3), and dried over Na_2SO_4 and then the solvent was evaporated. The product was crystallized from hot absolute ethanol and a white solid was obtained. The white solid thus obtained was then dissolved in ethanol (200 cm^3, 95%) and HCl (75 cm^3, 35%) was added. The solution was then refluxed for 4 hours. After cooling the reaction mixture to room temperature, it was filtered to yield solid 1. The filtrate was concentrated, cooled and filtered to yield solid 2. Both the solids 1 and 2 were combined together and to the solid residues water (100 cm3) was added followed by the addition of a solution of NaOH (2 mol/dm^3) until the pH = 12 was attained. The solid was filtered, dried and recrystallized from ethanol. Yield = 16.6 gm, 66 %, M.P. 65^{o}C.

IR analysis (data in cm^{-1}): 2955, 2602 (νCH); 1624, 830 (νN-H), 1260 (νC-N), 1521, 1475 (νC=Caromatic), 1045 (νCO). Molecular formula: $C_{16}H_{27}NO$; Mol. Wt.: 249; Elemental analysis: Estimated: C, 77.06; H, 10.91; N, 5.62; Found: C, 77.12; H, 10.85; N, 5.55.

3.4.3. Synthesis of alkoxyphenylazo phenol:

4-(4/-n-decyloxyphenylazo) phenol:



Scheme 3: i. HCl, $NaNO_2$, 0-5°C
ii. phenol, NaOH

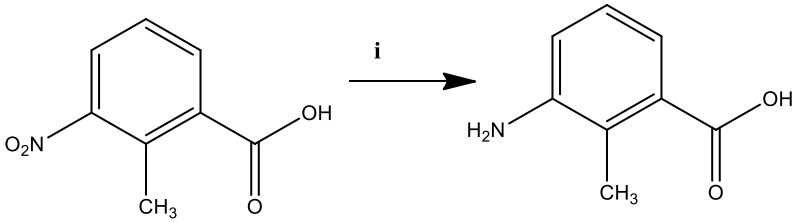
To a solution of 30ml of mixture of alcohol and water (1:1) containing hydrochloric acid (6.85 ml, 4.4M, 0.03mol) 4-n-decyloxy aniline (5.0 g, 0.02 mol) was added slowly to form a clear solution. The resulting solution was stirred and cooled to 0°C, and an aqueous cold solution of $NaNO_2$ (1.6g, 0.023mol) was added drop wise maintaining the temperature of the reaction mixture at 0-5°C, to yield the diazonium chloride. It was subsequently coupled with salicylaldehyde (2.44g, 0.02mol) which was dissolved in 23 ml of aqueous 2N NaOH (1.84g, 0.046mol) solution and ethanol (3ml) was added to the solution of diazonium salt. The reaction mixture was stirred for 1h at 0-5°C and then allowed to warm slowly to room temperature with stirring for over 1 h. The resulting yellow precipitate was filtered, washed with H_2O several times. The crude product was dissolved in CH_2Cl_2 dried over Na_2SO_4. After removal of the solvent under reduced pressure the sample was recrystallized to give yellow crystalline solid. Yield = 4.9 g, 69%.

IR ν_{max} in cm^{-1} : 1483 ($\nu_{N=N}$, azo), 3449 (ν_{O-H}, H-bonded).

^{1}H-NMR($CDCl_3$, 400 MHz): δ = 5.56 (s, 1H, Ar-**OH**); 7.92 (d, 2H, J = 10.2 Hz, Ar**H**); 7.86 (d, 2H, J = 10.2 Hz, Ar**H**); 7.01 (d, 2H, J = 10.2 Hz, Ar**H**); 6.96 (d, 2H, J = 10.2 Hz, Ar**H**); 4.06 (t, 2H, J = 6.3 Hz, -O-**CH_2**-); 1.86 (q, 2H, J = 6.6 Hz, - OCH_2-**CH_2**-); 1.34-1.53 (m, 14H, -(**CH_2**)$_7$-); 0.92 (t, 3H, J = 6.3 Hz, -**CH_3**).

Molecular formula: $C_{16}H_{27}NO$; Mol. Wt.: 354.4, Elemental analysis calculated for $C_{25}H_{34}N_2O_3$: C = 74.54%; H = 8.53%; N = 7.90%. Found C = 74.23%; H = 8.53%; N = 7.83%.

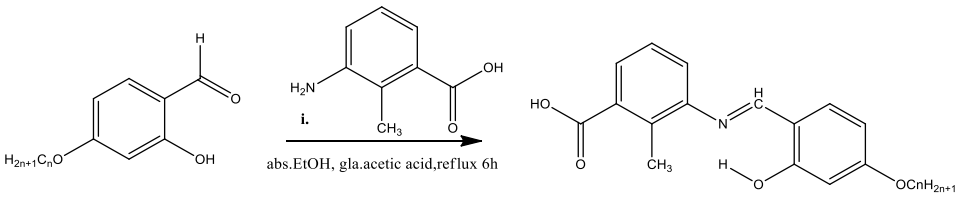
3.4.4. Synthesis of 2-Methyl-3-aminobenzoicacid:



Scheme 4: i. Dry ethyl acetate,10% Pd-C, stir 15h

Commercial 2-Methyl-3-nitrobenzoicacid (1.8 g, 10 mmol) was dissolved in dry ethylacetate in a two neck round bottom flask and 10% Pd-C (0.28 g) was added to it. The reaction mixture was stirred for 15 h under the hydrogen atmosphere. After completion of the reaction the solution was filtered and recrystallized from ethylacetate using animal charcoal to yield the pure product as white solid in quantitative yield. Yield: 1.36gm (90%).

