Chapter 3

Experimental: Materials and Methods

We describe the synthetic steps for efficient and elegant route towards the successful synthesis of the desired compound. Chemical characterization methods with spectral data of the synthesized compound and procedure involved for the synthesis mentioned. A brief outline about the experimental set up with working principles and methods involved for studying the phase behaviours, electro-optical properties and other associated physico-chemical properties of liquid crystals are also detailed.
3.1 **Experimental: Synthesis, Techniques and Methods**

3.2 **Synthesis:**

The target compounds are designed and the syntheses of different compounds at intermediate stages were carried out following the procedures well documented in literature [1-3]. The different reagents and reaction conditions are modified wherever they are necessary and experimented on a trial basis and then followed the same procedure for yielding the desired compounds. The compounds are recrystallized from suitable solvents or purified by column chromatography. The synthetic procedures for the intermediate as well as target compounds are depicted below. All the solvents are purified following standard procedures well documented in the literature [4-8]. Silica gel [(60-120 mesh) from Acme synthetic chemicals was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for TLC. Benzene, Chloroform, ethyl acetate, or Petroleum ether (refers to the fraction boiling between 60°C and 80°C) were used as eluents for chromatographic separation.

**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.).

**Table 3.1:** List of Commercially available Compounds.

1. 4,4'-diaminobenzophenone,

2. 4,4'-diaminophenylenesulfone,

3. 4-fluoro-1,3-phenylenediamine

4. 2-methyl-1,3-phenylenediamine
5. 4-methyl-1,3-phenylenediamine

6. 4-nitro-1,3-phenylenediamine

7. 4-chloro-1,3-phenylenediamine

8. 1,3-phenylenediamine,

9. 3,5-diaminobenzoic acid

The following intermediate compounds and final products had been synthesized in the laboratory and characterized for their molecular and material characteristics during the last few years and are furnished below.

**Intermediate compounds:**

**Table 3.2:** List of Intermediate compounds.

1. 4-n-butyloxysalicylaldehyde,

2. 4-n-hexyloxysalicylaldehyde,

3. 4-n-octyloxysalicylaldehyde,

4. 4-n-decyloxysalicylaldehyde,
5. 4-n-dodecylxysalicylaldehyde,

6. 4-n-tetradecylxysalicylaldehyde,

7. 4-n-hexadecyloxysalicylaldehyde,

8. 4-n-octadecyloxysalicylaldehyde,

9. 4-n-butyloxybenzoic acid,

10. 4-n-hexyloxybenzoic acid,

11. 4-n-octyloxybenzoic acid,

12. 4-n-decyloxybenzoic acid,

13. 4-n-dodecyloxybenzoic acid,

14. 4-n-tetradecyloxybenzoic acid,

15. 4-n-hexadecyloxybenzoic acid,

16. 4-n-octadecyloxybenzoic acid,

17. 4-(4'-n-hexyloxybenzoyloxy)salicylaldehyde,
18. 4-(4'-n-octyloxybenzoyloxy)salicylaldehyde,

19. 4-(4'-n-decyloxybenzoyloxy)salicylaldehyde,

20. 4-(4'-n-dodecyloxybenzoyloxy)salicylaldehyde,

21. 4-(4'-n-tetradecyloxybenzoyloxy)salicylaldehyde,

22. 4-(4'-n-hexadecyloxybenzoyloxy)salicylaldehyde,

23. 4-(4'-n-octadecyloxybenzoyloxy)salicylaldehyde,

24. 4-(4'-n-octyloxybenzoyloxy)benzaldehyde,

25. 4-(4'-n-decyloxybenzoyloxy)benzaldehyde,

26. 4-(4'-n-dodecyloxybenzoyloxy)benzaldehyde,

27. 4-(4'-n-tetradecyloxybenzoyloxy)benzaldehyde,

28. 4-(4'-n-hexadecyloxybenzoyloxy)benzaldehyde,

29. 4-n-dodecyloxyaniline,

30. 3-(4-n-dodecyloxyphenylazo)salicylaldehyde,

31. 3-nitrophenyl-4-nitrobenzoate
32. 4-nitrophenyl-3-nitrobenzoate.

33. 3-aminophenyl-4-aminobenzoate and

34. 4-aminophenyl-3-aminobenzoate.

Final Products

Table 3.3: List of final Compounds synthesized for the present study.

1. \[3-(N-4'-n-alkyloxysalicylidene)-aminophenyl]-[4-(N-4'-n-alkyloxysalicylidene-amino)-benzoate], 34-\textit{n}OH.

2. N, N'-bis[4-n-alkyloxysalicylidene]-4,4'-diaminobenzophenone, BP-\textit{n}OH.

3. N, N'-bis[4-n-alkyloxysalicylidene]-4,4'-diaminophenylenesulfone, PAS-\textit{n}OH.

4. N,N'-bis-[4-(4'-n-alkyloxybenzoyloxy)-salicylidene]-phenylene-4-fluoro-1,3-diamine, 4FnOH.
N,N'-bis[4-(4-n-alkyloxybenzoyloxy)-salicylidene]-phenylene-2-methyl-1,3-diamine, 2M-nOH.

N,N'-bis[4-(4-n-alkyloxybenzoyloxy)-salicylidene]-phenylene-4-methyl-1,3-diamine, 4M-10OH.

N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-phenylene-1,3-diamine, 10OHH.

N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-phenylene-4-chloro-1,3-diamine, 4Cl-10OH.
N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-phenylene-4-nitro-1,3-diamine, 4N-10OH.

N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-3,5-diaminobenzoic acid, 5Ba-10OH

N,N'-bis[2-hydroxy-5-(4'-n-dodecyloxyphenylazo)benzylidene]-phenylene-4-nitro-1,3-diamine, 134NPDO12.

[3-(N-4-(4'-n-alkyloxybenzoyloxy)salicylidene)-aminophenyl]-[4-(N-4-(4'-n-alkyloxybenzoyloxy)salicylidene)-amino]-benzoate, 34-nOH-6.

[4-(N-4-(4'-n-alkyloxybenzoyloxy)salicylidene)-aminophenyl]-[3-(N-4-(4'-n-alkyloxybenzoyloxy)salicylidene)-amino]-benzoate, 43-nOH-6
3.2.1. Synthesis of 4-n-alkyloxysalicylaldehyde, 1-8, (Scheme 1):

Scheme 1: i. acetone(dry), NaHCO$_3$, C$_n$H$_{2n+1}$Br, KI, reflux, 48 hrs.

4-n-octyloxysalicylaldehyde, 3:

The synthesis of 4-octyloxy-2-hydroxy benzaldehyde, (Scheme 1) viz., mono alkylation was performed by using a modification of a literature procedure to improve the product yield. 2,4-dihydroxybenzaldehyde (10 g, 72.4 mmol), 1-bromo octane (16.6 ml, 75 mmol), NaHCO$_3$ (6.30 g, 75 mmol) and KI (catalytic amount) were mixed in dry acetone (250ml) and then the mixture was refluxed for 48 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 solid. Yield: 12.6 gm, 70%.

IR v$_{\text{max}}$ in cm$^{-1}$: 1666 (vC=O, aldehyde), 3449 (vO-H, H-bonded).

$^1$H NMR (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, 10H, -(CH$_2$)$_5$-); 0.90 (t, 3H, J = 6.3 Hz, -CH$_3$).

Elemental analysis calculated for C$_{15}$H$_{22}$O$_3$: C = 71.97%; H = 8.86%; N = 19.17%. Found C = 71.95%; H = 8.86%; N = 19.14%.
Rest of the desired intermediate compounds \((n = 4, 6, 10, 12, 14, 16, 18)\) of this 4-n-alkyloxysalicylaldehyde homologous series were prepared according to the procedure described above with appropriate alkylbromide.

**3.2.2. Synthesis of 4-n-alkyloxybenzoic acid, (9-16), (Scheme 2):**

\[
\text{HO-} \underset{i}{\text{COC}_{2}H_{5}} \rightarrow \underset{ii}{H_{2n+1}C_{n}O-COC_{2}H_{5}} \rightarrow \underset{iii}{H_{2n+1}C_{n}O-\text{COOC}_{2}H_{5}} \rightarrow \text{H-O-} \underset{iv}{\text{COC}_{2}H_{5}}
\]

Scheme 2: i. absolute ethanol, KOH, \(C_{4}H_{9}Br\), KI, reflux, 40hrs, ii. OH\(^{-}\), H\(_{2}\)O; H\(^{+}\), H\(_{2}\)O

4-n-octyloxybenzoic acid, 11:

The synthesis of 4-octyloxy-2-hydroxy benzaldehyde, viz., mono alkylation was performed following the (Scheme 2). Ethyl-4-hydroxy benzoate (16.6 g, 0.1m) was refluxed with 1-bromooctane (22ml, 0.11m) and KOH (10g) in 200ml of ethanol (absolute) for 40 hours. Once the etherification reaction is complete then the excess ethanol was distilled out from the reaction mixture. After distillation, 200ml of water is added and then 8 g of NaOH is also added to this reaction mixture and refluxed for 10 hours. The reaction mixture was cooled to room temperature. After that the solution is taken in a 1000ml beaker and this solution is acidified with HCl (till pH = 2) with constant stirring. The solid white precipitate 4-n-octyloxy benzoic acid separates out from the reaction mixture and the separated white precipitate was filtered and washed with excess of water. The resulting solid was recrystallized from absolute ethanol using animal charcoal. The solid is dried to yield a pure white solid. Yield: 26.4g, (88%).

**IR** \(v_{\text{max}}\) in cm\(^{-1}\): 1054 (\(v_{\text{C-O-C}}\)); 1683 (\(v_{\text{C=O, ester}}\)); 3062 (\(v_{\text{O-H, acid}}\)).  

\(^{1}\text{H NMR}\) (CDCl\(_3\), 300MHz): \(\delta= 11.26\) (s, 1H, \(-\text{OH}\)); 8.06 (d, 2H, \(J = 8.7\) Hz, \(\text{ArH}\)); 7.25 (d, 2H, \(J = 8.7\) Hz, \(\text{ArH}\)); 4.02 (t, 2H, \(J = 6.3\) Hz, \(-\text{O-CH}_2\)); 1.76 (q, 2H, \(J = 6.6\) Hz, \(-\text{CH}_2-\text{CH}_2-\)); 1.41–1.28 (m, 10H, \(-\text{CH}_2\)), 0.90 (t, 3H, \(J = 6.6\) Hz, \(-\text{CH}_3\)).

**Elemental analysis** calculated for C\(_{15}\)H\(_{22}\)O\(_3\): C = 71.97%; H = 8.86%. Found C = 72.05%; H = 8.89%.

Rest of the desired intermediate compounds \((n = 4, 6, 10, 12, 14, 16, 18)\) of this 4-n-alkyloxysalicylaldehyde homologous series were prepared according to the procedure described above with appropriate alkylbromide.
3.2.3. 4-(4'-n-alkyloxybenzoyloxy)salicylaldehyde, 17-23, (Scheme 3):

![Chemical structure](image)

Scheme 3: i) SOCl₂, DCM, DMF; ii) 2,4-dihydroxybenzaldehyde, DCM, TEA

4-(4'-n-octyloxybenzoyloxy)salicylaldehyde, 18:

In a two-neck round bottom flask with a Teflon-coated magnetic stirrer was added 4-n-octyloxybenzoic acid (3.75g, 15mmol) in CH₂Cl₂, and a catalytic amount of DMF. The reaction flask was flushed with N₂, sealed with a rubber septum, and cooled in an ice bath. An excess of thionyl chloride, SOCl₂ (8ml, 2.0 equiv) was added dropwise to the cooled reaction mixture. The ice bath was removed and the reaction mixture was stirred for 1 h. The solvent was evaporated under reduced pressure and the resulting compound was dried under vacuum. The product was used for the next step without further purification. To the resulting acyl chloride which was dissolved in dichloromethane (30 ml) and in presence of few ml of trimethylamine (2ml) a solution of 2,4-dihydroxybenzaldehyde (2.07 g, 15 mmol) in dry dichloromethane was added dropwise with constant stirring. The resultant mixture was then vigorously stirred for 5-6 h maintaining the temperature at 10-20°C. The organic layer was dried over sodium sulphate. Evaporation of the solvent gave the crude product which was then purified by column chromatography (silica gel, eluent petroleum ether/ethyl acetate, 95:5, V/V) and the solvent was evaporated to give pure product. Further purification by recrystallization from ethanol afforded the pure product as white solid. Yield: 3.49 g (63%).

**IR** ν_max in cm⁻¹: 1680 (ν_C=O); 1736 (ν_C=O, ester); 3400 (ν_OH, H-bonded).

**¹H NMR** (CDCl₃, 300 MHz): δ = 11.26 (s, 1H, -OH); 9.89 (s, 1H, -CHO); 8.12 (dd, 2H, J = 2.4, 8.9 Hz, ArH); 7.60 (d, 1H, J = 8.4 Hz, ArH); 6.99 (dd, 2H, J = 2.4, 8.9 Hz, ArH); 6.90 (dd, 1H, J = 1.8, 8.5 Hz, ArH); 6.87 (d, 1H, J = 2.0 Hz, ArH), 4.05 (t, 2H, J = 6.6 Hz, -O-CH₂), 1.83 (q, 2H, J = 6.6 Hz, -CH₂- CH₂-), 1.58-1.28 (m, 10H, -(CH₂)₅-), 0.89 (t, 3H, J = 6.6 Hz, -CH₃).

**Elemental analysis** calculated for C₂₂H₂₆O₅: C = 71.33%; H = 7.07%. Found C = 71.45%; H = 6.99%.
Rest of the desired intermediate compounds (n = 6, 10, 12, 14, 16, 18) of this 4-(4'-n-octyloxybenzoyloxy)-salicylaldehyde homologous series were prepared according to the procedure described above with appropriate alkoxybenzoic acid.

3.2.4. 4-(4'-n-alkyloxybenzoyloxy)benzaldehyde, 24-28, (Scheme 4):

\[
\begin{align*}
H_{2n+1}C_nO-\text{COOH} & \xrightarrow{i} H_{2n+1}C_nO-\text{COCl} \\
& \xrightarrow{ii} H_{2n+1}C_nO-\text{C}=O
\end{align*}
\]

Scheme 4: i). SOCl₂, DCM, DMF; ii) 4-hydroxybenzaldehyde, DCM, TEA

4-(4'-n-octyloxybenzoyloxy)benzaldehyde, 24:

In a two-neck round bottom flask with a Teflon-coated magnetic stirrer was added 4-n-octyloxybenzoic acid (3.75g; 15mmol) in CH₂Cl₂, and a catalytic amount of DMF. The reaction flask was flushed with N₂, sealed with a rubber septum, and cooled in an ice bath. An excess of thionyl chloride, SOCl₂ (8ml, 2.0 equiv) was added drop wise to the cooled reaction mixture. The ice bath was removed and the reaction mixture was stirred for 1 h. The solvent was evaporated under reduced pressure and the resulting compound was dried under vacuum. The product was used for the next step without further purification. To the resulting acyl chloride which was dissolved in dichloromethane (30ml), an aqueous solution of 4-hydroxy benzaldehyde (1.83g; 15mmol) and K₂CO₃ (4.14g; 30mmol) was added. The resulting solution stirred for overnight with addition of catalytic amount of tetra butyl ammonium bromide. The organic layer was then separated out washed several times with the alkaline solution and 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) and the solvent was evaporated to give pure product. Further purification by recrystallization from ethanol afforded the pure product as white solid. Yield: 4.24 g, (80%)

IRν_max in cm⁻¹: 1709 (ν_C=O, aldehyde); 1736 (ν_C=O, ester).

¹HNMR (CDCl₃, 300MHz) δ = 10.01(s, 1H, -CHO); 8.13 (d, 2H, J=8.7 Hz, ArH); 7.96 (d, 2H, J=8.4 Hz, ArH); 7.39 (d, 2H, J=8.4 Hz, ArH); 6.58 (d, 2H, J=9.0 Hz, ArH); 4.05 (t, 2H, J=6.6 Hz, -O-CH₂-); 1.82 (q, 2H, J=6.9 Hz, CH₂-CH₂-); 1.54-1.26 (m, 10H, -(CH₂)₅-); 0.88 (t, 3H, J=7.2Hz, -CH₃).
Elemental analysis calculated for C$_{22}$H$_{26}$O$_4$: C = 74.55%; H = 7.39%. Found C = 74.45%; H = 7.29%.

Rest of the desired intermediate compounds (n = 10, 12, 14, 16) of this 4-(4'-n-alkyloxybenzoyloxy)benzaldehyde homologous series were prepared according to the procedure described above with appropriate alkoxybenzoic acid.

3.2.5. 4-n-dodecyloxyaniline, 29 (Scheme 5):

\[
\begin{align*}
\text{HO-} & \xrightarrow{\text{i}} \text{H}_{2n+1}C_n\text{O-} \xrightarrow{\text{ii}} \text{H}_{2n+1}C_n\text{O-} \xrightarrow{\text{NH}} \text{NH}_2
\end{align*}
\]

Scheme 5: i. dry Acetone, K$_2$CO$_3$, C$_{12}$H$_{25}$Br, KI, reflux, 40hrs, ii. H*, H$_2$O; OH*, H$_2$O

4-n-dodecyloxyaniline, 29:

A solution of 1-bromododecane (24.3g, 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 24 hours 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 residue in the funnel was washed with ether and the washing was evaporated to give the solid. Both solid were combined and dissolved in dichloromethane. The dichloromethane solution was washed with a solution of NaOH (2.10cm$^3$, 2mol/dm$^3$) and NaCl (2.10cm$^3$, 2mol/dm$^3$), and then dried over Na$_2$SO$_4$ and then the solvent was evaporated. The product was crystallized from hot absolute ethanol and a white solid was obtained. The solid was then dissolved in ethanol (200cm$^3$, 95%) and HCl (75cm$^3$, 35%) was added. The solution was then refluxed for 4 hours. After cooling to room temperature, the reaction mixture 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 residue water (100 cm$^3$) was added followed by the addition of a solution of NaOH (2mol/m3) until the pH=12 was attained. The solid was filtered, dried and recrystallized from ethanol. Yield = 16.6 gm, 60%.

IR $\nu$$_{\text{max}}$ in cm$^{-1}$: 1054 ($\nu$C-O-C); 3345 ($\nu$N-H, amine).

$^1$H NMR (CDCl$_3$, 300MHz): $\delta$ = 6.88 (d, 2H, J = 8.4 Hz, ArH); 6.70 (d, 2H, J = 8.7 Hz, ArH); 4.00 (t, 2H, J = 6.6 Hz, -O-CH$_2$), 3.57 (s, 2H, Ar-NH$_2$). 1.72 (q, 2H, J = 6.2 Hz, -CH$_2$- CH$_2$), 1.52–1.26 (m, 18H, -(CH$_2$)$_9$-), 0.89 (t, 3H, J = 6.6 Hz, -CH$_3$).
Elemental analysis calculated for C_{14}H_{23}NO: C = 75.97%; H = 10.47%; N = 6.33%. Found C = 75.98%; H = 10.49%; N = 6.31%.

3.2.6. 3-(4-n-dodecyloxyphenylazo)salicylaldehyde, 30, (Scheme 6):

Scheme 6: i) HCl, NaN\textsubscript{O} \textsubscript{2}, 0-5\textdegree C; ii) Salicylaldehyde, NaOH

3-(4-n-dodecyloxyphenylazo)salicylaldehyde, 30:

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-dodecyloxy aniline (5.54g, 0.02mol) was added slowly to form a clear solution. The resulting solution was stirred and cooled to 0\textdegree C, an aqueous cold solution of NaNO\textsubscript{2} (1.6g, 0.023mol) was added drop wise maintaining the temperature of the reaction mixture at 0-5\textdegree 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\textdegree 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\textsubscript{2}O several times. The crude product was dissolved in CH\textsubscript{2}Cl\textsubscript{2} dried over Na\textsubscript{2}SO\textsubscript{4}. After removal of the solvent under reduced pressure the sample was recrystallized to give yellow crystalline solid. Yield: 4.9 g, 60%.

IR $\nu_{\text{max}}$ in cm$^{-1}$: 1483 (vN-N, azo), 1666 (vC=O, aldehyde), 3449 (vO-H, H-bonded).

$^1$H NMR (CDCl\textsubscript{3}, 300 MHz): $\delta = 11.26$ (s, 1H, -OH); 10.02 (s, 1H, -CH=O); 8.14 (d, 1H, J = 8.2 Hz, ArH); 7.88 (d, 2H, J = 8.9 Hz, ArH); 7.11 (d, 2H, J = 9.6 Hz, ArH); 7.00 (d, 1H, J = 9.0 Hz, ArH); 4.00 (t, 2H, J = 6.5 Hz, -O-CH$_2$-); 1.60 (q, 2H, J = 6.6 Hz, -CH$_2$-CH$_2$-); 1.53-1.20 (m, 18H, -(CH$_2$)$_9$); 0.80 (t, 3H, J = 6.3 Hz, -CH$_3$).

Elemental analysis calculated for C$_{25}$H$_{34}$N$_2$O$_3$: C = 73.14%; H = 8.35%; N = 6.82%. Found C = 73.13%; H = 8.33%; N = 6.83%.
3.2.7. 3-nitrophenyl-4-nitrobenzoate, 31, (Scheme 7):

Scheme 7: i) SOCl₂, DCM; ii) 3-Nitrophenol, DCM, K₂CO₃, TBAB

3-nitrophenyl-4-nitrobenzoate, 31:

4-nitrobenzoic acid (2.50 g; 15 mmol) was dissolved in dichloromethane in a two neck round bottomed flask with a teflon coated magnetic stirrer and the reaction flask was flushed with N₂, sealed with a rubber septum and cooled in an ice bath. Thionyl chloride (2.0 ml, 1.65 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 1 h. 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 (30 ml), an aqueous solution of 3-nitrophenol (2.08 g; 15 mmol) and K₂CO₃ (4.14 g; 30 mmol) 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: 3.44 g, (80%). Purity (HPLC) 99+%.

IR νmax in cm⁻¹: 1737 (νC=O, ester), 1536 (νN-O, nitro).

¹H NMR (CDCl₃, 300 MHz): δ = 8.12 (d, 1H, J = 2.5 Hz, ArH); 8.00 (d, 2H, J = 8.1 Hz, ArH); 7.97 (d, 2H, J = 8.1 Hz, ArH); 7.77 (d, 1H, J = 8.7 Hz, ArH); 7.60 (t, 1H, J = 8.1 Hz, ArH); 7.20 (d, 1H, J = 8.7 Hz, ArH).

Elemental analysis calculated for C₁₃H₈O₆N₂: C = 54.18%; H = 2.80%; N = 9.72%. Found C = 54.16%; H = 2.82%; N = 9.70%.
3.2.8. 4-nitrophenyl-3-nitrobenzoate, 32 (Scheme 8):

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{i} \quad \text{O}_2\text{N} \\
\text{COOH} & \quad \text{Cl}^{-} \quad \text{O}_2\text{N} \\
\text{O}_2\text{N} & \quad \text{COCl} \\
\text{O}_2\text{N} & \quad \text{NO}_2
\end{align*}
\]

Scheme 8: i) SOCl$_2$, DCM; ii) 4-Nitrophenol, DCM, K$_2$CO$_3$, TBAB

4-nitrophenyl-3-nitrobenzoate:

Compound 4-nitrophenyl-3-nitrobenzoate was synthesized by the same procedure described for the preparation of 3-nitrophenyl-4-nitrobenzoate, using 3-nitrobenzoic acid (2.50 g; 15 mmol), thionyl chloride (2.0 ml, 1.65 mmol), 4-nitro phenol (2.08 g; 15 mmol) K$_2$CO$_3$ (4.14 g; 30 mmol) and catalytic amount of tetra butyl ammonium bromide. The compound was purified by column chromatography (silica gel, eluent petroleum ether/ethyl acetate, 97:3 v/v) and recrystallized from ethanol to yield the pure product as white solid.

Yield: 3.62 g, (84%). Purity (HPLC) 99+%

IR $\nu_{\text{max}}$ in cm$^{-1}$: 1737 (vC=O, ester), 1537 (vN$^>$), nitro).

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 8.22$ (d, 1H, J = 2.3 Hz, ArH); 8.18 (d, 1H, J = 8.1 Hz, ArH); 8.08 (d, 1H, J = 8.4 Hz, ArH); 7.97 (d, 2H, J = 8.7 Hz, ArH); 7.60 (t, 1H, J = 8.4 Hz, ArH); 7.21 (d, 2H, J = 8.1 Hz, ArH).

Elemental analysis calculated for C$_{13}$H$_8$O$_6$N$_2$ C = 54.18%; H = 2.80%; N = 9.72%.

Found C = 54.17%; H = 2.83%; N = 9.71%.

3.2.9. 3-aminophenyl-4-aminobenzoate, 33, (Scheme 9):

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{i} \quad \text{H}_2\text{N} \\
\text{O}_2\text{N} & \quad \text{Cl}^{-} \quad \text{O}_2\text{N} \\
\text{O}_2\text{N} & \quad \text{NH}_2
\end{align*}
\]

Scheme 9: i) Ethyl acetate, 10% Pd-C

3-aminophenyl-4-aminobenzoate, 33:

3-nitrophenyl-4-nitrobenzoate thus obtained is then subjected to catalytic reduction. 3-nitrophenyl-4-nitrobenzoate (1.44 g, 5 mmol) was dissolved in ethyl acetate in a two neck round bottom flask to it 10% Pd-C (0.14g). The reaction mixture is
stopped, well, stirred for 15 hrs under balloon pressure filled with hydrogen gas. On completion of the reaction the crude product was collected by evaporating the solvent under reduced pressure. Which was then purified by column chromatography (silica gel 60-120 mesh, eluent dichloromethane/ethanol, 99.5:0.5 v/v) and the solvent was evaporated to give pure product. Further purification by recrystallization from ethyl acetate afforded the pure product as white solid. Yield: 1.01 g, (89%).

IR \( \nu_{\text{max}} \) in cm\(^{-1} \): 1730 (\( \nu_{\text{C=O, ester}} \)), 3350 (\( \nu_{\text{N-H, amine}} \)).

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \( \delta = 7.56 \) (d, 2H, J = 7.5 Hz, ArH); 7.47 (d, 1H, J = 2.1 Hz, ArH); 7.25 (t, 1H, J = 9.9 Hz, ArH); 6.97 (d, 1H, J = 8.7 Hz, ArH); 6.90 (d, 2H, J = 8.1 Hz, ArH); 6.70 (d, 1H, J = 8.7 Hz, ArH); 3.80 and 3.66 (s, 4H, Ar-NH\(_2\)).

Elemental analysis calculated for C\(_{13}\)H\(_{12}\)N\(_2\)O\(_2\): C = 68.41%; H = 5.30%; N = 12.27%. Found C = 68.43%; H = 5.33%; N = 12.26%.

### 3.2.10. 4-aminophenyl-3-aminobenzoate, 34, (Scheme 10):

![Scheme 10: i) Ethyl acetate, 10% Pd-C](image)

4-aminophenyl-3-aminobenzoate, 34:

The synthesis of 4-aminophenyl-3-aminobenzoate was carried out following the same procedure adopted for 3-aminophenyl-4-aminobenzoate. 4-nitrophenyl-3-nitrobenzoate was reduced with 10% Pd-C to give 3-aminophenol-4-aminobenzoate in quantitative yield. Yield: 0.99 g, (87%).

IR \( \nu_{\text{max}} \) in cm\(^{-1} \): 1733 (\( \nu_{\text{C=O, ester}} \)), 3348 (\( \nu_{\text{N-H, amine}} \)).

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \( \delta = 7.58 \) (d, 1H, J = 8.4 Hz, ArH); 7.52 (d, 1H, J = 8.1 Hz, ArH); 7.21 (t, 1H, J = 8.9 Hz, ArH); 6.98 (d, 2H, J = 8.7 Hz, ArH); 6.95 (d, 2H, J = 8.4 Hz, ArH); 6.75 (d, 1H, J = 8.4 Hz, ArH); 3.80 and 3.69 (s, 4H, Ar-NH\(_2\)).

Elemental analysis calculated for C\(_{13}\)H\(_{12}\)N\(_2\)O\(_2\): C = 68.41%; H = 5.30%; N = 12.27%. Found C = 68.41%; H = 5.31%; N = 12.26%.
3.2.11. [3-(N-4'-n-alkyloxysalicylidene)-aminophenyl]-[4-(N-4'-n-alkyloxysalicylideneamino)-benzoate, 34-nOH, (Scheme 11):

![Chemical structure]

Scheme 11

[3-(N-4'-n-octyloxysalicylidene)-aminophenyl]-[4-(N-4'-n-octyloxysalicylideneamino)-benzoate, 34-8OH.

An ethanolic solution (20 ml) of 4-n-octyloxysalicyldehyde (0.62 g, 2.5 mmol) was added to an ethanolic solution of 3-aminophenyl-4-aminobenzoate (0.28 g, 1.25 mmol) as shown in scheme 11. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff's base [3-(N-4'-n-octyloxysalicylidene)-aminophenyl]-[4-(N-4'-n-octyloxysalicylidene-amino)-benzoate, 34-8OH. The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure compound. Yield: 0.49 g, 58%.

IR \(\nu_{\text{max}}\) in cm\(^{-1}\): 1625 (\(\nu_{\text{C-H}}, \text{imine}\)); 1726 (\(\nu_{\text{C=O}}, \text{ester}\)), 3430 (\(\nu_{\text{O-H}}, \text{H-bonded}\)).

\(^1\text{H NMR}\) (CDCl\(_3\), 300 MHz): \(\delta = 13.49 & 13.37\) (s, 2H, -OH); 8.57 & 5.54 (s, 2H, -CH=N-); 8.25 (d, 2H, J = 8.1Hz, ArH); 7.45 (t, 1H, J = 7.8 Hz, ArH); 7.35 (d, 2H, J = 8.4Hz, ArH); 7.32-7.25 (m, 3H, ArH); 7.17 (d, 2H, J = 8.7 Hz, ArH); 7.12 (d, 2H, J = 8.4 Hz, ArH); 6.49 (s, 2H, ArH); 4.00 (t, 4H, J = 6.0Hz, -O-CH\(_2\)-); 1.79 (q, 4H, J = 6.2Hz, -CH\(_2\)-CH\(_2\)-); 1.56-1.26 (m, 20H, -(CH\(_2\))\(_n\)-); 0.87 (t, 6H, J = 6.9Hz, -CH\(_3\)).

**Elemental analysis** calculated for C\(_{43}\)H\(_{52}\)N\(_2\)O\(_6\): C = 75.54%; H = 7.56%; N = 4.04%

Found. C = 75.51%; H = 7.55%; N = 4.01%.
[3-(N-4'-n-decyloxsalicylidene)-aminophenyl]-[4-(N-4'-n-decyloxsalicylidene-amino)-benzoate, 34-10OH]

34-10OH was prepared according to the procedure described for 34-8OH using 4-n-decyloxsalicylaldehyde (0.69 g, 2.5 mmol) and 3-aminophenyl-4-aminobenzoate (0.28g, 1.25 mmol). Yield: 0.62g; (67%)

IR v<sub>max</sub> in cm<sup>-1</sup>: 1628 (νC=N, imine); 1730 (νC=O, ester), 3445 (νO-H, H-bonded).

1H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 13.50 & 13.37 (s, 2H, -OH); 8.58 & 5.55 (s, 2H, -CH=N-); 8.25 (d, 2H, J = 8.1Hz, ArH); 7.46 (t, 1H, J = 8.1 Hz, ArH); 7.35 (d, 2H, J = 8.1Hz, ArH); 7.32-7.26 (m, 3H, ArH); 7.17 (d, 2H, J = 8.4 Hz, ArH); 7.12 (d, 2H, J = 8.4 Hz, ArH); 6.50 (s, 2H, ArH); 4.00 (t, 4H, J = 6.3Hz, -O-CH<sub>2</sub>-); 1.79 (q, 4H, J = 6.2Hz, -CH<sub>2</sub>-CH<sub>2</sub>-); 1.55-1.27 (m, 20H, -(CH<sub>2</sub>)<sub>7</sub>-); 0.88 (t, 6H, J = 6.6Hz, -CH<sub>3</sub>).

Elemental analysis calculated for C<sub>42</sub>H<sub>60</sub>N<sub>2</sub>O<sub>6</sub>: C = 75.37%; H = 8.07%; N = 3.74%

Found C = 75.36%; H = 8.05%; N = 3.76%.

[3-(N-4'-n-dodecyloxsalicylidene)-aminophenyl]-[4-(N-4'-n-dodecyloxsalicylidene-amino)-benzoate, 34-12OH]

34-12OH was prepared according to the procedure described for 34-8OH using 4-n-dodecyloxsalicylaldehyde (0.76 g, 2.5 mmol) and 3-aminophenyl-4-aminobenzoate (0.28g, 1.25 mmol). Yield: 0.62g; (62%)

IR v<sub>max</sub> in cm<sup>-1</sup>: 1626 (νCH=N, imine); 1731 (νC=O, ester), 3442 (νO-H, H-bonded).

1H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 13.51 & 13.36 (s, 2H, -OH); 8.56 & 5.54 (s, 2H, -CH=N-); 8.23 (d, 2H, J = 8.9 Hz, ArH); 7.43 (t, 1H, J = 8.4 Hz, ArH); 7.34 (d, 2H, J = 9.1 Hz, ArH); 7.33-7.28 (m, 3H, ArH); 7.15 (d, 2H, J = 8.4 Hz, ArH); 7.11 (d, 2H, J = 8.4 Hz, ArH); 6.51 (s, 2H, ArH); 4.03 (t, 4H, J = 6.6 Hz, -O-CH<sub>2</sub>-); 1.81 (q, 4H, J = 6.2 Hz, -CH<sub>2</sub>-CH<sub>2</sub>-); 1.53-1.26 (m, 20H, -(CH<sub>2</sub>)<sub>9</sub>-); 0.97 (t, 6H, J = 6.2 Hz, -CH<sub>3</sub>).