3.4.5. Synthesis of 3-[N-(4/-n-alkyloxysalicylideneamino)]-2-methyl-benzoicacid:



Scheme 5:

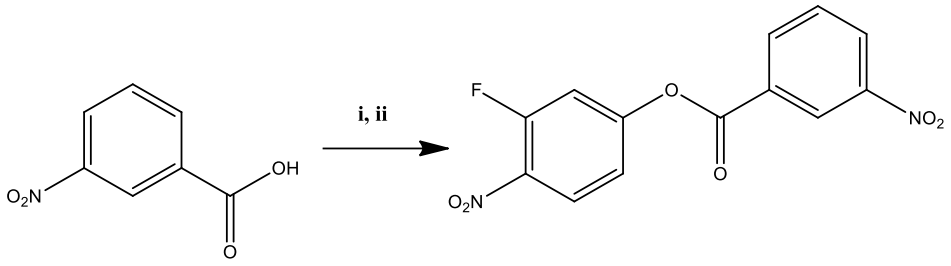
An ethanolic solution of 2-Methyl-3-aminobenzoicacid (0.45 g, 3 mmol) was added to an ethanolic solution (20 ml) of 4-n-alkyloxysalicyldehyde (0.92 g, 3 mmol). The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 6 hours to yield the yellow Schiff's base 3-(N-4/-n alkyloxysalicylideneimino) phenyl-2-methylbenzoicacid. The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure compound. Yield = 0.76 g, (58%).

The analytical data are follows for n=12: IR ν_{max} in cm^{-1}: 1625 ($\nu_{CH=N}$, imine); 1747 ($\nu_{C=O}$, ester), 3427(ν_{O-H}, H-bonded).

^1H NMR (400 MHz, $CDCl_3$: δ = 12.26 (s, 1H, Ar-COOH), 13.51 (s, 1H, Ar-OH), 8.01 (s, 1H, -CH=N-), 7.96 (d, 8.0Hz, 1H), 7.54 (d, 8.8Hz, 1H), 7.38 (d, 8.0 Hz, 1H), 7.32 (d, 8.8Hz, 1H), 7.04 (dd, 8.4Hz, 1H), 6.62 (d, 8.4Hz, 1H), 4.15 (t, Ar-CH_2, 2H), 2.72 (s, $ArCH_3$, 3H), 1.27-1.89 (m, -$(CH_2)_2$, 20H), 0.92 (t, 3H) ppm.

3.5 Synthesis of central core:

3.5.1 Synthesis of 3-fluoro-4-nitrophenyl 3-nitrobenzoate:



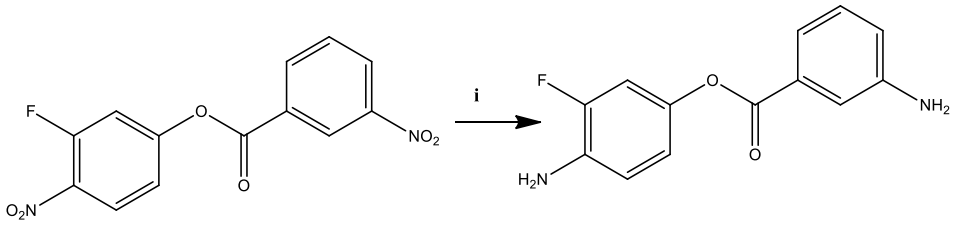
Scheme 7: i.$SOCl_2$, DCM, ii. 3, fluoro-4-nitro phenol, DCM, K_2CO_3, TBAB

3-nitrobenzoic acid (2.50g; 15mmol) was dissolved in dichloromethane in a two neck round bottomed flask with a teflon coated magnetic stirrer and the reaction flask was flushed with N_2, sealed with a rubber septum and cooled in an ice bath. Thionylchloride (2.0 ml, 16.5 mmol) was added drop wise slowly to the cooled reaction mixture. The ice bath was removed and the reaction mixture was vigorously stirred and refluxed for 3h. The solvent and excess thionyl chloride was evaporated under reduced pressure and the resulting compound was dried under vacuum. To the resulting acyl chloride dissolved in dichloromethane (30ml), an aqueous solution of 3,fluoro-4-nitro phenol (2.35g; 15mmol) and K_2CO_3 (4.14g; 30mmol) were added. The resulting solution was vigorously stirred for 24 h after adding a catalytic amount of tetra butyl ammonium bromide. After the stirring was complete, the organic layer was separated, washed several times with the alkaline solution and water and then dried over sodium sulphate. Evaporation of the solvent gives the crude product which was then purified by column chromatography (silica gel, eluent petroleum ether/ ethyl acetate, 97:3

v/v) followed by recrystallization from ethanol to obtain the pure product as white solid. Yield = 3.6 g, (80%).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 9.03 (d, 1H, J = 6 Hz, Ar**H**); 8.50 (d, 1H, J = 9.0 Hz, Ar**H**); 8.38 (d, 2H, J = 8.0 Hz, Ar**H**); 7.48 (d, 1H, J = 8.4 Hz, Ar**H**); 7.45 (d, 2H, J = 8.6 Hz, Ar**H).** Elemental analysis calculated for $C_{13}H_7FN_2O_6$: C = 50.99%; H =2.30%; N= 9.15% Found C = 50.94%; H = 2.32%; N = 9.06%.

3.5.2 Synthesis of 4-amino-3-fluorophenyl 3-aminobenzoate:



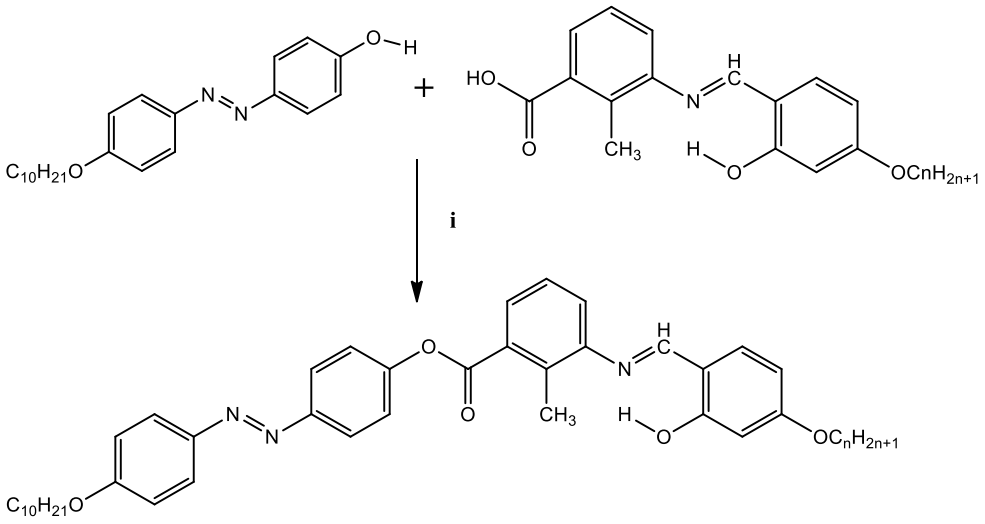
Scheme 8: i. Pd-C(10%), H_2, Dry ethyl acetate

3-fluoro-4-nitrophenyl 3-nitrobenzoate (3.06 g, 10 mmol) was dissolved in ethyl acetate in a two neck round bottom flask to it 10% Pd-C (0.28g). The reaction mixture is stirred for 15hrs under balloon pressure filled with hydrogen gas. On completion of the reaction the crude product was collected by evaporating the solvent under reduced pressure. The crude product was then purified by column chromatography (silica gel 60-120 mesh, using dichloromethane/ethanol, (99.5:0.5::V/V) as eluent to give pure product. Yield: 2.18 g (89%)

3.6. Synthesis of the target designed compounds:

3.6.1 Synthesis of 4-((E)-(4-(decyloxy)phenyl)diazenyl)phenyl 3-((E)-(4-(alkyloxy)-2-hydroxybenzylidene)amino)-2-methylbenzoate:

4-(4/-n-decyloxyphenylazo) phenyl-3-[N-(4/-n-dodecyloxysalicylideneamino)]-2-methyl-benzoate, 12-10 :



n= 4,5,10,11,12,13,14,16,18

Scheme 9: i) DCC, DMAP, DCM, Stirring 48 hr.

1 mmol of 3-[N-(4/-n-dodecyloxysalicylideneamino)]-2-methyl-benzoicacid (0.44 g) and 1 mmol of 4-(4/-n-decyloxyphenylazo) phenol (0.35g) were dissolved in100 ml of absolute dichloromethane. Dicyclohexylcarbodimide (3mmol) and a small amount of dimethylaminopyridine as catalyst were added. The mixture was stirred at room temperature for 48 hours. The solution was filtered off and the solvent was evaporated. The product **12-10** was recrystallized several times from acetone to obtain the pure product. Yield 0.40 g, (55%).

The analytical data are follows. IR ν_{max} in cm^{-1}: 1625 ($\nu_{CH=N}$, imine); 1467 ($\nu_{N=N}$azo); 1747 ($\nu_{C=O}$, ester), 3427(ν_{O-H}, H-bonded)

^{1}H NMR (400 MHz, $CDCl_3$) : δ = 13.51 (s, 1H, Ar-OH), 8.54 (s, 1H, -CH=N-), 7.99 (d, 8.0Hz, 1H), 7.97 (d,8.8 Hz, 2H), 7.92 (d, 8.8Hz, 2H), 7.37 (d, 8.4Hz, 2H), 7.30 (d, 8.8Hz, 1H), 7.27 (d, 8.0 Hz, 2H), 7.01 (d, 8.8Hz, 2H), 6.51 (dd, 8.4Hz,

2.4Hz, 2H), 7.92 (d, 8.4Hz, 2H), 4.03 (t, Ar-CH_2, 4H), 2.68 (s, $ArCH_3$, 3H), 1.59-1.80 (m, -$(CH_2)_{18}$, 36H), 0.88 (t, 6H) ppm.

Elemental analysis for $C_{49}H_{65}N_3O_5$ (776.06), Theoretical: C 75.84%, H 8.44%, N 5.41%; found C 75.55%, H 8.43%, N 5.32%.

Using the same procedure as described above (Scheme 9) the whole homologous series with varying number of carbon atoms (n) in the alkoxy chain (n = 4,5,10, 11,13, 14,16, 18) were synthesized. The IR, NMR and CHN data of other compounds of the homologous series are presented below.

4-(4′-n-decyloxyphenylazo)phenyl-3-[N-(4′-n-butyloxysalicylideneamino)]-2-methyl-benzoate, 4-10 :

The analytical data are follows. IR ν_{max} in cm^{-1}: 1620 ($\nu_{CH=N}$, imine); 1468 ($\nu_{N=N}$, azo); 1745 ($\nu_{C=O}$, ester), 3430(ν_{O-H}, H-bonded)

^{1}H NMR (400 MHz, $CDCl_3$) : δ = 13.50 (s, 1H, Ar-OH), 8.52 (s, 1H, -CH=N-), 7.95 (d, 8.0Hz, 1H), 7.93 (d,8.8 Hz, 2H), 7.92 (d, 8.8Hz, 2H), 7.38 (d, 8.4Hz, 2H), 7.29 (d, 8.8Hz, 1H), 7.27 (d, 8.0 Hz, 2H), 7.01 (d, 8.8Hz, 2H), 6.50 (dd, 8.4Hz, 2.4Hz, 2H), 7.92 (d, 8.4Hz, 2H), 4.01 (t, Ar-CH_2, 4H), 2.65 (s, $ArCH_3$, 3H), 1.59-1.70 (m, -$(CH_2)_{10}$, 20H), 0.89 (t, 6H) ppm.