Elemental analysis calculated for C<sub>51</sub>H<sub>68</sub>N<sub>2</sub>O<sub>6</sub>: C = 76.08%; H = 8.05%; N = 3.48%

Found C = 76.11%; H = 8.55%; N = 3.49%.

[3-(N-4'-n-tetradecyloxsalicylidene)-aminophenyl]-[4-(N-4'-n-tetradecyloxsalicylidene-amino)-benzoate, 34-14OH]

34-14OH was prepared according to the procedure described for 34-8OH using 4-n-tetradecyloxsalicylaldehyde (0.83 g, 2.5 mmol) and 3-aminophenyl-4-aminobenzoate (0.28g, 1.25 mmol). Yield: 0.58g; (54%)
**IR** $\nu_{\text{max}}$ in cm$^{-1}$: 1626 ($\nu_{\text{CH-N}}$, imine); 1735 ($\nu_{\text{C=O}}$, ester), 3445 ($\nu_{\text{O-H}}$, H-bonded).

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 13.59 & 13.44 (s, 2H, -OH); 8.61 & 5.54 (s, 2H, -CH=N-); 8.08 (d, 2H, $J$ = 8.1 Hz, ArH); 7.54 (t, 1H, $J$ = 8.1 Hz, ArH); 7.35 (d, 2H, $J$ = 8.1 Hz, ArH); 7.31-7.26 (m, 3H, ArH); 7.17 (d, 2H, $J$ = 8.4 Hz, ArH); 7.12 (d, 2H, $J$ = 8.4 Hz, ArH); 6.51 (s, 2H, ArH); 4.00 (t, 4H, $J$ = 6.3 Hz, -O-CH$_2$-); 1.80 (q, 4H, $J$ = 6.6 Hz, -CH$_2$-CH$_2$-); 1.54-1.26 (m, 44H, -(CH$_2$)$_n$-); 0.88 (t, 6H, $J$ = 6.6 Hz, -CH$_3$).

Elemental analysis calculated for C$_{55}$H$_{76}$N$_2$O$_6$: C = 76.71; H = 8.89%; N = 3.25%. Found C = 76.72%; H = 8.90%; N = 3.21%.

[3-(N-4'-n-hexadecyloxysalicylidene)-aminophenyl]-[4-(N-4'-n-hexadecyloxy-salicylidene-amino)-benzoate, 34-6OH:

34-6OH was prepared according to the procedure described for 34-8OH using 4-n-hexadecyloxsalicylaldehyde (0.90 g, 2.5 mmol) and 3-aminophenyl-4-amino benzoate (0.28g, 1.25 mmol). Yield: 0.78g, (68%).

**IR** $\nu_{\text{max}}$ in cm$^{-1}$: 1626 ($\nu_{\text{CH-N}}$, imine); 1735 ($\nu_{\text{C=O}}$, ester), 3442 ($\nu_{\text{O-H}}$, H-bonded).

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 13.47 & 13.39 (s, 2H, -OH); 8.56 & 5.51 (s, 2H, -CH=N-); 8.24 (d, 2H, $J$ = 8.1 Hz, ArH); 7.43 (t, 1H, $J$ = 8.4 Hz, ArH); 7.34 (d, 2H, $J$ = 8.9 Hz, ArH); 7.31-7.27 (m, 3H, ArH); 7.18 (d, 2H, $J$ = 8.1 Hz, ArH); 7.14 (d, 2H, $J$ = 7.8 Hz, ArH); 6.47 (s, 2H, ArH); 3.99 (t, 4H, $J$ = 6.2 Hz, -O-CH$_2$-); 1.77 (q, 4H, $J$ = 6.6 Hz, -CH$_2$-CH$_2$-); 1.58-1.22 (m, 52H, -(CH$_2$)$_n$-); 0.90 (t, 6H, $J$ = 6.6 Hz, -CH$_3$).

Elemental analysis calculated for C$_{59}$H$_{84}$N$_2$O$_6$: C = 77.25; H = 9.23%; N = 3.05%. Found C = 77.25%; H = 9.25%; N = 3.01%.

[3-(N-4'-n-octadecyloxsalicylidene)-aminophenyl]-[4-(N-4'-n-octadecyloxy-salicylidene-amino)-benzoate, 34-8OH:

34-8OH was prepared according to the procedure described for 34-8OH using 4-n-octadecyloxsalicylaldehyde (0.97 g, 2.5 mmol) and 3-aminophenyl-4-amino benzoate (0.28g, 1.25 mmol). Yield: 0.69g, (57%).

**IR** $\nu_{\text{max}}$ in cm$^{-1}$: 1623 ($\nu_{\text{CH-N}}$, imine); 1730 ($\nu_{\text{C=O}}$, ester), 3448 ($\nu_{\text{O-H}}$, H-bonded).

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 13.41 & 13.36 (s, 2H, -OH); 8.58 & 5.53 (s, 2H, -CH=N-); 8.24 (d, 2H, $J$ = 8.4 Hz, ArH); 7.46 (t, 1H, $J$ = 8.1 Hz, ArH); 7.36 (d, 2H, $J$ = 8.4 Hz, ArH); 7.31-7.26 (m, 3H, ArH); 7.15 (d, 2H, $J$ = 8.1 Hz, ArH); 7.11 (d,
2H, J = 8.7 Hz, ArH); 6.48 (s, 2H, ArH); 4.02 (t, 4H, J = 6.6 Hz, -O-CH₂-); 1.79 (q, 4H, J = 6.2 Hz, -CH₂-CH₂-); 1.55-1.24 (m, 60H, -(CH₂)₅s-); 0.88 (t, 6H, J = 6.2 Hz, -CH₃).

**Elemental analysis** calculated for C₆₃H₉₂N₂O₆: C = 77.73%; H = 9.53%; N = 2.88%. Found C = 77.71%; H = 9.55%; N = 2.91%.

3.2.12. **N,N'-bis[4-n-alkyloxysalicylidene]-4,4'-diaminobenzophenone, BP-nOH, (Scheme 12):**

N,N'-bis[4-n-octyloxysalicylidene]-4,4'-diaminobenzophenone, BP-8OH:

An ethanolic solution (20 ml) of 4-octyloxy-2-hydroxybenzaldehyde (0.62 g, 2.5 mmol) was added to an ethanolic solution of 4,4'-diaminobenzophenone (0.26 g, 1.25 mmol) as shown in scheme 12. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff's base N, N'-bis[4-n-octyloxysalicylidene]-4,4'-diaminobenzophenone. The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure compound. Yield: 0.59 g, (71%).

**IR** νmax in cm⁻¹: 1625 ( νCH=N, imine); 1637 ( νC=O, ketone), 3398(νO-H, H-bonded).

**¹H NMR** (CDCl₃, 300 MHz): δ = 13.41 (s, 2H, -OH); 8.55 (s, 2H, -CH=NH-); 7.86 (d, 2H, J = 8.7 Hz, ArH); 7.36 (d, 4H, J = 8.5 Hz, ArH); 7.31 (d, 4H, J = 8.6 Hz, ArH); 6.54 (d, 2H, J = 8.3 Hz, ArH); 6.46 (d, 2H, J = 2.1 Hz, ArH); 4.00 (t, 4H, J = 6.6 Hz, -
Elemental analysis calculated for C_{43}H_{52}N_{2}O_{5}: C = 76.30%; H = 7.74%; N = 4.14%.

Found C = 76.25%; H = 7.71%; N = 4.18%.

N, N'-bis[4-n-hexyloxy-4-salicylidene]-4,4'-diaminobenzophenone, BP-6OH:

BP-6OH was prepared following to the procedure described for BP-8OH using 4-n-decyloxy-4-salicylaldehyde (0.55g, 2.5 mmol) and 4,4'-diaminobenzophenone (0.26g, 1.25 mmol). Yield: 0.56 g, (73%).

IR \text{\textit{v}}_{\text{max}} \text{in cm}^{-1}: 1623 (\nu_{\text{C=O}}, \text{ketone}), 3444 (\nu_{\text{O-H}}, \text{H-bonded}).

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300MHz): \delta = 13.40 (s, 2H, -OH); 8.54 (s, 2H, -CH=N-); 7.85 (d, 2H, J = 8.3Hz, ArH); 7.38 (d, 4H, J = 8.1Hz, ArH); 7.36 (d, 4H, J = 8.6Hz, ArH); 6.56 (d, 2H, J = 8.4Hz, ArH); 6.51 (d, 2H, J = 2.1Hz, ArH); 4.01 (t, 4H, J = 6.2Hz, -O-CH\textsubscript{2}-); 1.81 (q, 4H, J = 6.6Hz, -CH\textsubscript{2}-CH\textsubscript{2}-); 1.56-1.25 (m, 12H, -CH\textsubscript{2}-(CH\textsubscript{2})\textsubscript{5}-); 0.87 (t, 6H, J = 6.4Hz, -CH\textsubscript{3}).

Elemental analysis calculated for C\textsubscript{49}H\textsubscript{46}N\textsubscript{2}O\textsubscript{5}: C = 75.46%; H = 7.14%; N = 4.51%. Found C = 75.49%; H = 7.20%; N = 4.47%.

N, N'-bis[4-n-decyloxy-salicylidene]-4,4'-diaminobenzophenone, BP-10OH:

BP-10OH was prepared following to the procedure described for BP-8OH using 4-n-decyloxy-salicylaldehyde (0.69g, 2.5 mmol) and 4,4'-diaminobenzophenone (0.26g, 1.25 mmol). Yield: 0.62 g, (69%).

IR \text{\textit{v}}_{\text{max}} \text{in cm}^{-1}: 1623 (\nu_{\text{C=CH}}, \text{imine}), 1641 (\nu_{\text{C=O}}, \text{ketone}), 3399 (\nu_{\text{O-H}}, \text{H-bonded}).

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300MHz): \delta = 13.45 (s, 2H, -OH); 8.52 (s, 2H, -CH=N-); 7.84 (d, 2H, J = 8.4Hz, ArH); 7.34 (d, 4H, J = 8.2Hz, ArH); 7.31 (d, 4H, J = 8.6Hz, ArH); 6.53 (d, 2H, J = 8.1Hz, ArH); 6.46 (d, 2H, J = 2.4Hz, ArH); 4.02 (t, 4H, J = 6.2Hz, -O-CH\textsubscript{2}-); 1.82 (q, 4H, J = 6.0Hz, -CH\textsubscript{2}-CH\textsubscript{2}-); 1.53-1.25 (m, 28H, -CH\textsubscript{2}-(CH\textsubscript{2})\textsubscript{5}-); 0.86 (t, 6H, J = 6.8Hz, -CH\textsubscript{3}).

Elemental analysis calculated for C\textsubscript{47}H\textsubscript{40}N\textsubscript{2}O\textsubscript{5}: C = 77.01%; H = 8.25%; N = 3.82%. Found C = 76.25%; H = 7.71%; N = 4.18%.

N, N'-bis[4-n-dodecyloxy-salicylidene]-4,4'-diaminobenzophenone, BP-12OH:

BP-12OH was prepared following to the procedure described for BP-8OH using 4-
n-dodecyloxy salicylaldehyde (0.76 g, 2.5 mmol) and 4,4'-diaminobenzophenone (0.26 g, 1.25 mmol). Yield: 0.67 g, (69%)  

**IR** $v_{\text{max}}$ cm$^{-1}$: 1623 ($v_{\text{CH}=\text{N}, \text{imine}}$), 1638 ($v_{\text{C}=\text{O}, \text{ketone}}$), 3399 ($v_{\text{O-H}, \text{H-bonded}}$).  

**$^1H$ NMR** (CDCl$_3$, 300 MHz): $\delta$ = 13.45 (s, 2H, -OH); 8.52 (s, 2H, -CH=N-); 7.84 (d, 2H, $J = 8.4$Hz, ArH); 7.34 (d, 4H, $J = 8.2$Hz, ArH); 7.31 (d, 4H, $J = 8.6$Hz, ArH); 6.53 (d, 2H, $J = 8.1$Hz, ArH); 6.46 (d, 2H, $J = 2.4$Hz, ArH); 4.02 (t, 4H, $J = 6.2$Hz, -O-CH$_2$-); 1.82 (q, 4H, $J = 6.0$Hz, -CH$_2$-CH$_2$-); 1.53-1.25 (m, 36H, -CH$_2$-(CH$_2$)$_9$-); 0.86 (t, 6H, $J = 6.8$Hz, -CH$_3$).  

**Elemental analysis** calculated for C$_{51}$H$_{68}$N$_2$O$_5$: C = 77.63%; H = 8.69%; N = 3.55%. Found C = 77.62%; H = 8.71%; N = 3.54%.  

**N, N'-bis[4-n-tetradecyloxy salicylidene]-4,4'-diaminobenzophenone, BP-14OH:**  

**BP-14OH** was prepared following to the procedure described for BP-8OH using 4-n-tetradecyloxy salicylaldehyde (0.83 g, 2.5 mmol) and 4,4'-diaminobenzophenone (0.26 g, 1.25 mmol). Yield: 0.77 g, (74%)  

**IR** $v_{\text{max}}$ cm$^{-1}$: 1626 ($v_{\text{CH}=\text{N}, \text{imine}}$), 1637 ($v_{\text{C}=\text{O}, \text{ketone}}$), 3444 ($v_{\text{O-H}, \text{H-bonded}}$).  

**$^1H$ NMR** (CDCl$_3$, 300 MHz): $\delta$ = 13.43 (s, 2H, -OH); 8.58 (s, 2H, -CH=N-); 7.88 (d, 2H, $J = 8.1$Hz, ArH); 7.36 (d, 4H, $J = 8.1$Hz, ArH); 7.32 (d, 4H, $J = 8.1$Hz, ArH); 6.50 (d, 2H, $J = 7.8$Hz, ArH); 6.48 (d, 2H, $J = 2.3$Hz, ArH); 4.01 (t, 4H, $J = 6.6$Hz, -O-CH$_2$-); 1.80 (q, 4H, $J = 7.2$Hz, -CH$_2$-CH$_2$-); 1.56-1.25 (m, 44H, -CH$_2$-(CH$_2$)$_{11}$-); 0.89 (t, 6H, $J = 6.0$Hz, -CH$_3$).  

**Elemental analysis** calculated for C$_{55}$H$_{76}$N$_2$O$_5$: C = 78.16%; H = 9.06%; N = 3.31%. Found C = 78.18%; H = 9.02%; N = 3.32%.  

**N, N'-bis[4-n-hexadecyloxy salicylidene]-4,4'-diaminobenzophenone, BP-16OH:**  

**BP-16OH** was prepared following to the procedure described for BP-8OH using 4-n-hexadecyloxy salicylaldehyde (0.90 g, 2.5 mmol) and 4,4'-diaminobenzophenone (0.26 g, 1.25 mmol). Yield: 0.77 g, (69%)  

**IR** $v_{\text{max}}$ cm$^{-1}$: 1621 ($v_{\text{CH}=\text{N}, \text{imine}}$), 1636 ($v_{\text{C}=\text{O}, \text{ketone}}$), 3411($v_{\text{O-H}, \text{H-bonded}}$).  

**$^1H$ NMR** (CDCl$_3$, 300 MHz): $\delta$ = 13.45 (s, 2H, -OH); 8.52 (s, 2H, -CH=N-); 7.84 (d, 2H, $J = 8.4$Hz, ArH); 7.38 (d, 4H, $J = 8.2$Hz, ArH); 7.35 (d, 4H, $J = 8.6$Hz, ArH); 6.53 (d, 2H, $J = 8.1$Hz, ArH); 6.46 (d, 2H, $J = 2.4$Hz, ArH); 4.02 (t, 4H, $J = 6.8$Hz, ArH).
6.2\, Hz, -O-\text{CH}_2-); 1.82 (q, 4H, J = 6.0\, Hz, -\text{CH}_2-\text{CH}_2-); 1.53-1.25 (m, 52H, -(\text{CH}_2)_{13-}); 0.86 (t, 6H, J = 6.8\, Hz, -\text{CH}_3).

**Elemental analysis** calculated for C$_{59}$H$_{84}$N$_2$O$_5$: C = 78.62%; H = 9.39%; N = 3.11%. Found C = 76.25%; H = 7.71%; N = 4.18%.

N, N'-bis[4-n-octadecyloxysalicylidene]-4,4'-diaminobenzophenone, BP-\textit{i}OH:

BP-\textit{i}OH was prepared following the procedure described for BP-\textit{o}OH using 4-n-octadecyloxy salicylaldehyde (0.97 g, 2.5 mmol) and 4,4'-diaminobenzophenone (0.26 g, 1.25 mmol). Yield: 0.93 g, (79%)

IR $\nu_{\text{max}}$ in cm$^{-1}$: 1623 (\text{v}_\text{C}H=N, imine), 1638 (\text{v}_\text{C}=\text{o}, ketone), 3438 (\text{v}_\text{O}-\text{H}, \text{H-bonded}).

$^1$H NMR (CDCl$_3$, 300MHz): $\delta$ = 13.48 (s, 2H, -OH); 8.54 (s, 2H, -\text{CH}=\text{N}-); 7.85 (d, 2H, J = 8.3\, Hz, \text{ArH}); 7.38 (d, 4H, J = 8.6\, Hz, \text{ArH}); 7.33 (d, 4H, J = 8.6\, Hz, \text{ArH}); 6.58 (d, 2H, J = 8.4\, Hz, \text{ArH}); 6.51 (d, 2H, J = 2.1\, Hz, \text{ArH}); 4.01 (t, 4H, J = 6.2\, Hz, -O-\text{CH}_2-); 1.81 (q, 4H, J = 6.6\, Hz, -\text{CH}_2-\text{CH}_2-); 1.54-1.25 (m, 60H, - \text{CH}_2-(\text{CH}_2)_{13-}); 0.88 (t, 6H, J = 6.4\, Hz, -\text{CH}_3).

**Elemental analysis** calculated for C$_{63}$H$_{92}$N$_2$O$_5$: C = 79.03%; H = 9.69%; N = 2.93%. Found C = 79.24%; H = 9.72%; N = 2.95%.

3.2.13. N,N'-bis[4-n-alkyloxysalicylidene]-4,4'-diaminophenylene sulfone, (PAS-\textit{n}OH), Scheme 13:
N, N’-bis[4-n-octyloxy salicylidene]-4,4’-diaminophenylensulfone, PAS-8OH:

An ethanolic solution (20 ml) of 4-n-octyloxy salicylaldehyde (0.62 g, 2.5 mmol) was added to an ethanolic solution of 4-aminophenyl sulfone (0.31 g, 1.25 mmol) as shown in scheme 13. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff’s base N,N’-bis[4-n-octyloxy salicylidene]-4,4’-diaminophenylensulfone. The precipitate was collected by filtration from the hot solution and recrystallised several times from absolute ethanol to give a pure compound. Yield: 0.64 g, (73%)

IR: v_{max} in cm^{-1}: 1367 (v_{S=O}, sulfone), 1625 (v_{C=N}, imine), 3424 (v_{O-H}, H-bonded).

^1H NMR (CDCl_3, 300 MHz): δ = 13.25 (s, 2H, -OH); 8.48 (s, 2H, -CH=N-); 7.97 (d, 4H, J = 8.2Hz, ArH); 7.32 (d, 4H, J = 8.9Hz, ArH); 7.28 (d, 2H, J = 8.3Hz, ArH); 6.50 (d, 2H, J = 7.9Hz, ArH); 6.47 (d, 2H, J = 2.1Hz, ArH); 4.00 (t, 4H, J = 6.6Hz, -O-CH_2-); 1.77 (q, 4H, J = 6.2Hz, -CH_2-CH_2-); 1.52-1.26 (m, 20H, -(CH_2)_5-); 0.97 (t, 6H, J = 6.4Hz, CH_2-CH_3).

Elemental analysis calculated for C_{42}H_{52}N_2O_6S: C = 70.76%; H = 7.35%; N = 3.93%. Found C = 70.72%; H = 7.38%; N = 3.94%.

N,N’-bis[4-n-hexyloxy salicylidene]-4,4’-diaminophenylensulfone, PAS-6OH:

PAS-6OH was prepared following the procedure described for PAS-8OH using 4-n-hexyloxy salicylaldehyde (0.55 g, 2.5 mmol) and 4,4’-diaminophenylsulphone (0.31 g, 1.25 mmol). Yield: 0.56 g, (69%)

IR: v_{max} in cm^{-1}: 1367 (v_{S=O}, sulfone), 1626 (v_{C=N}, imine), 3424 (v_{O-H}, H-bonded).

^1H NMR (CDCl_3, 300 MHz): δ = 13.25 (s, 2H, -OH); 8.49 (s, 2H, -CH=N-); 7.96 (d, 4H, J = 8.2Hz, ArH); 7.33 (d, 4H, J = 8.4Hz, ArH); 7.27 (d, 2H, J = 8.6Hz, ArH); 6.51 (d, 2H, J = 8.3Hz, ArH); 6.48 (d, 2H, J = 2.3Hz, ArH); 4.02 (t, 4H, J = 6.2Hz, -O-CH_2-); 1.75 (q, 4H, J = 6.2Hz, -CH_2-CH_2-); 1.50-1.26 (m, 12H, -(CH_2)_3-); 0.99 (t, 6H, J = 6.2Hz, CH_2-CH_3).

Elemental analysis calculated for C_{38}H_{44}N_2O_6S: C = 69.49%; H = 6.75%; N = 4.26%. Found C = 69.50%; H = 6.78%; N = 4.23%.

N, N’-bis[4-n-decyloxy salicylidene]-4,4’-diaminophenylensulfone, PAS-10OH:

PAS-10OH was prepared following the procedure described for PAS-8OH using 4-n-decyloxy salicylaldehyde (0.69 g, 2.5 mmol) and 4,4’-diaminophenylsulphone (0.31 g, 1.25 mmol). Yield: 0.67 g, (71%)
IR $v_{\text{max}}$ in cm$^{-1}$: 1367 ($v_{\text{S=O, sulfone}}$), 1625 ($v_{\text{CH=N, imine}}$), 3424 ($v_{\text{O-H, H-bonded}}$).

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 13.25 (s, 2H, -OH); 8.48 (s, 2H, -CH=N-); 7.97 (d, 4H, $J$ = 8.2Hz, ArH); 7.32 (d, 4H, $J$ = 8.9Hz, ArH); 7.28 (d, 2H, $J$ = 8.3Hz, ArH); 6.50 (d, 2H, $J$ = 7.9Hz, ArH); 6.47 (d, 2H, $J$ = 2.1 Hz, ArH); 4.00 (t, 4H, $J$ = 6.6Hz, -O-CH$_2$-); 1.77 (q, 4H, $J$ = 6.2Hz, -CH$_2$-CH$_2$-); 1.52-1.26 (m, 28H, -(CH$_2$)$_7$-); 0.97 (t, 6H, $J$ = 6.4Hz, -CH$_3$).

**Elemental analysis** calculated for C$_{46}$H$_{60}$N$_2$O$_6$S: C = 71.84%; H = 7.86%; N = 3.64%. Found C = 71.82%; H = 7.88%; N = 3.63%.

N,N'-bis[4-n-dodecyloxy salicylidene]-4,4'-diaminophenylanesulfone, PAS-J2OH:

PAS-J2OH was prepared following the procedure described for PAS-8OH using 4-n-dodecyloxy salicylaldehyde (0.76 g, 2.5 mmol) and 4,4'-diaminophenylsulphone (0.31 g, 1.25 mmol). Yield: 0.69 g, (68%).

IR $v_{\text{max}}$ in cm$^{-1}$: 1367 ($v_{\text{S=O, sulfone}}$), 1625 ($v_{\text{CH=N, imine}}$), 3424 ($v_{\text{O-H, H-bonded}}$). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 13.22 (s, 2H, -OH); 8.47 (s, 2H, -CH=N-); 7.93 (d, 4H, $J$ = 8.4Hz, ArH); 7.32 (d, 4H, $J$ = 8.9Hz, ArH); 7.25 (d, 2H, $J$ = 8.1Hz, ArH); 6.59 (d, 2H, $J$ = 7.8 Hz, ArH); 6.46 (d, 2H, $J$ = 2.1 Hz, ArH); 4.02 (t, 4H, $J$ = 6.6Hz, -O-CH$_2$-); 1.74 (q, 4H, $J$ = 6.2 Hz, -CH$_2$-CH$_2$-); 1.58-1.24 (m, 36H, -(CH$_2$)$_9$-); 0.88 (t, 6H, $J$ = 6.6Hz, -CH$_3$).

**Elemental analysis** calculated for C$_{50}$H$_{72}$N$_2$O$_6$S: C = 72.43%; H = 8.75%; N = 3.38%. Found C = 72.42%; H = 8.73%; N = 3.39%.

N,N'-bis[4-n-tetradecyloxy salicylidene]-4,4'-diaminophenylanesulfone, PAS-J4OH:

PAS-J4OH was prepared following the procedure described for PAS-8OH using 4-n-tetradecyloxy salicylaldehyde (0.83 g, 2.5 mmol) and 4,4'-diaminophenylsulphone (0.31 g, 1.25 mmol). Yield: 0.67 g, (62%).

IR $v_{\text{max}}$ in cm$^{-1}$: 1322 ($v_{\text{S=O, sulfone}}$), 1621 ($v_{\text{CH=N, imine}}$), 3444 ($v_{\text{O-H, H-bonded}}$). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 13.11 (s, 2H, -OH); 8.48 (s, 2H, -CH=N-); 7.97 (d, 4H, $J$ = 8.1Hz, ArH); 7.31 (d, 4H, $J$ = 8.4Hz, ArH); 7.27 (d, 2H, $J$ = 8.3Hz, ArH); 6.65 (d, 2H, $J$ = 7.9Hz, ArH); 6.49 (d, 2H, $J$ = 2.4 Hz, ArH); 4.01 (t, 4H, $J$ = 6.3Hz, -O-CH$_2$-); 1.78 (q, 4H, $J$ = 6.9Hz, -CH$_2$-CH$_2$-); 1.62-1.26 (m, 44H, -(CH$_2$)$_{11}$-); 0.87 (t, 6H, $J$ = 6.0Hz, -CH$_3$).

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Elemental analysis calculated for C_{54}H_{76}N_{2}O_{6}S: C = 73.60%; H = 8.69%; N = 3.18%. Found C = 76.62%; H = 8.70%; N = 3.20%.

N,N'-bis[4-n-hexadecyloxysalicylidene]-4,4'-diaminophenylenesulfone, PAS-16OH:

PAS-16OH was prepared following the procedure described for PAS-8OH using 4-n-hexadecyloxy salicylaldehyde (0.90 g, 2.5 mmol) and 4,4'-diaminophenyl-sulphone (0.31 g, 1.25 mmol). Yield: 0.76 g, (66%).

IR v_{max} in cm\(^{-1}\): 1365 (vs=O, sulfone), 1613 (v_{CH=N}, imine), 3364 (v_{O-H}, H-bonded).

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 13.17\) (s, 2H, -OH); 8.47 (s, 2H, -CH=N-); 7.91 (d, 4H, J = 8.4Hz, ArH); 7.31 (d, 4H, J = 8.4Hz, ArH); 7.25 (d, 2H, J = 8.3Hz, ArH); 6.66 (d, 2H, J = 8.4 Hz, ArH); 6.48 (d, 2H, J = 2.2 Hz, ArH); 4.00 (t, 4H, J = 6.3Hz, -O-CH\(_2\)-); 1.79 (q, 4H, J = 6.2Hz, -CH\(_2\)-CH\(_2\)-); 1.54-1.25 (m, 52H, -(CH\(_2\))\(_{13}\)-); 0.87 (t, 6H, J = 6.0Hz, -CH\(_3\)).

Elemental analysis calculated for C_{58}H_{84}N_{2}O_{8}S: C = 74.32%; H = 9.03%; N = 2.99%. Found C = 74.32%; H = 9.05%; N = 2.98%.

N,N'-bis[4-n-octadecyloxysalicylidene]-4,4'-diaminophenylenesulfone, PAS-18OH:

PAS-18OH was prepared following the procedure described for PAS-8OH using 4-n-octadecyloxy salicylaldehyde (0.97 g, 2.5 mmol) and 4,4'-diaminophenyl-sulphone (0.31 g, 1.25 mmol). Yield: 0.91 g, (74%).

IR v_{max} in cm\(^{-1}\): 1367 (vs=O, sulfone), 1634 (v_{CH=N}, imine), 3436 (v_{O-H}, H-bonded).

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 13.21\) (s, 2H, -OH); 8.48 (s, 2H, -CH=N-); 7.95 (d, 4H, J = 8.4 Hz, ArH); 7.30 (d, 4H, J = 8.4 Hz, ArH); 7.23 (d, 2H, J = 8.9 Hz, ArH); 6.55 (d, 2H, J = 7.8 Hz, ArH); 6.44 (d, 2H, J = 2.1 Hz, ArH); 3.98 (t, 4H, J = 6.6 Hz, -O-CH\(_2\)-); 1.81 (q, 4H, J = 6.2 Hz, -CH\(_2\)-CH\(_2\)-); 1.53-1.25 (m, 60H, -(CH\(_2\))\(_{13}\)-); 0.98 (t, 6H, J = 6.6 Hz, -CH\(_3\)).

Elemental analysis calculated for C_{62}H_{92}N_{2}O_{6}S: C = 74.96%; H = 9.33%; N = 2.82%. Found C = 74.95%; H = 9.31%; N = 2.83%.
3.2.14. \( N,N'\)-bis-[4-(4-n-alkyloxybenzoyloxy)-salicylidene]-phenylene-4-fluoro-1,3-diamines, 4F-nOH, (Scheme 14):

\[
\begin{align*}
\text{Scheme 14} \\
N,N'\text{-bis[4-(4-n-octyloxybenzoyloxy)-salicylidene]-phenylene-4-fluoro-1,3-diamine, 4F-SOH.}
\end{align*}
\]

An ethanolic solution (20 ml) of 4-(4'-n-octyloxybenzoyloxy)salicylaldehyde (0.92 g, 2.5 mmol) was added to an ethanolic solution of 4-fluoro-1,3-phenylene diamine (0.15 g, 1.25 mmol), Scheme 14. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 h to yield the Schiff's base \( N,N'\)-bis[4-(4-n-octyloxybenzoyloxy)-salicylidene]-phenylene-4-fluoro-1,3-diamine. The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure compound. Yield: 0.70 g, (68%).

**IR** \( \nu_{max} \) in cm\(^{-1} \): 1632 (\( \nu_{C=N} \), imine); 1734 (\( \nu_{C=O} \), ester); 3444 (\( \nu_{OH} \), H-bonded).

**\(^1\)H NMR** (CDCl\(_3\)): 6 = 13.24 (bs, 2H, -OH); 8.75 and 8.60 (s, 2H, -CH=N-); 8.11 (d, 4H, J = 8.7 Hz, \( \text{ArH} \)); 8.08 (d, 2H, J = 8.4 Hz, \( \text{ArH} \)); 7.45 (d, 1H, J = 7.6 Hz, \( \text{ArH} \)); 7.16 (d, 2H, J = 8.8 Hz, \( \text{ArH} \)); 7.10 (d, 1H, J = 2.1 Hz, \( \text{ArH} \)); 6.95 (d, 1H, J = 7.6 Hz, \( \text{ArH} \)); 6.89 (d, 2H, J = 2.3 Hz, \( \text{ArH} \)); 6.85 (d, 4H, J = 8.7 Hz, \( \text{ArH} \)); 4.03 (t, 4H, J = 6.4 Hz, -O-CH\(_2\)); 1.82 (q, 4H, J = 6.8 Hz, -CH\(_2\)-CH\(_2\)-); 1.60-1.24 (m, 20H, -(CH\(_2\))\(_5\)-); 0.98 (t, 6H, J = 6.8 Hz, -CH\(_3\)).

**Elemental analysis** calculated for C\(_{50}\)H\(_{55}\)O\(_8\)N\(_2\)F: C = 72.27%; H = 6.67%; N = 3.37%. Found C = 72.80%; H = 6.89%; N = 3.52%.
N,N'-bis[4-(4-n-decyl oxybenzoyloxy)salicylidene]-phenylene-4-fluoro-1,3-diamine, 4F-10OH:

4F-10OH was prepared following the procedure described for 4F-8OH with 4-(4'-n-decyl oxybenzoyloxy)salicylaldehyde (0.99 g, 2.5 mmol) and 4-fluoro-1,3-phenylenediamine (0.15 g, 1.25 mmol). Yield 0.73 g, (66%).

IR νmax in cm⁻¹; 1626 (νC=N, imine); 1738 (νC=O, ester); 3423 (νOH, H-bonded).

¹H NMR (CDCl₃): δ = 13.26 (bs, 2H, -OH); 8.77 and 8.64 (s, 2H, -CH=N-); 8.13 (d, 4H, J = 7.8 Hz, ArH); 8.11 (d, 2H, J = 8.4 Hz, ArH); 7.46 (d, 1H, J = 7.2 Hz, ArH); 7.11 (d, 2H, J = 8.4, ArH); 6.98 (d, 1H, J = 2.4 Hz, ArH); 6.96 (d, 1H, J = 8.4 Hz, ArH); 6.91 (d, 2H, J = 2.8 Hz, ArH); 6.82 (d, 4H, J = 8.4 Hz, ArH); 4.04 (t, 4H, J = 6.0 Hz, -O-CH₂); 1.82 (q, 4H, J = 6.6 Hz, -CH₂-CH₂-); 1.60-1.28 (m, 28H, -(CH₂)₇-); 0.88 (t, 6H, J = 6.6 Hz, -CH₃).

Elemental analysis calculated for C₅₄H₆₀O₈N₂F: C=73.11%; H=7.16%; N=3.16%. Found C=73.53%; H=7.24%; N=3.21%.

N,N'-bis[4-(4-n-dodecyloxybenzoyloxy)salicylidene]-phenylene-4-fluoro-1,3-diamine, 4F-12OH:

4F-12OH was prepared following the procedure described for 4F-8OH with 4-(4'-n-dodecyloxybenzoyloxy)salicylaldehyde (1.00 g, 2.5 mmol) and 4-fluoro-1,3-phenylenediamine (0.15 g, 1.25 mmol). Yield: 0.76 g, (61%).