4-(4′-n-decyloxyphenylazo)phenyl-3-[N-(4′-n-pentyloxysalicylideneamino)]-2-methyl-benzoate, 5-10 :

The analytical data are follows. IR ν_{max} in cm^{-1}: 1618 ($\nu_{CH=N}$, imine); 1467 ($\nu_{N=N}$, azo); 1743 ($\nu_{C=O}$, ester), 3434(ν_{O-H}, H-bonded)

^{1}H NMR (400 MHz, $CDCl_3$) : δ = 13.50 (s, 1H, Ar-OH), 8.52 (s, 1H, -CH=N-), 7.96 (d, 8.0Hz, 1H), 7.93 (d,8.8 Hz, 2H), 7.91 (d, 8.8Hz, 2H), 7.40 (d, 8.4Hz, 2H), 7.28 (d, 8.8Hz, 1H), 7.27 (d, 8.0 Hz, 2H), 7.03 (d, 8.8Hz, 2H), 6.52 (dd, 8.4Hz, 2.4Hz, 2H), 7.92 (d, 8.4Hz, 2H), 4.02 (t, Ar-CH_2, 4H), 2.67 (s, $ArCH_3$, 3H), 1.59-1.77 (m, -$(CH_2)_{11}$, 22H), 0.89 (t, 6H) ppm.

4-(4′-n-decyloxyphenylazo)phenyl-3-[N-(4′-n-decyloxysalicylideneamino)]-2-methyl-benzoate, 10-10 :

The analytical data are follows. IR ν_{max} in cm^{-1}: 1618 ($\nu_{CH=N}$, imine); 1469 ($\nu_{N=N}$, azo); 1742 ($\nu_{C=O}$, ester), 3433(ν_{O-H}, H-bonded)

^1H NMR (400 MHz, $CDCl_3$) : δ = 13.48 (s, 1H, Ar-OH), 8.52 (s, 1H, -CH=N-), 7.97 (d, 8.0Hz, 1H), 7.92 (d,8.8 Hz, 2H), 7.91 (d, 8.8Hz, 2H), 7.40 (d, 8.4Hz, 2H), 7.29 (d, 8.8Hz, 1H), 7.27 (d, 8.0 Hz, 2H), 7.04 (d, 8.8Hz, 2H), 6.53 (dd, 8.4Hz, 2.4Hz, 2H), 7.92 (d, 8.4Hz, 2H), 4.00 (t, Ar-CH_2, 4H), 2.69 (s, $ArCH_3$, 3H), 1.55-1.77 (m, -$(CH_2)_{16}$, 32H), 0.88 (t, 6H) ppm.

4-(4′-n-decyloxyphenylazo)phenyl-3-[N-(4′-n-undecyloxysalicylideneamino)]-2-methyl-benzoate, 11-10 :

The analytical data are follows. IR ν_{max} in cm^{-1}: 1624 ($\nu_{CH=N}$, imine); 1467 ($\nu_{N=N}$, azo); 1743 ($\nu_{C=O}$, ester), 3432(ν_{O-H}, H-bonded)

^1H NMR (400 MHz, $CDCl_3$) : δ = 13.48 (s, 1H, Ar-OH), 8.51 (s, 1H, -CH=N-), 7.94 (d, 8.0Hz, 1H), 7.91 (d,8.8 Hz, 2H), 7.90 (d, 8.8Hz, 2H), 7.40 (d, 8.4Hz, 2H), 7.29 (d, 8.8Hz, 1H), 7.27 (d, 8.0 Hz, 2H), 7.04 (d, 8.8Hz, 2H), 6.52 (dd, 8.4Hz, 2.4Hz, 2H), 7.92 (d, 8.4Hz, 2H), 4.00 (t, Ar-CH_2, 4H), 2.67 (s, $ArCH_3$, 3H), 1.55-1.77 (m, -$(CH_2)_{17}$, 34H), 0.89 (t, 6H) ppm.

4-(4′-n-decyloxyphenylazo)phenyl-3-[N-(4′-n-tridecyloxysalicylideneamino)]-2-methyl-benzoate, 13-10 :

The analytical data are follows. IR ν_{max} in cm^{-1}: 1625 ($\nu_{CH=N}$, imine); 1469 ($\nu_{N=N}$, azo); 1744 ($\nu_{C=O}$, ester), 3433(ν_{O-H}, H-bonded)

^1H NMR (400 MHz, $CDCl_3$) : δ = 13.50 (s, 1H, Ar-OH), 8.52 (s, 1H, -CH=N-), 7.94 (d, 8.0Hz, 1H), 7.93 (d,8.8 Hz, 2H), 7.90 (d, 8.8Hz, 2H), 7.40 (d, 8.4Hz, 2H), 7.29 (d, 8.8Hz, 1H), 7.27 (d, 8.0 Hz, 2H), 7.06 (d, 8.8Hz, 2H), 6.58 (dd, 8.4Hz, 2.4Hz, 2H), 7.92 (d, 8.4Hz, 2H), 4.00 (t, Ar-CH_2, 4H), 2.68 (s, $ArCH_3$, 3H), 1.55-1.77 (m, -$(CH_2)_{19}$, 38H), 0.86 (t, 6H) ppm.