IR νmax in cm⁻¹; 1632 (νC=N, imine); 1733 (νC=O, ester); 3422 (νOH, H-bonded).

¹H NMR (CDCl₃): δ = 13.26 (bs, 2H, -OH); 8.77 & 8.65 (s, 2H, -CH=N-); 8.14 (d, 4H, J = 8.7 Hz, ArH); 8.12 (d, 2H, J = 8.2 Hz, ArH); 7.47 (d, 1H, J = 8.1 Hz, ArH); 7.45 (d, 2H, J = 8.4 Hz, ArH); 7.13 (d, 1H, J = 2.1 Hz, ArH); 6.97 (d, 1H, J = 8.4 Hz, ArH); 6.94 (d, 2H, J = 2.1 Hz, ArH); 6.85 (d, 4H, J = 8.4 Hz, ArH); 4.05 (t, 4H, J = 6.6 Hz, -O-CH₂); 1.82 (q, 4H, J = 6.6 Hz, -CH₂-CH₂-); 1.55-1.26 (m, 36H, -(CH₂)₉-); 0.88 (t, 6H, J = 6.6 Hz, -CH₃).

Elemental analysis calculated for C₅₈H₇₁O₈N₂F: C=73.86%; H=7.16%; N=3.16%. Found C=73.53%; H=7.49%; N=3.21%.

N,N'-bis[4-(4-n-tetradecyloxybenzoyloxy)salicylidene]-phenylene-4-fluoro-1,3-diamines, 4F-14OH:

4F-14OH was prepared following the procedure described for 4F-8OH with 4-(4'-n-
tetradecyloxybenzoyloxy)salicylaldehyde (1.13 g, 2.5 mmol) and 4-fluoro-1,3-phenylenediamine (0.15 g, 1.25 mmol). Yield: 0.85 g (65%).

IR $v_{\text{max}}$ in cm$^{-1}$; 1625 (vC=N, imine); 1742 (vC=O, ester); 3444 (vOH, H-bonded).

$^1$H NMR (CDCl$_3$): $\delta = 13.26$ (bs, 2H, -OH); 8.77 and 8.65 (s, 2H, -CH=N-); 8.13 (d, 4H, J = 8.6 Hz, ArH); 8.11 (d, 2H, J = 8.4 Hz, ArH); 7.47 (d, 1H, J = 8.5 Hz, ArH); 7.44 (d, 2H, J = 8.4 Hz, ArH); 7.11 (d, 1H, J = 2.4 Hz, ArH); 6.99 (d, 1H, J = 8.8 Hz, ArH); 6.96 (d, 2H, J = 2.5 Hz, ArH); 6.85 (d, 4H, J = 8.4 Hz, ArH); 4.05 (t, 4H, J = 6.4 Hz, -O-CH$_2$); 1.82 (q, 4H, J = 6.7 Hz, -CH$_2$- CH$_2$-); 1.55-1.26 (m, 44H, -(CH$_2$)$_{11}$-); 0.88 (t, 6H, J = 6.6 Hz, -CH$_3$).

Elemental analysis calculated for C$_{62}$H$_{79}$O$_8$N$_2$F: C = 74.52%; H = 7.97%; N=2.80%. Found C = 74.60%; H = 7.93%; N = 2.91%.

N,N'-bis[4-(4-n-hexadecyloxybenzoyloxy)salicylidene]-phenylene-4-fluoro-1,3-diamines, 4F-/60H:

4F-/60H was prepared following the procedure described for 4F-SOH with 4-(4'-n-hexadecyloxybenzoyloxy)salicylaldehyde (1.20 g, 2.5 mmol) and 4-fluoro-1,3-phenylenediamine (0.15 g, 1.25 mmol). Yield: 0.81 g, (65%).

IR $v_{\text{max}}$ in cm$^{-1}$; 1629 (vC=N, imine); 1733 (vC=O, ester); 3421 (vOH, H-bonded).

$^1$H NMR (CDCl$_3$): $\delta = 13.29$ (bs, 2H, -OH); 8.72 and 8.63 (s, 2H, -CH=N-); 8.14 (d, 4H, J = 8.2 Hz, ArH); 8.09 (d, 2H, J = 8.6 Hz, ArH); 7.45 (d, 1H, J = 8.6 Hz, ArH); 7.41 (d, 2H, J = 8.3 Hz, ArH); 7.08 (d, 1H, J = 2.1 Hz, ArH); 6.98 (d, 1H, J = 8.7 Hz, ArH); 6.96 (d, 2H, J = 2.3 Hz, ArH); 6.84 (d, 4H, J = 8.1 Hz, ArH); 4.08 (t, 4H, J = 6.3 Hz, -O-CH$_2$); 1.81 (q, 4H, J = 6.6 Hz, -CH$_2$- CH$_2$-); 1.53-1.25 (m, 52H, -(CH$_2$)$_{11}$-); 0.87 (t, 6H, J = 6.3 Hz, -CH$_3$).

Elemental analysis calculated for C$_{66}$H$_{87}$O$_8$N$_2$F: C = 75.11%; H = 8.31%; N = 2.65%. Found C = 75.10%; H = 8.36%; N = 2.66%.

N,N'-bis[4-(4-n-octadecyloxybenzoyloxy)salicylidene]-phenylene-4-fluoro-1,3-diamines, 4F-/16OH:

4F-/16OH was prepared following the procedure described for 4F-SOH with 4-(4'-n-octadecyloxybenzoyloxy)salicylaldehyde (1.27 g, 2.5 mmol) and 4-fluoro-1,3-phenylenediamine (0.15 g, 1.25 mmol). Yield: 0.93 g, (65%).

IR $v_{\text{max}}$ in cm$^{-1}$; 1630 (vC=N, imine); 1733 (vC=O, ester); 3399 (vOH, H-bonded).
$^1$H NMR (CDCl$_3$): $\delta = 13.28$ (bs, 2H, -OH); 8.69 and 8.61 (s, 2H, -CH=N-); 8.16 (d, 4H, $J = 8.8$ Hz, ArH); 8.12 (d, 2H, $J = 8.4$ Hz, ArH); 7.43 (d, 1H, $J = 8.2$ Hz, ArH); 7.44 (d, 2H, $J = 8.5$ Hz, ArH); 7.12 (d, 1H, $J = 2.5$ Hz, ArH); 6.99 (d, 1H, $J = 8.7$ Hz, ArH); 6.94 (d, 2H, $J = 2.6$ Hz, ArH); 6.81 (d, 4H, $J = 8.7$ Hz, ArH); 4.08 (t, 4H, $J = 6.4$ Hz, -CH$_2$-CH$_2$-); 1.56-1.24 (m, 60H, -(CH$_2$)$_{15}$-); 0.86 (t, 6H, $J = 6.6$ Hz, -CH$_3$).

Elemental analysis calculated for C$_{70}$H$_{95}$O$_8$N$_2$: C = 75.64%; H = 8.61%; N = 2.52%. Found C = 75.67%; H = 8.63%; N = 2.55%.

3.2.15. N,N'-bis[4-(4-n-alkyloxybenzoyloxy)-salicylidene]-phenylene-2-methyl-1,3-diamines, 2M-nOH, (Scheme 15):

An ethanolic solution (20 ml) of 4-(4'-n-octyloxybenzoyloxy)salicylaldehyde (0.92 g, 2.5 mmol) was added to an ethanolic solution of 2-methyl-1,3-phenylene diamine (0.15 g, 1.25 mmol) as shown in Scheme 15. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff’s base N,N'-Bis[4-(4-n-octyloxy-benzoyloxy)-salicylidene]-phenylene-2-methyl-1,3-diamine.
The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure compound 2M-8OH.

Yield: 0.71g, (69%).

IR ν_{max} in cm\(^{-1}\): 1622 (ν_{C=N}, imine); 1739 (ν_{C=O}, ester); 3445 (ν_{OH}, H-bonded).

\(^1\)H NMR (CDCl\(_3\)): δ = 13.55 (bs, 2H, -OH); 8.58 (s, 2H, -CH=N-); 8.14 (d, 2H, J = 8.7 Hz, ArH); 7.46 (d, 2H, J = 8.4 Hz, ArH); 7.33 (t, 1H, J = 7.8 Hz, ArH); 7.02 (d, 2H, J = 7.8 Hz, ArH); 6.98 (d, 4H, J = 8.7 Hz, ArH); 6.90 (s, 2H, ArH); 6.85 (d, 4H, J = 8.4 Hz, ArH); 4.05 (t, 4H, J = 6.3 Hz, -O-CH\(_2\)-); 2.42 (s, 3H, Ar-CH\(_3\)); 1.83 (q, 4H, J = 6.6 Hz, -CH\(_2\)-CH\(_2\)-); 1.55-1.35 (m, 20H, -(CH\(_2\))\(_5\)-); 0.92 (t, 6H, J = 6.23 Hz, -CH\(_3\)).

Elemental analysis calculated for C\(_{51}\)H\(_{58}\)O\(_8\)N\(_2\): C = 74.07%; H = 7.07%; N = 3.39%.

Found C = 74.10%; H = 7.06%; N = 3.35%.

N,N'-bis[4-(4-n-hexyloxybenzoyloxy)-salicylidene]-phenylene-2-methyl-1,3-diamine, 2M-6OH:

2M-6OH was prepared according to the procedure described for 2M-8OH using 4-(4'-n-hexyloxybenzoyloxy)salicylaldehyde (0.85 g, 2.5 mmol) and 2-methyl-1,3-phenylenediamine (0.15 g, 1.25 mmol). Yield: 0.60 g, (62%).

IR ν_{max} in cm\(^{-1}\): 1625 (ν_{C=N}, imine); 1737 (ν_{C=O}, ester); 3438 (ν_{OH}, H-bonded).

\(^1\)H NMR (CDCl\(_3\)): δ = 13.54 (bs, 2H, -OH); 8.57 (s, 2H, -CH=N-); 8.13 (d, 2H, J = 8.7 Hz, ArH); 7.45 (d, 2H, J = 8.4 Hz, ArH); 7.32 (t, 1H, J = 7.8 Hz, ArH); 7.02 (d, 2H, J = 8.1 Hz, ArH); 6.97 (d, 4H, J = 8.7 Hz, ArH); 6.90 (s, 2H, ArH); 6.84 (d, 4H, J = 8.4 Hz, ArH); 4.04 (t, 4H, J = 6.3 Hz, -O-CH\(_2\)-); 2.42 (s, 3H, Ar-CH\(_3\)); 1.82 (q, 4H, J = 6.9 Hz, -CH\(_2\)-CH\(_2\)-); 1.57-1.35 (m, 20H, -(CH\(_2\))\(_3\)-); 0.92 (t, 6H, J = 6.3 Hz, -CH\(_3\)).

Elemental analysis calculated for C\(_{47}\)H\(_{50}\)O\(_9\)N\(_2\): C = 73.23%; H = 6.54%; N = 3.63%.

Found C = 73.21%; H = 6.53%; N = 3.65%.

N,N'-bis[4-(4-n-decyloxybenzoyloxy)-salicylidene]-phenylene-2-methyl-1,3-diamine, 2M-10OH:

2M-10OH was prepared according to the procedure described for 2M-8OH using 4-(4'-n-decyloxybenzoyloxy)salicylaldehyde (0.99 g, 2.5 mmol).and 2-methyl-1,3-phenylenediamine (0.15 g, 1.25 mmol). Yield: 0.79 g, (72%).

IR ν_{max} in cm\(^{-1}\): 1625 (ν_{C=N}, imine); 1739 (ν_{C=O}, ester); 3445 (ν_{OH}, H-bonded).
$^1$H NMR (CDCl$_3$): $\delta = 13.54$ (bs, 2H, -OH); 8.57 (s, 2H, -CH=N-); 8.13 (d, 2H, J = 8.7 Hz, ArH); 7.45 (d, 2H, J = 8.4 Hz, ArH); 7.32 (t, 1H, J = 7.8 Hz, ArH); 7.02 (d, 2H, J = 8.1 Hz, ArH); 6.97 (d, 4H, J = 8.7 Hz, ArH); 6.90 (s, 2H, ArH); 6.84 (d, 4H, J = 8.4 Hz, ArH); 4.05 (t, 4H, J = 6.3 Hz, -O-CH$_2$); 2.42 (s, 3H, Ar-CH$_3$); 1.81 (q, 4H, J = 6.9 Hz, -CH$_2$-CH$_2$-); 1.55-1.29 (m, 28H, -(CH$_2$)$_7$-); 0.89 (t, 6H, J = 6.9 Hz, -CH$_3$).

Elemental analysis calculated for C$_{55}$H$_{66}$O$_8$N$_2$: C = 74.80%; H = 7.53%; N = 3.17%. Found C = 74.81%; H = 7.54%; N = 3.15%.

N,N'-bis[4-(4-n-dodecyloxybenzoyloxy)-salicylidene]-phenylene-2-methyl-1,3-diamine, 2M-/20H:

2M-/20H was prepared according to the procedure described for 2M-8OH using 4-(4'-n-dodecyloxybenzoyloxy)salicylaldehyde (1.00 g, 2.5 mmol) and 2-methyl-1,3-phenylenediamine (0.15 g, 1.25 mmol). Yield: 0.82 g (70%).

IR $v_{max}$ in cm$^{-1}$: 1622 ($v$C=N, imine); 1740 ($v$C=O, ester); 3445 ($v$OH, H-bonded).

$^1$H NMR (CDCl$_3$): $\delta = 13.53$ (bs, 2H, -OH); 8.55 (s, 2H, -CH=N-); 8.13 (d, 2H, J = 8.6 Hz, ArH); 7.42 (d, 2H, J = 8.1 Hz, ArH); 7.30 (t, 1H, J = 8.4 Hz, ArH); 7.02 (d, 2H, J = 8.8 Hz, ArH); 6.96 (d, 4H, J = 8.7 Hz, ArH); 6.89 (s, 2H, ArH); 6.82 (d, 4H, J = 8.1 Hz, ArH); 4.03 (t, 4H, J = 6.6 Hz, -O-CH$_2$); 2.41 (s, 3H, Ar-CH$_3$); 1.84 (q, 4H, J = 6.3 Hz, -CH$_2$-CH$_2$-); 1.52-1.26 (m, 36H, -(CH$_2$)$_9$-); 0.88 (t, 6H, J = 6.6 Hz, -CH$_3$).

Elemental analysis calculated for C$_{59}$H$_{74}$O$_8$N$_2$: C = 75.45%; H = 7.94%; N = 2.98%. Found C = 75.48%; H = 7.94%; N = 3.00%.

N,N'-bis[4-(4-n-tetradecyloxybenzoyloxy)-salicylidene]-phenylene-2-methyl-1,3-diamine, 2M-/40H:

2M-/40H was prepared according to the procedure described for 2M-/8OH using 4-(4'-n-tetradecyloxybenzoyloxy)salicylaldehyde (1.13 g, 2.5 mmol) and 2-methyl-1,3-phenylenediamine (0.15 g, 1.25 mmol). Yield: 0.80 g (65%).

IR $v_{max}$ in cm$^{-1}$: 1622 ($v$C=N, imine); 1740 ($v$C=O, ester); 3445 ($v$OH, H-bonded).

$^1$H NMR (CDCl$_3$): $\delta = 13.55$ (bs, 2H, -OH); 8.58 (s, 2H, -CH=N-); 8.14 (d, 2H, J = 8.7 Hz, ArH); 7.46 (d, 2H, J = 8.4 Hz, ArH); 7.31 (t, 1H, J = 8.7 Hz, ArH); 7.03 (d, 2H, J = 8.4 Hz, ArH); 6.97 (d, 4H, J = 9.0 Hz, ArH); 6.90 (s, 2H, ArH); 6.85 (d, 4H, J = 8.4 Hz, ArH); 4.05 (t, 4H, J = 6.2 Hz, -O-CH$_2$); 2.43 (s, 3H, Ar-CH$_3$); 1.81
N,N'-bis[4-(4-n-hexadecyloxybenzoyloxy)-salicylidene]-phenylene-2-methyl-1,3-diamine, 2M-16OH:

2M-16OH was prepared according to the procedure described for 2M-8OH using 4-(4'-n-hexadecyloxybenzoyloxy)salicylaldehyde (1.20 g, 2.5 mmol) and 2-methyl-1,3-phenylenediamine (0.15 g, 1.25 mmol). Yield: 0.91 g, (69%).

\[ \text{IR } v_{\text{max}} \text{ in cm}^{-1}; 1626 (v_{CN}, \text{ imine}); 1739 (v_{CO}, \text{ ester}); 3382 (v_{OH}, \text{ H-bonded}). \]

\[ ^{1}H \text{ NMR } (\text{CDCl}_3): \delta = 13.55 (bs, 2H, -OH); 8.58 (s, 2H, -CH=N-); 8.14 (d, 2H, J = 8.4 Hz, ArH); 7.46 (d, 2H, J = 8.4 Hz, ArH); 7.32 (t, 1H, J = 7.8 Hz, ArH); 7.03 (d, 2H, J = 7.8 Hz, ArH); 6.97 (d, 4H, J = 8.4 Hz, ArH); 6.90 (s, 2H, ArH); 6.85 (d, 4H, J = 8.4 Hz, ArH); 4.04 (t, 4H, J = 6.6 Hz, -O-CH\textsubscript{2}); 2.42 (s, 3H, Ar-CH\textsubscript{3}); 1.82 (q, 4H, J = 6.9 Hz, -CH\textsubscript{2}-CH\textsubscript{2}-); 1.57-1.26 (m, 52H, -(CH\textsubscript{2})\textsubscript{15}); 0.88 (t, 6H, J = 6.3 Hz, -CH\textsubscript{3}). \]

Elemental analysis calculated for C\textsubscript{63}H\textsubscript{80}O\textsubscript{8}N\textsubscript{2}: C = 76.02%; H = 8.30%; N = 2.81%. Found C = 76.01%; H = 8.29%; N = 2.82%.