4-(4′-n-decyloxyphenylazo)phenyl-3-[N-(4′-n-tetradecyloxysalicylideneamino)]-2-methyl-benzoate, 14-10 :

The analytical data are follows. IR ν_{max} in cm^{-1}: 1618 ($\nu_{CH=N}$, imine); 1469 ($\nu_{N=N}$, azo); 1744 ($\nu_{C=O}$, ester), 3434(ν_{O-H}, H-bonded)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.52 (s, 1H, Ar-OH), 8.53 (s, 1H, -CH=N-), 7.94 (d, 8.0Hz, 1H), 7.93 (d,8.8 Hz, 2H), 7.92 (d, 8.8Hz, 2H), 7.40 (d, 8.4Hz, 2H), 7.29 (d, 8.8Hz, 1H), 7.27 (d, 8.0 Hz, 2H), 7.06 (d, 8.8Hz, 2H), 6.59 (dd, 8.4Hz, 2.4Hz, 2H), 7.92 (d, 8.4Hz, 2H), 4.00 (t, Ar-CH_2, 4H), 2.69 (s, $ArCH_3$, 3H), 1.55-1.77 (m, -$(CH_2)_{20}$, 40H), 0.89 (t, 6H) ppm.

4-(4′-n-decyloxyphenylazo)phenyl-3-[N-(4′-n-hexadecyloxysalicylideneamino)]-2-methyl-benzoate, 16-10 :

The analytical data are follows. IR ν_{max} in cm^{-1}: 1620 ($\nu_{CH=N}$, imine); 1469 ($\nu_{N=N}$, azo); 1744 ($\nu_{C=O}$, ester), 3437(ν_{O-H}, H-bonded)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.53 (s, 1H, Ar-OH), 8.52 (s, 1H, -CH=N-), 7.94 (d, 8.0Hz, 1H), 7.94 (d,8.8 Hz, 2H), 7.91 (d, 8.8Hz, 2H), 7.40 (d, 8.4Hz, 2H), 7.29 (d, 8.8Hz, 1H), 7.27 (d, 8.0 Hz, 2H), 7.06 (d, 8.8Hz, 2H), 6.59 (dd, 8.4Hz, 2.4Hz, 2H), 7.92 (d, 8.4Hz, 2H), 4.00 (t, Ar-CH_2, 4H), 2.68 (s, $ArCH_3$, 3H), 1.55-1.77 (m, -$(CH_2)_{22}$, 44H), 0.89 (t, 6H) ppm.

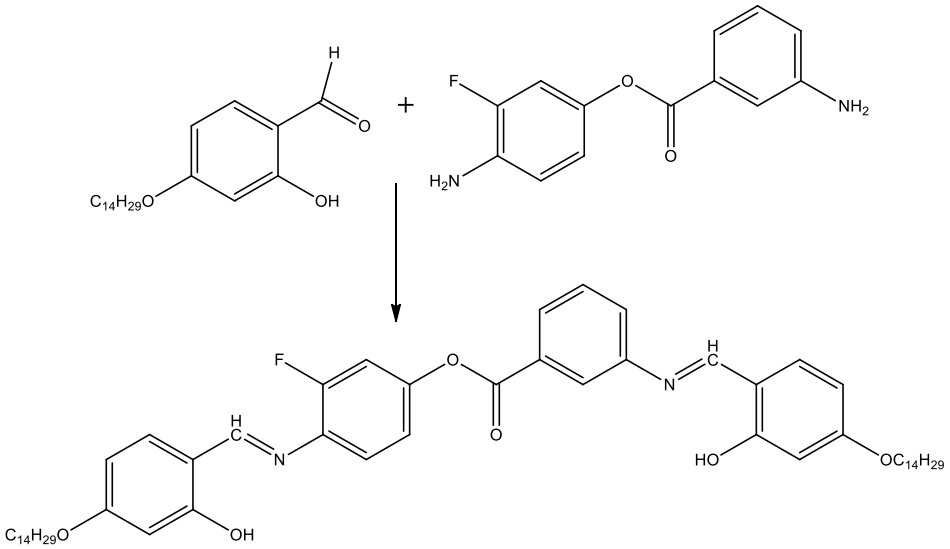
4-(4′-n-decyloxyphenylazo)phenyl-3-[N-(4′-n-octadecyloxysalicylideneamino)]-2-methyl-benzoate, 18-10 :

^{1}HNMR (400MHz, $CDCl_3$): δ = 13.51 (s, 1H, Ar-OH), 8.53 (s, 1H, -CH=N-), 7.99 (d, 8.0Hz, 1H), 7.97 (d,8.8 Hz, 2H), 7.92 (d, 8.8Hz, 2H), 7.38 (d, 8.4Hz, 2H), 7.30 (d, 8.8Hz, 1H), 7.27 (d, 8.0 Hz, 2H), 7.01 (d, 8.8Hz, 2H), 6.53 (dd, 8.4Hz, 2.4Hz, 2H), , 7.92 (d, 8.4Hz, 2H), 4.01 (t, Ar-CH_2, 4H), 2.68 (s, $ArCH_3$, 3H), 1.59-1.80 (m, -$(CH_2)_{24}$, 48H), 0.88 (t, 6H) ppm.

Elemental analysis for $C_{55}H_{77}N_3O_5$ (859.5), Theoretical: C 76.79%, H 9.02%, N 4.88%; found C 76.43%, H 8.99%, N 4.82%.

3.6.2Synthesis of 3-fluoro-4-((E)-(2-hydroxy-4(alkyloxy)benzylidene)amino)phenyl3-((E)-(2-hydroxy-4-(alkyloxy)benzylidene)amino)benzoate:

3-fluoro-4-(-(2-hydroxy-4-(tetradecyloxy)benzylidene)amino)phenyl 3-(-(2-hydroxy-4-(tetradecyloxy)benzylidene)amino)benzoate, 2-14-2F:



n = 10,11,12,13.

Scheme 10: abs EtOH, glacial acetic acid (2-3 drops), reflux 3h.

An ethanolic solution of 4-amino-3-fluorophenyl 3-aminobenzoate (0.61 g, 2.5 mmol) was added to an ethanolic solution (20 ml) of 4-n-tetradecyloxysalicylaldehyde (1.67 g, 5 mmol). The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff's base. The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure compound. Yield = 1.26g, (58%).

IR ν_{max} in cm^{-1}: 1627 ($\nu_{CH=N}$, imine); 1729 ($\nu_{C=O}$, ester), 3437(ν_{O-H}, H-bonded).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 13.46 & 13.43 (s, 2H, -**OH**); 8.62 & 8.08 (s, 2H, -**CH**=N-); 7.59 (d, 1H, J = 8.0 Hz, Ar**H**); 7.54 (d, 1H, Ar**H**); 7.34 (d, 2H, J = 9.2 Hz, Ar**H**); 7.26 (d, 1H, J = 12.0 Hz, Ar**H**); 7.15 (d, 1H, Ar**H**); 7.12 (d, 1H, Ar**H**); 7.10 (d, 1H, Ar**H**); 7.08 (d, 1H, Ar**H**); 6.62 (d, 2H, Ar**H**); 6.49 (d, 2H, Ar**H**); 4.00 (t, 4H, J = 6.0Hz, -O-**CH_2**-); 1.83 (q, 4H, J = 6.6Hz, - OCH_2-**CH_2**-); 1.80 (m, 4H, - CH_2-**CH_2**-); 1.78-1.26 (m, 40H, -**$(CH_2)_{20}$**-); 0.88 (t, 6H, J = 6.4 Hz, -**CH_3**).

Elemental analysis calculated for $C_{55}H_{75}N_2O_6F$: C = 75.14%; H = 8.60%; N = 3.19% Found. C = 75.10 %; H = 8.58%; N = 3.18%.

Using the same procedure as described above (Scheme 10) the whole homologous series with varying number of carbon atoms (n) in the alkoxy chain (n = 10, 11, 12, 13) were synthesized. The IR, NMR and CHN data of other compounds of the homologous series are presented below.

3-fluoro-4-(-(2-hydroxy-4-(tridecyloxy)benzylidene)amino)phenyl 3-(-(2-hydroxy-4-(tridecyloxy)benzylidene)amino)benzoate, 2-13-2F:

IR ν_{max} in cm^{-1}: 1625 ($\nu_{CH=N}$, imine); 1725 ($\nu_{C=O}$, ester), 3434(ν_{O-H}, H-bonded).
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 13.50 & 13.43 (s, 2H, -**OH**); 8.62 & 8.09 (s, 2H, -**CH**=N-); 7.59 (d, 1H, J = 8.0 Hz, Ar**H**); 7.54 (d, 1H, Ar**H**); 7.34 (d, 2H, J = 9.2 Hz, Ar**H**); 7.26 (d, 1H, J = 12.0 Hz, Ar**H**); 7.15 (d, 1H, Ar**H**); 7.11 (d, 1H, Ar**H**); 7.10 (d, 1H, Ar**H**); 7.08 (d, 1H, Ar**H**); 6.62 (d, 2H, Ar**H**); 6.48 (d, 2H, Ar**H**); 4.02 (t, 4H, J = 6.0Hz, -O-**CH_2**-); 1.83 (q, 4H, J = 6.6Hz, - OCH_2-**CH_2**-); 1.84 (m, 4H, - CH_2-**CH_2**-); 1.78-1.26 (m, 36H, -**$(CH_2)_{18}$**-); 0.89 (t, 6H, J = 6.4 Hz, -**CH_3**).
Elemental analysis calculated for $C_{53}H_{71}N_2O_6F$: C = 74.79%; H = 8.41%; N = 3.29% Found. C = 74.75 %; H = 8.40%; N = 3.23%.

3-fluoro-4-(-(2-hydroxy-4-(dodecyloxy)benzylidene)amino)phenyl 3-(-(2-hydroxy-4-(dodecyloxy)benzylidene)amino)benzoate, 2-12-2F:

IR ν_{max} in cm^{-1}: 1620 ($\nu_{CH=N}$, imine); 1723 ($\nu_{C=O}$, ester), 3433(ν_{O-H}, H-bonded).
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 13.48 & 13.45 (s, 2H, -**OH**); 8.62 & 8.09 (s, 2H, -**CH**=N-); 7.59 (d, 1H, J = 8.0 Hz, Ar**H**); 7.54 (d, 1H, Ar**H**); 7.34 (d, 2H, J = 9.2 Hz, Ar**H**); 7.26 (d, 1H, J = 12.0 Hz, Ar**H**); 7.15 (d, 1H, Ar**H**); 7.11 (d, 1H, Ar**H**); 7.10 (d, 1H, Ar**H**); 7.08 (d, 1H, Ar**H**); 6.53 (d, 2H, Ar**H**); 6.49 (d, 2H, Ar**H**); 4.02 (t, 4H, J = 6.0Hz, -O-**CH_2**-); 1.82 (q, 4H, J = 6.6Hz, - OCH_2-**CH_2**-); 1.78 (m, 4H, - CH_2-**CH_2**-); 1.59-1.16 (m, 32H, -**$(CH_2)_{16}$**-); 0.89 (t, 6H, J = 6.4 Hz, -**CH_3**).
Elemental analysis calculated for $C_{51}H_{67}N_2O_6F$: C = 74.42%; H = 8.20%; N = 3.40% Found. C = 74.40 %; H = 8.18%; N = 3.35%.