N,N'-bis[4-(4-n-octadecyloxybenzoyloxy)-salicylidene]-phenylene-2-methyl-1,3-diamine, 2M-18OH:

2M-18OH was prepared according to the procedure described for 2M-8OH using 4-(4'-n-octadecyloxybenzoyloxy)salicylaldehyde (1.27 g, 2.5 mmol) and 2-methyl-1,3-phenylenediamine (0.15 g, 1.25 mmol). Yield: 0.87 g, (63%).

\[ \text{IR } v_{\text{max}} \text{ in cm}^{-1}; 1627 (v_{CN}, \text{ imine}); 1738 (v_{CO}, \text{ ester}); 3441 (v_{OH}, \text{ H-bonded}). \]

\[ ^{1}H \text{ NMR } (\text{CDCl}_3): \delta = 13.49 (bs, 2H, -OH); 8.55 (s, 2H, -CH=N-); 8.15 (d, 2H, J = 8.8 Hz, ArH); 7.43 (d, 2H, J = 8.1 Hz, ArH); 7.31 (t, 1H, J = 8.1 Hz, ArH); 7.03 (d, 2H, J = 8.4 Hz, ArH); 6.95 (d, 4H, J = 8.6 Hz, ArH); 6.91 (s, 2H, ArH); 6.82 (d, 4H, J = 8.1 Hz, ArH); 4.01 (t, 4H, J = 6.6 Hz, -O-CH\textsubscript{2}); 2.40 (s, 3H, Ar-CH\textsubscript{3}); 1.80 (q, 4H, J = 6.6 Hz, -CH\textsubscript{2}-CH\textsubscript{2}-); 1.51-1.26 (m, 52H, -(CH\textsubscript{2})\textsubscript{15}); 0.90 (t, 6H, J = 6.9 Hz, -CH\textsubscript{3}). \]

Elemental analysis calculated for C\textsubscript{71}H\textsubscript{98}O\textsubscript{8}N\textsubscript{2}: C = 77.00%; H = 8.92%; N = 2.53%. Found C = 77.04%; H = 8.94%; N = 2.50%.
3.2.16. N,N'-bis[4-(4-n-alkyloxybenzoyloxy)benzylidene]-phenylene-4-fluoro-1,3-diamines, 4F-nH, (Scheme 16):

![Chemical Structure](image)

Scheme 16

**N,N'-bis[4-(4-n-octyloxybenzoyloxy)benzylidene]-phenylene-4-fluoro-1,3-diamine, 4F-8H:**

An ethanolic solution (20ml) of 4-(4'-n-octyloxybenzoyloxy)benzaldehyde (0.88 g, 2.5 mmol) was added to an ethanolic solution of 4-fluoro-1,3-phenylene diamine (0.15 g, 1.25 mmol), Scheme 16. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3h to yield the Schiff's base N,N'-bis[4-(4'-n-octyloxybenzoyloxy)-benzylidene]-phenylene-4-fluoro-1,3-diamine. The precipitate of 4F-8H was collected by filtration and recrystallized several times from absolute ethanol to give pure compound. Yield: 0.57g, (58%).

**IR v**<sub>max</sub> **in cm**<sup>−1</sup>: 1629 (ν<sub>ν=ν</sub>, imine); 1730 (ν<sub>c=ν</sub>, ester).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 300MHz) δ = 8.55 & 8.50 (s, 2H, -CH=N-); 8.13 (d, 4H, J = 7.5Hz, ArH); 8.00 (d, 4H, J = 9.4Hz, ArH); 7.95 (d, 1H, J = 9.1 Hz, ArH); 7.35 (d, 4H, J = 8.4Hz, ArH); 7.18 (d, 1H, J = 2.1 Hz, ArH); 7.03 (d, 1H, J = 8.7 Hz, ArH); 6.95 (d, 4H, J = 7.5 Hz, ArH); 4.15 (t, 4H, J = 6.2 Hz, -O-CH₂-); 1.80 (q, 4H, J = 6.2 Hz, CH₂-CH₂-); 1.52-1.25 (m, 20H, -(CH₂)₅-); 0.88 (t, 6H, J = 6.2Hz, -CH₃).

**Elemental analysis** calculated for C₅₀H₅₅N₂O₆F: C = 75.18; H = 6.89; N = 3.50. Found: C = 75.01; H = 6.69; N = 3.48.

**N,N'-bis[4-(4-n-decyloxybenzoyloxy)benzylidene]-phenylene-4-fluoro-1,3-diamine, 4F-10H:**
4F-10H was prepared following to the procedure described for 4F-8H using 4-(4'-n-decyloxybenzoyloxy)benzaldehyde (0.95 g, 2.5 mmol) and 4-fluoro-1,3-phenylene diamine (0.15 g, 1.25 mmol). Yield: 0.65 g, (61%).

IR $\nu_{\text{max}}$ in cm$^{-1}$: 1628 ($\nu_{\text{C=O}}$ imine); 1730 ($\nu_{\text{C=O}}$ ester).

$^1$H NMR (CDCl$_3$, 300MHz) $\delta = 8.59$ & 8.51 (s, 2H, -CH=N-); 8.15 (d, 4H, J = 7.5Hz, ArH); 8.00 (d, 4H, J = 9.3Hz, ArH); 7.97 (d, 1H, J = 9.1Hz, ArH); 7.34 (d, 4H, J = 8.1Hz, ArH); 7.18 (d, 1H, J = 2.1 Hz, ArH); 7.09 (d, 1H, J = 8.7 Hz, ArH); 6.98 (d, 4H, J = 7.5 Hz, ArH); 4.05 (t, 4H, J = 6.0 Hz, -O-CH$_2$-); 1.81 (q, 4H, J = 6.6 Hz, -CH$_2$-); 1.55-1.27 (m, 28H, -(CH$_2$)$_7$-); 0.88 (t, 6H, J = 6.3Hz, -CH$_3$).

Elemental analysis calculated for C$_{54}$H$_{63}$N$_2$O$_6$F: C = 75.87; H = 7.37; N = 3.27. Found: C = 75.76; H = 7.21; N = 3.19.

N,N'-bis[4-(4-n-dodecyloxybenzoyloxy)benzylidene]-phenylene-4-fluoro-1,3-diamine, 4F-12H

4F-12H was prepared following to the procedure described for 4F-8H using 4-(4'-n-dodecyloxybenzoyloxy)benzaldehyde (1.02 g, 2.5 mmol) and 4-fluoro-1,3-phenylene diamine (0.15 g, 1.25 mmol). Yield: 0.74 g, (66%).

IR $\nu_{\text{max}}$ in cm$^{-1}$: 1733 ($\nu_{\text{C=O}}$ ester); 1628 ($\nu_{\text{C=O}}$ imine).

$^1$H NMR (CDCl$_3$, 300MHz) $\delta = 8.59$ & 8.50 (s, 2H, -CH=N-); 8.16 (d, 4H, J = 8.2Hz, ArH); 7.99 (d, 4H, J = 8.9Hz, ArH); 7.93 (d, 1H, J = 9.1Hz, ArH); 7.36 (d, 4H, J = 8.2Hz, ArH); 7.12 (d, 1H, J = 2.3 Hz, ArH); 6.99 (d, 1H, J = 8.8 Hz, ArH); 6.96 (d, 4H, J = 8.0 Hz, ArH); 4.06 (t, 4H, J = 6.0 Hz, -O-CH$_2$-); 1.83 (q, 4H, J = 6.6 Hz, -CH$_2$-); 1.55-1.27 (m, 36H, -(CH$_2$)$_9$-); 0.88 (t, 6H, J = 6.6Hz, -CH$_3$).

Elemental analysis calculated for C$_{58}$H$_{71}$N$_2$O$_6$F: C = 76.48; H = 7.80; N = 3.07. Found: C = 76.38; H = 7.69; N = 3.04.

N,N'-bis[4-(4-n-tetradecyloxybenzoyloxy)benzylidene]-phenylene-4-fluoro-1,3-diamine, 4F-14H

4F-14H was prepared following to the procedure described for 4F-8H using 4-(4'-n-tetradecyloxybenzoyloxy)benzaldehyde (1.09 g, 2.5 mmol) and 4-fluoro-1,3-phenylene diamine (0.15 g, 1.25 mmol). Yield: 0.76 g, (63%).

IR $\nu_{\text{max}}$ in cm$^{-1}$: 1730 ($\nu_{\text{C=O}}$ ester), 1629 ($\nu_{\text{C=O}}$ imine).

$^1$H NMR (CDCl$_3$, 300MHz) $\delta = 8.59$ & 8.51 (s, 2H, -CH=N-); 8.15 (d, 4H, J = 7.5Hz, ArH); 8.01 (d, 4H, J = 9.3Hz, ArH); 7.96 (d, 1H, J = 9.6 Hz, ArH); 7.35 (d,
4H, J = 8.4 Hz, ArH); 7.07 (d, 1H, J = 2.5 Hz, ArH); 7.02 (d, 1H, J = 8.4 Hz, ArH); 6.98 (d, 4H, J = 7.5 Hz, ArH); 4.05 (t, 4H, J = 6.0 Hz, -O-CH$_2$-); 1.81 (q, 4H, J = 6.6 Hz, -CH$_2$-CH$_2$-); 1.55-1.28 (m, 44H, -(CH$_2$)$_{44}$-); 0.88 (t, 6H, J = 6.3 Hz, -CH$_3$).

**Elemental analysis** calculated for C$_{62}$H$_{79}$N$_2$O$_{16}$F: C = 77.01; H = 8.17; N = 2.89. Found: C = 76.96; H = 8.16; N = 2.87.

N,N'-bis[4-(4-n-hexadecyloxybenzoyloxy)benzylidene]-phenylene-4-fluoro-1,3-diamine, 4F-16H

4F-16H was prepared following to the procedure described for 4F-8H using 4-(4'-n-hexadecyloxybenzoyloxy)benzaldehyde (1.16 g, 2.5 mmol) and 4-fluoro-1,3-phenylene diamine (0.15 g, 1.25 mmol). Yield: 0.76 g, (60%) 

IR $v_{max}$ in cm$^{-1}$: 1733 (vC=O, ester); 1625 (vC=N, imine).

$^1$H NMR (CDCl$_3$, 300MHz) δ = 8.59 & 8.50 (s, 2H, -CH=N-); 8.15 (d, 4H, J = 8.7 Hz, ArH); 8.08 (d, 4H, J = 8.4 Hz, ArH); 7.97 (d, 1H, J = 8.4 Hz, ArH); 7.36 (d, 4H, J = 8.8 Hz, ArH); 7.12 (d, 1H, J = 2.8 Hz, ArH); 6.99 (d, 1H, J = 8.5 Hz, ArH); 6.96 (d, 4H, J = 8.2 Hz, ArH); 4.05 (t, 4H, J = 6.3 Hz, -O-CH$_2$-); 1.82 (q, 4H, J = 6.9 Hz, -CH$_2$-CH$_2$-); 1.55-1.26 (m, 56H, -(CH$_2$)$_{56}$-); 0.88 (t, 6H, J = 6.6 Hz, -CH$_3$).

**Elemental analysis** calculated for C$_{66}$H$_{87}$N$_2$O$_{12}$F: C = 77.49; H = 8.51; N = 2.73. Found: C = 77.45; H = 8.46; N = 2.68.

### 3.2.17. N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-phenylene-1,3-diamine (10OHHH), Scheme 17:

![Scheme 17](image-url)

-82-
N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-phenylene-1,3-diamine (10OH):

An ethanolic solution (20 ml) of 4-(4'-n-decyloxybenzoyloxy)salicylaldehyde (0.99 g, 2.5 mmol) was added to an ethanolic solution of m-phenylene diamine (0.13 g, 1.25 mmol) as shown in Scheme 17. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff's base N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-phenylene-1,3-diamine. The precipitate was collected by filtration from the hot solution and recrystallised several times from absolute ethanol to give a pure compound. Yield: 0.77 g, (72%).

IR νmax in cm⁻¹: 1625 (νC=N, imine); 1736 (νC=O, ester); 3443 (νOH, H-bonded).

¹H NMR (CDCl₃): δ = 8.39 (s, 2H, -CH=N-); 8.17 (d, 4H, J = 8.7 Hz, ArH); 7.95 (d, 2H, J = 8.7 Hz, ArH); 7.35 (d, 4H, J = 8.7 Hz, ArH); 6.98 (d, 1H, J = 9.3, ArH); 6.52 (d, 2H, J = 2.1 Hz, ArH); 6.49-6.48 (m, 3H, ArH); 6.16 (d, 2H, J = 8.4 Hz, ArH); 4.05 (t, 4H, J = 6.6 Hz, -O-CH₂); 1.82 (q, 4H, J = 6.6 Hz, -CH₂- CH₂-); 1.54-1.26 (m, 28H, -(CH₂)₇); 0.88 (t, 6H, J = 6.6 Hz, -CH₃).

Elemental analysis calculated for C₅₄H₆₄O₈N₂: C = 74.63%; H = 7.42%; N = 3.22%. Found C = 74.61%; H = 7.44%; N = 3.21%.

3.2.18. N,N'-bis[4-(4'-n-decyloxybenzoyloxy)salicylidene]-phenylene-4-methyl-1,3-diamine, 4M-10OH, (Scheme 18):

![Scheme 18](image-url)
N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-4-methyl-1,3-phenylene-
diamine, 4M-10OH:

An ethanolic solution (20 ml) of 4-(4'-n-decyloxybenzoyloxy)salicylaldehyde (0.99 g, 2.5 mmol) was added to an ethanolic solution of 4-methyl-1,3-phenylene diamine (0.15 g, 1.25 mmol) as shown in scheme 18. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff’s base N,N’-
Bis[4-(4-n-decyloxybenzoyloxy)-salicylidene]-phenylene-4-methyl-1,3-diamine.
The precipitate was collected by filtration from the hot solution and recrystallised several times from absolute ethanol to give a pure compound. Yield: 0.72 g, (66%).

IR \nu_{\text{max}} \text{ in cm}^{-1}: 1618 (\nu_{C=N}, \text{imine}); 1731 (\nu_{C=O}, \text{ester}); 3426 (\nu_{OH}, \text{H-bonded}).

1H NMR (CDCl3): \delta = 13.59 and 13.54 (bs, 2H, -OH); 8.67 and 8.63 (s, 2H, -CH=N-); 8.13 (d, 4H, J = 7.8 Hz, ArH); 8.11 (d, 2H, J = 8.4 Hz, ArH); 7.46 (d, 1H, J = 8.4 Hz, ArH); 7.30 (d, 2H, J = 8.4, ArH); 6.13 (d, 2H, J = 8.0 Hz, ArH); 7.04 (d, 1H, J = 8.4 Hz, ArH); 6.88 (d, 1H, J = 2.8 Hz, ArH); 6.81 (d, 4H, J = 8.4 Hz, ArH); 4.03 (t, 4H, J = 6.8 Hz, -O-CH2); 2.40 (s, 3H, Ar-CH3); 1.80 (q, 4H, J = 6.8 Hz, -CH2- CH2-); 1.55-1.25 (m, 28H, -(CH2)7-); 0.86 (t, 6H, J = 6.4 Hz, -CH3).

Elemental analysis calculated for C_{55}H_{66}O_{8}N_{2}: C = 74.80%; H = 7.53%; N = 3.17%.
Found C = 74.79%; H = 7.54%; N = 3.19%.

3.2.19. N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-phenylene-
4-chloro-1,3- -diamine, 4Cl-10OH, Scheme 19:
N,N'-bis[4-(4-n-decylbenzoyloxy)salicylidene]-phenylene-4-chloro-1,3-diamine 4Cl-10OH:

An ethanolic solution (20 ml) of 4-(4'-n-decylbenzoyloxy)salicylaldehyde (0.99 g, 2.5 mmol) was added to an ethanolic solution of 4-chloro-1,3-phenylene diamine (0.17 g, 1.25 mmol), Scheme 19. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff’s base N,N'-Bis[4-(4-n-decylbenzoyloxy)salicylidene]-phenylene-4-chloro-1,3-diamine. The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure compound. Yield: 0.74 g, (66%).

IR ν<sub>max</sub> in cm<sup>-1</sup>; 1617 (ν<sub>c=N</sub>, imine); 1727 (ν<sub>νO</sub>, ester); 3485 (ν<sub>OH</sub>, H-bonded);

<sup>1</sup>HNMR(CDC<sub>3</sub>): δ = 13.41 (bs, 2H, -OH); 8.69 (s, 2H, -CH=N-); 8.13 (d, 4H, J = 8.7 Hz, ArH); 8.08 (d, 2H, J = 8.4 Hz, ArH); 7.47 (d, 1H, J = 7.6 Hz, ArH); 7.44 (d, 2H, J = 8.7 Hz, ArH); 7.20 (d, 1H, J = 2.1 Hz, ArH); 6.97 (d, 1H, J = 8.4 Hz, ArH); 6.90 (d, 2H, J = 2.3 Hz, ArH); 6.85 (d, 4H, J = 8.1 Hz, ArH); 4.04 (t, 4H, J = 6.3 Hz, -O-CH<sub>2</sub>); 1.82 (q, 4H, J = 6.6 Hz, -CH<sub>2</sub>-CH<sub>2</sub>-); 1.54-1.26 (m, 28H, -(CH<sub>2</sub>)<sub>7</sub>-); 0.88 (t, 6H, J = 6.6 Hz, -CH<sub>3</sub>).

Elemental analysis calculated for C<sub>54</sub>H<sub>50</sub>O<sub>8</sub>N<sub>2</sub>C: C = 71.78%; H = 7.03%; N = 3.10%. Found C = 71.77%; H = 7.00%; N = 3.12%.

3.2.20. N,N'-bis[4-(4-n-decylbenzoyloxy)salicylidene]-phenylene-4-nitro-1,3-diamine 4N-10OH, Scheme 20:

Scheme 20
N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-phenylene-4-nitro-1,3-diamine 4N-10OH:

An ethanolic solution (20 ml) of 4-(4'-n-decyloxybenzoyloxy)salicylaldehyde (0.99 g, 2.5 mmol) was added to an ethanolic solution of 4-nitro-1,3-phenylene diamine (0.19 g, 1.25 mmol) as shown in Scheme 20. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff’s base N,N'-bis[4-(4-n-decyloxybenzoyloxy)-salicylidene]-phenylene-4-nitro-1,3-diamine. The precipitate was collected by filtration from the hot solution and recrystallised several times from absolute ethanol to give a pure compound. Yield: 0.63 g, (56%).

IR $v_{max}$ in cm$^{-1}$: 1672 ($\nu_{C=\text{N}, \text{imine}}$); 1734 ($\nu_{C=\text{O}, \text{ester}}$); 3365 ($\nu_{\text{OH}, \text{H-bonded}}$).

$^1$H NMR (CDCl$_3$): $\delta = 12.89$ (bs, 2H, -OH); 8.60 (s, 2H, -CH=N); 8.19 (d, 4H, J = 9.1 Hz, ArH); 8.12 (d, 1H, J = 8.7 Hz, ArH); 7.44 (d, 1H, J = 8.4 Hz, ArH); 6.97 (d, 1H, J = 8.7 Hz, ArH); 6.89 (d, 2H, J = 8.4 Hz, ArH); 6.86 (d, 4H, J = 8.4 Hz, ArH); 6.61 (d, 2H, J = 7.5 Hz, ArH); 6.18 (d, 2H, J = 2.1 Hz, ArH); 4.85 (t, 4H, J = 6.3 Hz, -O-CH$_2$); 1.82 (q, 4H, J = 6.6 Hz, -CH$_2$-CH$_2$); 1.54-1.24 (m, 28H, -(CH$_2$)$_7$); 0.88 (t, 6H, J = 6.6 Hz, -CH$_3$).

Elemental analysis calculated for C$_{54}$H$_{63}$O$_{10}$N$_3$: C = 70.95%; H = 6.95%; N = 4.60%. Found C = 70.94%; H = 6.94%; N = 4.58%.

3.2.21. N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-3,5-diamino benzoic-acid, 5Ba-10OH, Scheme 21:
N,N'-bis[4-(4-n-decyloxybenzoyloxy)salicylidene]-3,5-diaminobenzoic acid, 5Ba10OH:

An ethanolic solution (20 ml) of 4-(4'-n-decyloxybenzoyloxy)salicylaldehyde (0.99 g, 2.5 mmol) was added to an ethanolic solution of 3,5-diaminobenzoic acid (0.19 g, 1.25 mmol) as shown in Scheme 21. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff's base N,N'-bis[4-(4'-n-decyloxybenzoyloxy)salicylidene]-3,5-diaminobenzoic acid. The precipitate was collected by filtration from the hot solution and recrystallised several times from absolute ethanol to give a pure compound. Yield: 0.69 g, (61%).

IR $\nu_{\text{max}}$ in cm$^{-1}$: 1620 ($\nu_{\text{C=N, imine}}$); 1730 ($\nu_{\text{C=O, ester}}$); 3365 ($\nu_{\text{OH, H-bonded}}$).

$^1$H NMR (CDCl$_3$): $\delta = 8.74$ (s, 2H, -CH=N-); 8.13 (d, 4H, $J = 8.7$ Hz, ArH); 7.94 (d, 2H, $J = 8.7$ Hz, ArH); 7.49 (d, 1H, $J = 2.4$ Hz, ArH); 7.45 (d, 2H, $J = 8.7$ Hz, ArH); 6.97 (d, 4H, $J = 8.4$ Hz, ArH); 6.92 (d, 2H, $J = 2.1$ Hz, ArH); 6.87 (d, 2H, $J = 8.4$ Hz, ArH); 4.85 (t, 4H, $J = 6.3$ Hz, -O-CH$_2$); 1.82 (q, 4H, $J = 6.6$ Hz, -CH$_2$-CH$_2$-); 1.48-1.26 (m, 28H, -(CH$_2$)$_7$-); 0.88 (t, 6H, $J = 6.6$ Hz, -CH$_3$).

Elemental analysis calculated for $C_{55}H_{64}O_{10}N_2$: $C = 72.35\%$; $H = 7.06\%$; $N = 3.07\%$. Found $C = 72.34\%$; $H = 7.04\%$; $N = 3.08\%$.

3.2.22.N,N'-bis[2-hydroxy-5-(4'-n-dodecyloxyphenylazo)benzylidene]-4-nitro-1,3-phenylenediamine, 134NPDO12, Scheme 22:
N,N'-bis[[2-hydroxy-5-(4'-n-dodecyloxyphenyIazo)benzylidene]-4-nitro-1,3-phenylenediamine, 134NPDO12:

3-(4-n-dodecyloxyphenyIazo)salicylaldehyde (1.02g, 2.5 mmol) was dissolved in minimum volume of absolute alcohol. 4-nitro-1,3-phenylenediamine (0.19 g, 1.25 mmol) were also dissolved in absolute ethanol. Then both of these are mixed together in presence of 2-3 drops of glacial acetic acid and refluxed for 3 h. The reaction mixture was then cooled and filtered. The precipitate thus obtained in hot condition was dried and recrystallized from absolute ethanol. Yield: 0.18 g, 40%.

**IR** $\nu_{\text{max}}$ in cm$^{-1}$: 1480 ($\nu_{\text{N-N \, azo}}$), 1638 ($\nu_{\text{C=N \, imine}}$), 3483 ($\nu_{\text{O-H \, H-bonded}}$).

**$^1$H NMR** (CDCl$_3$, 300 MHz): $\delta$ = 13.00 (s, 2H, -OH); 8.71 (s, 2H, -CH=N); 8.21 (d, 1H, J = 9.1 Hz, ArH); 8.06 (d, 2H, J = 2.2 Hz, ArH); 8.03 (d, 1H, J = 2.3 Hz, ArH); 8.02 (d, 1H, J = 7.8 Hz, ArH); 8.01 (d, 1H, J = 8.0 Hz, ArH); 7.74 (d, 4H, J = 8.5 Hz, ArH); 7.02 (d, 4H, J = 9.0 Hz, ArH); 6.64 (d, 2H, J = 8.6 Hz, ArH); 4.00 (t, 4H, J = 6.5 Hz, -O-CH$_2$); 1.60 (q, 4H, J = 6.8 Hz, -CH$_2$-CH$_2$-); 1.53-1.20 (m, 36H, -(CH$_2$)$_9$-); 0.80 (t, 3H, J = 6.8 Hz, -CH$_3$).

**Elemental analysis** calculated for C$_{58}$H$_{71}$N$_7$O$_5$: C = 71.69%; H = 7.63%; N = 10.45%. Found C = 71.68%; H = 7.62%; N = 10.43%.

3.2.23. [3-(N-4-(4'-n-alkyloxybenzoyloxy)salicylidene)-amino-phenyl]-[4-(N-4-(4'-n-alkyloxybenzoyloxy)-salicylidene)-amino]-benzoate], 34-nOH-6, Scheme 23:

![Scheme 23](image-url)
[3-(N-4-(4'-n-decyl-4'-oxybenzoylbenzoxyloxy)salicylidene)-aminophenyl]-[4-(N-4-(4'-n-decyl-4'-oxybenzoylbenzoxyloxy)salicylidene)-amino]-benzoate 34-1OH-6:

To a slurry of 4-(4'-n-decyl-4'-oxybenzoylbenzoxyloxy)salicylaldehyde (0.99 g, 2.5 mmol) and 3-aminophenol-4-aminobenzoate (0.28 g, 1.25 mmol) in ethanol (60 ml), a catalytic amount of acetic acid was added. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff's base [3-(N-4-(4'-n-decyl-4'-oxybenzoylbenzoxyloxy)salicylidene)-aminophenyl]-[4-(N-4-(4-n-decyl-4'-oxybenzoylbenzoxyloxy)salicylidene)-amino]-benzoate]. The precipitate was collected by filtration from the hot solution and recrystallised several times from absolute ethanol to give a pure compound of bright yellow crystals. Yield: 0.90 g, (74%).

\[ \text{IR } \nu_{\text{max}} \text{ in cm}^{-1} : 1625 (\nu_{\text{CH}=\text{N}}, \text{ imine}); 1728 (\nu_{\text{C}=\text{O}}, \text{ ester}), 3434 (\nu_{\text{O}-\text{H}}, \text{ H-bonded}). \]

\[ ^1\text{H NMR (CDCl}_3, 300 MHz) : \delta = 13.33 \& 13.17 (s, 2H, -OH); 8.68 \& 8.66 (s, 2H, -CH=\text{N}-); 8.28 (d, 4H, J = 8.1 Hz, ArH); 8.13 (d, 2H, J = 7.5 Hz, ArH); 7.61 (t, 1H, J = 8.4 Hz, ArH); 7.48 (d, 2H, J = 8.1 Hz, ArH); 7.40 (d, 4H, J = 8.4 Hz, ArH); 7.20 (d, 2H, J = 8.1 Hz, ArH); 6.97 (d, 2H, J = 7.5 Hz, ArH); 6.93-6.90 (m, 3H, ArH); 6.85 (d, 2H, J = 8.1 Hz, ArH); 4.04 (t, 4H, J = 6.2 Hz, -O-\text{CH}_2-); 1.82 (q, 4H, J = 6.6 Hz, -CH_2-CH_2-); 1.55-1.26 (m, 36H, -(CH_2)_9-); 0.88 (t, 6H, J = 6.6 Hz, -CH_3). \]

Elemental analysis calculated for C_{61}H_{68}N_2O_{10}: C = 74.07%; H = 6.93%; N = 2.83%. Found C = 74.02%; H = 6.91%; N = 2.81%.

[3-(N-4-(4'-n-dodecyl-decyl-4'-oxybenzoylbenzoxyloxy)salicylidene)-aminophenyl]-[4-(N-4-(4'-n-dodecyl-decyl-4'-oxybenzoylbenzoxyloxy)salicylidene)-amino]-benzoate 34-12OH-6:

34-12OH-6 was prepared according to the procedure described for 34-1OH-6 using 4-(4'-n-dodecyl-decyl-4'-oxybenzoylbenzoxyloxy)salicylaldehyde (1.07 g, 2.5 mmol) and 3-aminophenol-4-aminobenzoate (0.28 g, 1.25 mmol). Yield: 0.91 g, (70%).

\[ \text{IR } \nu_{\text{max}} \text{ in cm}^{-1} : 1623 (\nu_{\text{CH}=\text{N}}, \text{ imine}); 1731 (\nu_{\text{C}=\text{O}}, \text{ ester}), 3438 (\nu_{\text{O}-\text{H}}, \text{ H-bonded}). \]

\[ ^1\text{H NMR (CDCl}_3, 300 MHz) : \delta = 13.29 \& 13.15 (s, 2H, -OH); 8.66 \& 8.63 (s, 2H, -CH=\text{N}-); 8.26 (d, 4H, J = 8.1 Hz, ArH); 8.11 (d, 2H, J = 8.7 Hz, ArH); 7.60 (t, 1H, J = 8.1 Hz, ArH); 7.47 (d, 2H, J = 8.4 Hz, ArH); 7.39 (d, 4H, J = 8.7 Hz, ArH); 7.21 (d, 2H, J = 8.1 Hz, ArH); 6.96 (d, 2H, J = 7.2 Hz, ArH); 6.93-6.90 (m, 3H, ArH); 6.84 (d, 2H, J = 8.1 Hz, ArH); 4.04 (t, 4H, J = 6.6 Hz, -O-\text{CH}_2-); 1.82 (q, 4H, J = 6.2 Hz, -CH_2-CH_2-); 1.55-1.25 (m, 36H, -(CH_2)_9-); 0.87 (t, 6H, J = 6.6 Hz, -CH_3). \]

Elemental analysis calculated for C_{65}H_{76}N_2O_{10}: C = 74.69%; H = 7.33%; N = 2.68%. Found C = 74.70%; H = 7.35%; N = 2.66%. 

-89-
[3-(N-4-(4'-n-tetradecyloxybenzoyloxy)salicylidene)-aminophenyl]-[4-(N-4-(4'-n-tetradecyloxybenzoyloxy)salicylidene)-amino]-benzoate 34-I4OH-6:

34-I4OH-6 was prepared according to the procedure described for 34-I0OH-6 using 4-(4'-n-tetradecyloxybenzoyloxy)salicylaldehyde (1.13 g, 2.5 mmol) and 3-aminophenol-4-aminobenzoate (0.28g, 1.25 mmol). Yield: 1.01 g, (74%).

IR \( \nu_{\text{max}} \) in cm\(^{-1}\): 1625 (\( \nu \text{CH}=\text{N}, \text{imine} \)); 1726 (\( \nu \text{C}=\text{O}, \text{ester} \)), 3435 (\( \nu \text{O}=\text{H}, \text{H-bonded} \)).

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \( \delta = 13.33 \& 13.17 \) (s, 2H, -OH); 8.68 \& 8.66 (s, 2H, -CH=\text{N}); 8.28 (d, 4H, \( J = 8.4 \) Hz, ArH); 8.13 (d, 2H, \( J = 7.2 \) Hz, ArH); 7.60 (t, 1H, \( J = 8.1 \) Hz, ArH); 7.48 (d, 2H, \( J = 8.4 \) Hz, ArH); 7.39 (d, 4H, \( J = 8.4 \) Hz, ArH); 7.20 (d, 2H, \( J = 7.2 \) Hz, ArH); 6.97 (d, 2H, \( J = 7.5 \) Hz, ArH); 6.93-6.90 (m, 3H, ArH); 6.85 (d, 2H, \( J = 7.2 \) Hz, ArH); 4.04 (t, 4H, \( J = 6.6 \) Hz, -O-CH\(_2\)-); 1.82 (q, 4H, \( J = 6.2 \) Hz, -CH\(_2\)-CH\(_2\)-); 1.54-1.25 (m, 44H, -(CH\(_2\))\(_n\)-); 0.88 (t, 6H, \( J = 6.6 \) Hz, -CH\(_3\)).

Elemental analysis calculated for C\(_{69}\)H\(_{84}\)N\(_2\)O\(_{10}\): C = 75.24\%; H = 7.69\%; N = 2.54\%.

Found C = 75.22\%; H = 7.70\%; N = 2.51\%.