3-fluoro-4-(-(2-hydroxy-4-(undecyloxy)benzylidene)amino)phenyl 3-(-(2-hydroxy-4-(undecyloxy)benzylidene)amino)benzoate, 2-11-2F:

IR ν_{max} in cm^{-1}: 1618 ($\nu_{CH=N}$, imine); 1724 ($\nu_{C=O}$, ester), 3437(ν_{O-H}, H-bonded).
^1H NMR ($CDCl_3$, 400 MHz): δ = 13.46 & 13.45 (s, 2H, **-OH**); 8.62 & 8.08 (s, 2H, **-CH**=N-); 7.58 (d, 1H, J = 8.0 Hz, Ar**H**); 7.54 (d, 1H, Ar**H**); 7.34 (d, 2H, J = 9.2 Hz, Ar**H**); 7.26 (d, 1H, J = 12.0 Hz, Ar**H**); 7.14 (d, 1H, Ar**H**); 7.11 (d, 1H, Ar**H**); 7.09 (d, 1H, Ar**H**); 7.08 (d, 1H, Ar**H**); 6.52 (d, 2H, Ar**H**); 6.49 (d, 2H, Ar**H**); 4.02 (t, 4H, J = 6.0Hz, -O-**CH_2**-); 1.83 (q, 4H, J = 6.6Hz, - OCH_2-**CH_2**-); 1.78 (m, 4H, - CH_2-**CH_2**-); 1.58-1.27 (m, 28H, **-$(CH_2)_{14}$**-); 0.88 (t, 6H, J = 6.4 Hz, **-CH_3**).
Elemental analysis calculated for $C_{49}H_{63}N_2O_6F$: C = 74.03%; H = 7.99%; N = 3.52% Found. C = 74.01 %; H = 7.95%; N = 3.50%.

3-fluoro-4-(-(2-hydroxy-4-(decyloxy)benzylidene)amino)phenyl 3-(-(2-hydroxy-4-(decyloxy)benzylidene)amino)benzoate, 2-10-2F:

IR ν_{max} in cm^{-1}: 1619 ($\nu_{CH=N}$, imine); 1727 ($\nu_{C=O}$, ester), 3434(ν_{O-H}, H-bonded).
^1H NMR ($CDCl_3$, 400 MHz): δ = 13.42 & 13.40 (s, 2H, **-OH**); 8.61 & 8.09 (s, 2H, **-CH**=N-); 7.58 (d, 1H, J = 8.0 Hz, Ar**H**); 7.54 (d, 1H, Ar**H**); 7.32 (d, 2H, J = 9.2 Hz, Ar**H**); 7.26 (d, 1H, J = 12.0 Hz, Ar**H**); 7.14 (d, 1H, Ar**H**); 7.10 (d, 1H, Ar**H**); 7.09 (d, 1H, Ar**H**); 7.08 (d, 1H, Ar**H**); 6.62 (d, 2H, Ar**H**); 6.50 (d, 2H, Ar**H**); 4.02 (t, 4H, J = 6.0Hz, -O-**CH_2**-); 1.83 (q, 4H, J = 6.6Hz, - OCH_2-**CH_2**-); 1.74 (m, 4H, - CH_2-**CH_2**-); 1.67-1.30 (m, 24H, **-$(CH_2)_{12}$**-); 0.88 (t, 6H, J = 6.4 Hz, **-CH_3**).
Elemental analysis calculated for $C_{47}H_{59}N_2O_6F$: C = 73.60%; H = 7.75%; N = 3.65% Found. C = 73.56 %; H = 7.70%; N = 3.62%.

3.7. Experimental techniques:

3.7.1. Infrared Spectroscopy:

IR spectra were recorded on a Perkin-Elmer L 120-000A spectrometer and Shimadzu IR Prestige-21, FTIR-8400S (ν_{max} in cm^{-1}) on KBr disks. The representative IR spectra of the final compounds are provided in appendix.

3.7.2. ^{1}HNMR:

The ^{1}H nuclear magnetic resonance spectra were recorded either on JEOL FX-90Q (500 MHz) multinuclear spectrometer or Bruker DPX-400 spectrometer in $CDCl_3$ (chemical shift in δ) solution with TMS as internal standard. The representative NMR spectra of the final compounds are provided in appendix.

3.7.3. CHN analysis:

The elemental analysis was carried out using PE2400 elemental analyzer.

3.7.4. UV-visible spectroscopy:

UV visible absorption spectra of the compounds in $CHCl_3$ at different concentrations were recorded on a Shimadzu UV-1601PC spectrophotometer (λ_{max} in nm).

3.7.5. Fluorescence Studies:

Emission spectra of the synthesized compounds were recorded in a RF-5301PC spectrofluoro- photometer in Chloroform.

3.7.6. Texture Observation Using an Optical Polarized Microscope:

The optical properties of liquid crystal phases often directly reflect the symmetry of their structures. Birefringence, anisotropy of the refractive index, is one of characteristic physical properties of liquid crystals, and it allows for the visualization of the macroscopic molecular orientation. In thin liquid crystal sample cells placed between two crossed polarizers under an optical microscope, various textures and birefringence colors will be observed. These textures and colors not only look beautiful but also involve a lot of information about the macroscopic structure of the LC phases. Although there are many experimental techniques to investigate the structure and physical properties of LC phases, microscope observations often give enough information to determine the structure even if a well-aligned domain would not be obtained. The thermal behavior of the compounds is studied using a thin film of liquid crystalline material sandwiched between glass plate and a cover slip kept in the path of white light beam crossed with polarizers with a polarizing microscope (Nikon LV-100 eclipse) attached with Instec STC200 temperature controller configured for HCS302 from Instec Inc. USA. The accuracies in temperatures are 0.001^{0}C. The textures were recorded using Nikon NIS elements attached with the polarizing microscope.

3.7.7. Differential Scanning Calorimetry:

The thermal behavior of the compounds was examined using Differential Scanning Calorimetry. A Perkin-Elmer differential scanning calorimeter (DSC) Pyris-1 spectrometer using Indium as standard was used to measure the phase transition temperatures of materials and the corresponding transition enthalpies. The equipment measures heat difference between the sample pan (containing testing sample) and the reference pan at certain heat rate.

As two pans (the reference pan and the pan with sample) are heated or cooled at same rate, extra heat will release or absorb at sample's pan when there are phase transitions happen in samples. Thus peaks will appear in the heat flow curve corresponding to the temperatures where phase transitions happen. From the peak position the exact phase transition temperatures can be determined. Integrating the peak above the baseline gives the total heat released or absorbed at the transition.

3.7.8. X-ray Diffraction Studies:

X-ray diffraction is useful and powerful method to investigate microscopic structure of the material. The positional and orientational ordering in the LC phases has been well investigated by means of this x-ray diffraction. Though liquid crystals are fluids and smectic layer ordering is almost sinusoidal unlike the regular positional ordering in a crystal, electron density wave along the layer normal direction give an enough high contrast to produce a sharp diffraction (and harmonics) at the angle satisfied Bragg's law, $2d \sin\theta = n\lambda$ where d is wavelength of electron density function in the media, θ is diffraction angle, λ is wavelength of x-ray and integer number n. Unoriented powdered sample was used for the variable temperature X-ray diffraction analyses. The powder X-ray diffraction patterns of the liquid crystalline phases were recorded on a Rigaku Rotaflex RTP 300 diffractometer. The wavelength of the incident beam was $\lambda = 1.5418$ Å and the sample-to-detector distance was 120 cm for both small angle (SAXS) and wide angle (WAXS) measurements. Uniform orientation of the sample, placed in thin capillaries of 1 mm diameter perpendicular to the X-ray beam, was obtained with alignment in a magnetic field of medium strength B = 0.386 T. The capillaries (1 mm diameter) were standing orthogonal to the incident X-ray beam

and The temperature of the sample was controlled by thermo-controller having ± 0.1 ^{O}C precision and cooling rate of 0.5 ^{O}C/min.

3.7.9. Density Functional Theory study:

As suitable X-ray quality crystal could not be grown, quantum chemical calculation based on density functional theory (DFT) has been performed to investigate the electronic structure of the 2F-14 (figure 1). Full geometry optimization has been carried out without imposing any constrain with the Gaussian 09 program package [15]. Spin-restricted DFT calculation has been carried out in the framework of the generalized gradient approximation (GGA) using Becke3-Lee-Yang-Parr exchange-correlation functional i.e. B3LYP [16,17] hybrid functional and 6-31G (d, p) basis set.

References:

[1] M. Ghedini, B. Panuzi and A. Roviello, *Liq. Cryst.*, **25**, 225, (1998).

[2] N. Hoshino, A. Kodama, T. Shibuya, Y. Matsunaga and S. Miyajima, *Inorg. Chem.*, **30**, 3091, (1991).

[3] S. F. Tandel, M.W. Schoder, G. Pelzl, U. Baumeister, W. Weissflog, S. Stern, A. Nemes, R. Stannarius, and A. Eremin, *Eur. Phys. J.* E, **25**, 395, (2008).

[4] *Vogel's Textbook of Practical Organic Chemistry*, Ed B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tachell, Longman Scientific and Technical, UK (1989).

[5] D. L. Pavia, G. M. Lampman, G. S. Kriz, and J. R. Vyvyan, *Introduction to Spectroscopy*, 4th Ed., Brooks/Cole, Cengage Learning, (2009, 2001)

[6] R. A. Meyers, *Encyclopaedia of Analytical Chemistry*, John Wiley & Sons Ltd.

[7] R. Deb, R. K. Nath, M. K. Paul, N. V. S. Rao, F. Tuluri, Y. Shen, R. Shao, D. Chen, C. Zhu, I. I. Smalyukh and N. A. Clark, *J. Mater. Chem*., 20, 7332-7336, (2010).

[8] V. Prasad, S. W. Kang, K. A. Suresh, L. Joshi, Q. Wang and S. Kumar, *J. Am. Chem. Soc*., 127, 17224-17227, (2005).

[9] G. Shanker and C. Tschierske, *Tetrahedron*, 67, 8635-8638, (2011).

[10] O. Francescangeli, F. Vita, C. Ferrero, T. Dingemans and E. T. Samulski, S*oft Mater*, 7, 895-901, (2011).

[11] G. Shanker, M. Nagaraj, A. Kocot, J. K. Vij, M. Prehm and C. Tschierske, *Adv. Funct. Mater.* **22**, 1671-1683, (2012).

[12] C. Keith, A. Lehmann, U. Baumeister, M. Prehm and C. Tschierske, S*oft Mater*, 6, 1704-1721, (2010).

[13] R. A. Reddy, C. Zhu, R. Shao, E. Korblova, T. Gong, Y. Shen, E. Garcia, M. A. Glaser, J. E. Maclennan, D. M. Walba and N. A. Clark, S*cience*, vol-332, (2011).

[14] (a) R. I. Nessim, M. M. Naoum, S. Z. Mohamed and M. I. Nessim *Liq. Cryst.*, **31,** 649-654, (2004). (b) M. Guillevic, M.E. Light, S. E. Coles, T. Gelbrich, M.B. Hursthouse and D. W. Bruce, *J. Chem. Soc., Dalton Trans.*, 1437-1445, (2000). (c) C. K. Lai, C. H. Chang and C. H. Tsai, *J. Mater. Chem.*

8, 599-602, (1998).

[15] Gaussian 09, Revision B.01,M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochters R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, (2010).

[16] K. Kim and K. D. Jordan "Comparison of Density Functional and MP2 Calculations on the Water Monomer and Dimer". *J. Phys. Chem.* **98**, (40), 10089 (1994).

[17] P.J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch "Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields". *J. Phys. Chem.* **98**, (45), 11623 (1994).