3.2.24. [4-(N-4-(4'-n-alkyloxybenzoyloxy)salicylidene)-aminophenyl]-[3-(N-4-(4'-n-alkyloxybenzoyloxy)salicylidene)-amino]-benzoate, 43-nOH-6, Scheme 24:

[4-(N-4-(4'-n-decyloxybenzoyloxy)salicylidene)-aminophenyl]-[3-(N-4-(4'-n-decyloxybenzoyloxy)salicylidene)-amino]-benzoate 43-I0OH-6:

To a slurry of 4-(4'-n-decyloxybenzoyloxy)salicylaldehyde (0.99g, 2.5 mmol) and 4-aminophenol-3-aminobenzoate (0.28g, 1.25 mmol) in ethanol (60ml), a catalytic
amount of acetic acid was added. The mixture was refluxed with a few drops of
glacial acetic acid as catalyst for 3 hours to yield the Schiff’s base [3-(N-4-(4′-n-
decyloxybenzoyloxy)salicylidene)-aminophenyl]-[4-(N-4-(4′-n-decyloxybenzoyloxy )-salicylidene)-amino]-benzoate]. The precipitate was collected by filtration from the
hot solution and recrystallised several times from absolute ethanol to give a pure
compound of bright yellow crystals. Yield: 0.88 g, (72%).

\[ \text{IR } \nu_{\text{max}} \text{ in cm}^{-1}: 1627 (\nu_{\text{C=H}}, \text{ imine}); 1728 (\nu_{\text{C=O}}, \text{ ester}), 3445 (\nu_{\text{O-H}}, \text{ H-bonded}). \]

\[ ^1H \text{ NMR (CDCl}_3, 300 MHz): \delta = 13.44 & 13.27 (s, 2H, -OH); 8.70 & 8.65 (s, 2H, -CH=N-); 8.19 (d, 4H, J = 8.7 Hz, ArH); 8.15 (d, 1H, J = 8.7 Hz, ArH); 7.61 (d, 1H, J = 8.1 Hz, ArH); 7.47 (t, 1H, J = 8.7 Hz, ArH); 7.35 (d, 2H, J = 8.1 Hz, ArH); 7.31 (d, 4H, J = 8.1 Hz, ArH); 7.00 (d, 2H, J = 8.1 Hz, ArH); 6.95-6.88 (m, 5H, ArH); 6.85 (d, 2H, J = 8.7 Hz, ArH); 4.01 (t, 4H, J = 6.2 Hz, -O-CH\textsubscript{2}-); 1.85 (q, 4H, J = 6.6 Hz, -CH\textsubscript{2}-CH\textsubscript{2}-); 1.56-1.26 (m, 28H, -(CH\textsubscript{2})\textsubscript{7}-); 0.89 (t, 6H, J = 6.3 Hz, -CH\textsubscript{3}). \]

Elemental analysis calculated for C\textsubscript{65}H\textsubscript{68}N\textsubscript{2}O\textsubscript{10}: C = 74.07%; H = 6.93%; N = 2.83%.

\[ \text{Found C = 74.06%; H = 6.95%; N = 2.81%.} \]

\[ [4-(N-4-(4′-n-dodecyloxybenzoyloxy)salicylidene)-aminophenyl]-[3-(N-4-(4′-n-
decyloxybenzoyloxy)salicylidene)-amino]-benzoate] 43-720H-6: \]

\[ 43-720H-6 \text{ was prepared according to the procedure described for 43-10OH-6 using} \]

4-(4′-n-dodecyloxybenzoyloxy)salicylaldehyde (1.07 g, 2.5 mmol) and 4-amino-
phenol-3-aminobenzoate (0.28g, 1.25 mmol). Yield: 0.88 g, (68%).

\[ \text{IR } \nu_{\text{max}} \text{ in cm}^{-1}: 1623 (\nu_{\text{C=H}}, \text{ imine}); 1731 (\nu_{\text{C=O}}, \text{ ester}), 3444 (\nu_{\text{O-H}}, \text{ H-bonded}). \]

\[ ^1H \text{ NMR (CDCl}_3, 300 MHz): \delta = 13.43 & 13.29 (s, 2H, -OH); 8.72 & 8.66 (s, 2H, -CH=N-); 8.17 (d, 4H, J = 8.4 Hz, ArH); 8.13 (d, 1H, J = 8.4 Hz, ArH); 7.60 (d, 1H, J = 7.2 Hz, ArH); 7.45 (t, 1H, J = 8.1 Hz, ArH); 7.36 (d, 2H, J = 8.4 Hz, ArH); 7.30 (d, 4H, J = 8.7 Hz, ArH); 7.00 (d, 2H, J = 8.1 Hz, ArH); 6.96-6.89 (m, 5H, ArH); 6.85 (d, 2H, J = 8.1 Hz, ArH); 4.04 (t, 4H, J = 6.6 Hz, -O-CH\textsubscript{2}-); 1.82 (q, 4H, J = 6.6 Hz, -CH\textsubscript{2}-CH\textsubscript{2}-); 1.55-1.26 (m, 36H, -(CH\textsubscript{2})\textsubscript{9}-); 0.89 (t, 6H, J = 6.3 Hz, -CH\textsubscript{3}). \]

Elemental analysis calculated for C\textsubscript{61}H\textsubscript{68}N\textsubscript{2}O\textsubscript{10}: C = 74.69%; H = 7.33%; N = 2.68%.

\[ \text{Found C = 74.70%; H = 7.35%; N = 2.66%.} \]

\[ [4-(N-4-(4′-n-tetradecyloxybenzoyloxy)salicylidene)-aminophenyl]-[3-(N-4-(4′-n-
tetradecyloxybenzoyloxy)salicylidene)-amino]-benzoate] 43-12OH-6: \]
43-140H-6 was prepared according to the procedure described for 43-10OH-6 using 4-(4'-n-tetradecyloxybenzoyloxy)salicylaldehyde (1.13 g, 2.5 mmol) and 4-amino-phenol-3-aminobenzoate (0.28g, 1.25 mmol). Yield: 1.03 g, (75%)

**IR** $v_{\text{max}}$ in cm$^{-1}$: 1627 ($\nu_{\text{C-H=N}}$, imine); 1728 ($\nu_{\text{C=O}}$, ester), 3445 ($\nu_{\text{O-H}}$, H-bonded).

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 13.44 \& 13.29$ (s, 2H, -OH); $8.73 \& 8.65$ (s, 2H, -CH=N-); 8.15 (d, 4H, $J = 8.7$ Hz, ArH); 8.13 (d, 1H, $J = 8.1$ Hz, ArH); 7.59 (d, 1H, $J = 6.4$ Hz, ArH); 7.46 (t, 1H, $J = 8.7$ Hz, ArH); 7.37 (d, 2H, $J = 8.7$ Hz, ArH); 7.31 (d, 4H, $J = 7.2$ Hz, ArH); 6.99 (d, 2H, $J = 8.4$ Hz, ArH); 6.96-6.90 (m, 5H, ArH); 6.86 (d, 2H, $J = 6.3$ Hz, -O-CH$_2$-); 1.82 (q, 4H, $J = 6.6$ Hz, -CH$_2$-CH$_2$-); 1.55-1.27 (m, 44H, -(CH$_2$)$_n$-); 0.88 (t, 6H, $J = 6.0$ Hz, -CH$_3$).

**Elemental analysis** calculated for C$_{46}$H$_{34}$N$_2$O$_{10}$: C = 75.24%; H = 7.69%; N = 2.54%. Found C = 75.22%; H = 7.68%; N = 2.55%.

### 3.2.25. N,N'-bis[4-(4'-n-alkyloxybenzoyloxy)benzylidene]-4,4'-diaminobenzophenone, BP-nH-6, Scheme 25:

![Scheme 25](image)

$N,N'$-Bis[4-(4-n-dodecyloxybenzoyloxy)benzylidene]-4,4'-diaminobenzophenone, BP-12H-6

To a slurry of 4-(4'-n-dodecyloxybenzoyloxy)benzaldehyde (1.02 g, 2.5 mmol) and 4,4'-diaminobenzophenone (0.26 g, 1.25 mmol) in ethanol (60ml), a catalytic amount of acetic acid was added. The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff’s base $N,N'$-Bis[4-(4-n-
octyloxybenzoyloxy)-benzylidene]-4,4'-diaminobenzophenone. The precipitate was collected by filtration from the hot solution and recrystallised several times from absolute ethanol to give a pure compound of bright yellow crystals. Yield: 0.84 g, (68%).

IR $v_{\text{max}}$ in cm$^{-1}$: 1628 ($\nu_{\text{C=CH=N}}$, imine); 1736 ($\nu_{\text{C=O}}$, ester);

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 8.45 (s, 2H, $\text{-CH=N-}$); 8.12 (d, 4H, $J = 8.7$ Hz, ArH); 8.00 (d, 4H, $J = 8.1$ Hz, ArH); 7.92 (d, 4H, $J = 8.4$ Hz, ArH); 7.33 (d, 4H, $J = 8.1$ Hz, ArH); 7.28 (d, 4H, $J = 8.1$ Hz, ArH); 6.97 (d, 4H, $J = 8.7$ Hz, ArH); 4.04 (t, 4H, $J = 6.2$ Hz, $\text{-O-CH}_2$-); 1.88 (q, 4H, $J = 7.2$ Hz, $\text{-CH}_2$-$\text{CH}_2$-); 1.57-1.25 (m, 36H, $\text{-\{(CH}_2\}_9\text{-}$); 0.90 (t, 6H, $J = 6.6$ Hz, $\text{-CH}_3$).

Elemental analysis calculated for C$_{65}$H$_{76}$N$_2$O$_7$: C = 78.28%; H = 7.68%; N = 2.81%. Found C = 78.25%; H = 7.69%; N = 2.80%.

N,N'-Bis[4-(4-n-tetradecyloxybenzoyloxy)benzylidene]-4,4'-diaminobenzophenone, BP-14H-6:

BP-14H-6 was prepared according to the procedure described for BP-12H-6 using 4-(4'-n-tetradecyloxybenzoyloxy)benzaldehyde (1.09 g, 2.5 mmol) and 4,4'-diamino benzophenone (0.26 g, 1.25 mmol). Yield: 0.86 g, (66%)

IR $v_{\text{max}}$ in cm$^{-1}$: 1623 ($\nu_{\text{C=CH=N}}$, imine); 1739 ($\nu_{\text{C=O}}$, ester).

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 8.49 (s, 2H, $\text{-CH=N-}$); 8.15 (d, 4H, $J = 8.7$ Hz, ArH); 8.00 (d, 4H, $J = 8.1$ Hz, ArH); 7.90 (d, 4H, $J = 8.4$ Hz, ArH); 7.36 (d, 4H, $J = 8.4$ Hz, ArH); 7.30 (d, 4H, $J = 8.7$ Hz, ArH); 6.98 (d, 4H, $J = 8.7$ Hz, ArH); 4.05 (t, 4H, $J = 6.3$ Hz, $\text{-O-CH}_2$-); 1.83 (q, 4H, $J = 7.2$ Hz, $\text{-CH}_2$-$\text{CH}_2$-); 1.55-1.26 (m, 44H, $\text{-\{(CH}_2\}_9\text{-}$); 0.88 (t, 6H, $J = 6.9$ Hz, $\text{-CH}_3$).

Elemental analysis calculated for C$_{69}$H$_{84}$N$_2$O$_7$: C = 78.67%; H = 8.04%; N = 2.66%. Found C = 78.65%; H = 8.05%; N = 2.63%.

N,N'-Bis[4-(4-n-hexadecyloxybenzoyloxy)benzylidene]-4,4'-diaminobenzophenone, BP-16H-6:

BP-16H-6 was prepared according to the procedure described for BP-12H-6 using 4-(4'-n-hexadecyloxybenzoyloxy)benzaldehyde (1.16 g, 2.5 mmol) and 4,4'-diamino benzophenone (0.26 g, 1.25 mmol). Yield: 0.97 g, (70%)

IR $v_{\text{max}}$ in cm$^{-1}$: 1626 ($\nu_{\text{C=CH=N}}$, imine); 1739 ($\nu_{\text{C=O}}$, ester).
\(^1\)H NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta = 8.50 \text{ (s, 2H, -CH=N-); 8.14 \text{ (d, 4H, J = 8.0 Hz, ArH); 7.99 \text{ (d, 4H, J = 8.4 Hz, ArH); 7.90 \text{ (d, 4H, J = 8.1 Hz, ArH); 7.35 \text{ (d, 4H, J = 8.4 Hz, ArH); 7.31 \text{ (d, 4H, J = 8.4 Hz, ArH); 6.97 \text{ (d, 4H, J = 8.1 Hz, ArH); 4.04 \text{ (t, 4H, J = 6.6 Hz, -O-CH}_{2}\text{-}); 1.81 \text{ (q, 4H, J = 6.2 Hz, -CH}_{2}\text{-CH}_{2}\text{-); 1.56-1.23 \text{ (m, 52H, -(CH}_{2}\text{)}_{13}\text{-); 0.87 \text{ (t, 6H, J = 6.3 Hz, -CH}_{3}\text{).}}}

Elemental analysis calculated for C\textsubscript{73}H\textsubscript{92}N\textsubscript{2}O\textsubscript{7}: C = 79.02; H = 8.36%; N = 2.52%. Found C = 79.06%; H = 8.35%; N = 2.53%.
3.3. Experimental techniques:

3.3.1. Infrared Spectroscopy:

IR spectra were recorded on a Perkin-Elmer L 120-000A spectrometer ($\nu_{\text{max}}$ in cm$^{-1}$) on KBr disks. The representative IR spectra of the final compound from each series are provided in Appendix I [9, 10].

3.3.2. $^1$H NMR:

The $^1$H nuclear magnetic resonance spectra were recorded either on JEOL FX-90Q multinuclear spectrometer or Bruker DPX-300 spectrometer in CDCl$_3$ (chemical shift in $\delta$) solution with TMS as standard. The representative $^1$H NMR spectra of the final compound from each series are provided in Appendix I [9-11].

3.3.3. CHN analysis:

The elemental analysis was carried out using PE2400 elemental analyzer.

3.3.4. UV-visible spectroscopy:

UV visible absorption spectra of the compounds in CHCl$_3$ at different concentrations were recorded on a Shimadzu UV-1601PC spectrophotometer ($\lambda_{\text{max}}$ in nm).

3.3.5. Fluorescence Studies:

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

3.3.6. 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 [12, 13]. In thin liquid crystal sample cells placed between two crossed polarizers under an optical microscope, various textures and birefringence colours will be observed. 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 behaviour 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 optiphot-2-pol) attached with Instec
hot and cold stage HCS302, with STC200 temperature controller configured for
HCS302. The accuracies in temperatures are 0.1°C. The textures were recorded using
photo micrographic equipment attached with the polarizing microscope.

3.3.7. Differential Scanning Calorimetry:

The thermal behaviour of the compounds was examined using Differential Scanning
Calorimetry [14]. 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 (shown in Figure 3.1). 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 (shown in Figure 3.1). 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.

![Figure 3.1: Schematic illustration of DSC Instrument](image)

The representative DSC thermograms of the final compound from each sries are
provided in Appendix I.

3.3.8. 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 low, \(2d \sin \theta = n \lambda\) where \(d\) is wavelength of electron density function in the media, \(\theta\) is diffraction angle, \(\lambda\) is wavelength of x-ray and integer number \(n\).

Unoriented powdered sample was used for the variable temperature X-ray diffraction analyses. In situ desired temperature experiment were carried out by placing the sample in 1 mm diameter quartz capillary tubes and data were collected using a point detector mounted on a Huber four-circle goniometer at Cu K(\(\alpha\)) radiation from a 8 kW Rigaku UltraX-18 rotating anode x-ray generator(Cu anode, wavelength = 1.54 Å). High sensitivity scintillation detector (Crismatec) was used as detector while SPEC software was used for data collection in a Linux PC. Optics, 4 sets of motorized and 1 set of manual vacuum slits for adjusting resolution, diffracted beam bent graphite monochromator, and beam size at sample was 1 x 1 mm\(^2\) (adjustable to 1x3 mm\(^2\)). The heating/cooling rate was 10 °C/min., followed by data collection at the specified temperature.

**Figure 3.2:** A custom-built wide angle x-ray spectrometer

### 3.3.9. Fluorescence Confocal Polarizing Microscopy (FCPM):

Fluorescence confocal polarizing microscopy (FCPM) studies were made by using Olympus Fluoview FV5-PSU confocal microscope, modified by a linear polarizer \(P\) that sets polarization \(P_e \parallel P\) of the excitation beam and the polarisation \(P_f \parallel P\) of the detected fluorescent light (see Figure 3.3) [15, 16]. The excitation beam (488 nm, Ar laser) is focused by an objective into a small submicron volume in the cell. We use the 10X dry objective of numerical aperture \(N A = 0.3\). The emitted fluorescent light
from this volume is detected by a photomultiplier tube (PMT 1) in the spectral region 510-550 nm. The direction of polarization of the incident laser beam is rotated by 90° using a TN cell in order to get vertical polarization. The focus beam scan the sample both in the horizontal plane, located at a fixed depth and in the vertical plane. The intensity of the fluorescence is measured and stored in the computer memory as a thin optical slice. The thickness of the slice is defined by the resolution of the FCPM. The resolution is about 1 μm for slabs of small birefringence and thickness 20 μm or less. Simultaneously with the FCPM image, a usual transmitted PM texture of the sample is recorded by measuring the intensity of light (spectral region 585-610 nm PMT 2) under crossed polarizer and analyzer condition.

**Figure 3.3:** a) Confocal Microscope with detector Unit b) Scheme of FCPM (details in text)[15, 16]

### 3.3.10. Polarization reversal current technique:

The electro-optical studies were carried out using standard triangular-wave method [17, 18]. The triangular waves were generated employing a 20 MHz Function Waveform Generator (Agilent, model 33220A), fitted with a Trek Model 601E amplifier. The current was measured across a 10 k Ω resistor and the waveforms recorded using an Agilent Oscilloscope (54642A). The d.c. field experiments were carried out using a Regulated Dual d.c. Power Supply (ITL; TSD-150 1). Commercially obtained ITO cells (Instec, USA) were used for these experiments. Polarization reversal current curve for the SmCP phase of the synthesized compounds were obtained on applying triangular wave voltage. The spontaneous polarization value was also measured. The optical textures of the phase before and after the application of an external electric field were recorded.
References: