Fluorine containing nonsymmetrical five-ring achiral banana-shaped compounds with columnar and synclinic antiferroelectric layered phases

Channabasaveshwar V. Yelamaggad*, Indudhara Swamy Shashikala, Uma S. Hiremath, Guangxun Liao§, Antal Jakli§, Doddamane S. Shankar Rao Subbarao Krishna Prasad and Quan Li§

*Centre for Liquid Crystal Research, Jalalalli, Bangalore-560013, India
§Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA

Experimental

Synthetic and molecular structural characterization details

The procedure for the synthesis of 2,3-difluoro1-decyloxybenzene (4)

A solution of 2,3-difluorobenzene (1 g, 7.6 m.mol, 1 equiv.), 1-bromodecane (1.2 g, 9.12 m.mol, 1.2 equiv.), potassium carbonate (4.1 g, 30.4 m.mol, 4 equiv.) was taken in dry DMF (20 ml) solvent. The resulting mixture was stirred for 16 h under dry nitrogen atmosphere at 80 °C. The reaction was quenched by adding ice water (300 ml) and the crude product was extracted with dichloromethane (2 × 200 ml). The combined organic extracts was washed with water (200 ml) followed by brine and dried over anhydrous Na2SO4. Evaporation of solvent furnished the crude product, which was further purified by column chromatography using silica gel (100-200 mesh). The column was initially eluted with hexanes to remove the unreac ted 1-bromodecane and then with 5% EtOAc-hexanes to get the pure product. Yield: 90%. A colourless liquid; \( R_f = 0.55 \) (10% EtOAc-hexanes); IR (neat) \( \nu_{\text{max}} \) in cm\(^{-1}\) 2928, 2857, 1727, 1514, 1289 and 1074; \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta \) 6.99-6.84 (m, 1H, Ar), 6.77-6.69 (m, 2H, Ar), 4.02 (t, \( J = 6.6 \) Hz, 2H, 1 × OCH\(_2\)), 1.98-1.71 (m, 2H, 1 × CH\(_2\)), 1.69-1.00 (m, 14H, 7 × CH\(_2\)) and 0.88 (t, \( J = 6.88 \) Hz, 3H, 1 × CH\(_3\)); Elemental analysis: Calculated (Found)%: C 71.08 (71.08) ; H 8.95 (8.46) for C\(_{16}\)H\(_{24}\)F\(_2\)O.

*Author for correspondence; Tel: 91-80-28381119; Fax: 91-80-28382044; e-mail: yelamaggad@yahoo.com
The procedure for the synthesis of 2,3-difluoro-4-decyloxybenzoic acid (3)

*n*-Butyllithium (0.28 ml, 0.44 m.mol, 1.2 equiv. in hexanes) was added dropwise to a stirred, cooled (-40 °C) solution of 2,3-difluoro1-decyloxybenzene (4) (100 mg, 0.37 m.mol, 1.0 equiv.) in dry tetrahydrofuran (10 ml) under nitrogen atmosphere. The resulting solution was kept at ca. -40 °C for 2 h before being poured onto stirred slurry of crushed solid CO₂ and dry tetrahydrofuran (5 ml) and the reaction mixture was allowed to warm up to room temperature. The solution was acidified with 3N hydrochloric acid. The product was extracted with dichloromethane (2 × 25 ml), the combined organic extracts was washed with water (2 × 25 ml), brine (2 × 25 ml) and dried over anhydrous Na₂SO₄. The crude compound was purified by repeated recrystallizations with a mixture of dichloromethane-hexanes (1:10) to obtain a constant isotropic temperature. Yield: 95%. A white solid; R f = 0.12 (20% EtOAc-hexanes); m.p. 111-112 °C; (KBr Pellet) ν_max in cm⁻¹ 2918, 2848, 1690, 1621, 1305 and 1092; ¹H NMR (400MHz, CDCl₃): δ 7.81-7.71 (m, 1H, Ar), 6.82-6.74 (m, 1H, Ar), 4.11 (t, J = 6.6 Hz, 2H, 1 × OCH₂), 1.88-1.78 (m, 2H, 1 × CH₂), 1.47-1.27 (m, 14H, 7 × CH₂) and 0.88 (t, J = 6.6 Hz, 3H, 1 × CH₃); Elemental analysis: Calculated (Found)%: C 64.95 (65.07) ; H 7.69 (7.64) for C₁₇H₂₄F₂O₃.

The procedure for the synthesis of 4-formyl-3-hydroxyphenyl 4-(decyloxy)-2,3-difluorobenzoate (1a)

2,4-dihydroxybenzaldehyde (0.28 mg, 0.73 m.mol, 1 equiv.) and 2,3-difluoro-4-decyloxybenzoic acid (3) (1 g, 0.8 m.mol, 1.1 equiv.) were dissolved in dry dichloromethane (20 ml). To this DCC (0.47 mg, 0.73 m.mol, 1.1 equiv.) and a catalytic amount of DMAP was added and the mixture was stirred at room temperature for about 2 h. The precipitate dicyclohexylurea was filtered off and washed thoroughly with dichloromethane. The combined filtrate was washed with water, brine and dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography using
silica gel (100-200 mesh) and 10% EtOAc-hexanes elution afforded the product. Yield: 80%. A white solid; Rf = 0.30 (10% EtOAc-hexanes); m.p. 101-102 °C; (KBr Pellet) νmax in cm⁻¹ 2915, 2849, 1736, 1475, 1275 and 1084; ¹H NMR (400MHz, CDCl₃): δ 11.25 (s, 1H, 1× OH), 9.89 (s, 1H, 1x CHO), 7.87-7.78 (m, 1H, Ar), 7.62 (d, J = 8.0 Hz, 1H, Ar), 6.95-6.79 (m, 3H, Ar), 4.14 (t, J = 6.6 Hz, 2H, 1 × OCH₂), 1.91-1.80 (m, 2H, 1 × CH₂), 1.50-1.28 (m, 14H, 7 × CH₂) and 0.89 (t, J = 6.0 Hz, 3H, 1 × CH₃); Elemental analysis: Calculated (Found)%: C 67.25 (67.15 ); H 6.32 (6.29) for C₂₄H₂₈F₂O₅.

The preparation of 4-formylphenyl 4-(decyloxy)-2,3-difluorobenzoate (1b)

4-hydroxybenzaldehyde (0.25 g, 2.09 m.mol, 1 equiv.) and 2,3-difluoro-4-decyloxybenzoic acid (3) (1g, 2.30 m.mol, 1.1 equiv.) were dissolved in dry dichloromethane (20 ml). To this DCC (0.47 mg, 2.3 m.mol, 1.1 equiv.) and a catalytic amount of DMAP was added and the mixture was stirred at room temperature for about 2 h. The precipitate dicyclohexylurea was filtered off and washed thoroughly with dichloromethane. The combined filtrate was washed with water, brine and dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography using silica gel (100-200 mesh) and 10% EtOAc-hexanes elution afforded the product. Yield: 80%. A white solid; Rf = 0.30 (10% EtOAc-hexanes); m.p. 65-66 °C; (KBr Pellet) νmax in cm⁻¹ 2917, 2851, 1732, 1625, 1476, 1293 and 1086; ¹H NMR (200MHz, CDCl₃): δ 10.03 (s, 1H, 1× CHO), 7.97 (d, J = 8.5 Hz, 2H, Ar), 7.89-7.80 (m, 1H, Ar), 7.42 (d, J = 8.5 Hz, 2H, Ar), 6.87-6.80 (m, 1H, Ar), 4.14 (t, J = 6.5 Hz, 2H, 1 × OCH₂), 1.91-1.80 (m, 2H, 1 × CH₂), 1.49-1.28 (m, 14H, 7 × CH₂) and 0.89 (t, J = 6.0 Hz, 3H, 1 × CH₃); Elemental analysis: Calculated (Found)%: C 68.88( 69.02 ); H 6.74 (6.49) for C₂₄H₂₈F₂O₅.

The General preparation of 4-((3-(4-(4-(alkoxy)benzoyloxy)benzoyloxy)phenyl imino)methyl)-3-hydroxyphenyl 4-(decyloxy)-2,3-difluorobenzoate (I-6 to I-10)
A mixture of 4-(decyloxy)-2,3-difluorophenyl 4-formyl–3-hydroxybenzoate (1a) (0.18 m.mol, 1.0 equiv.), 4-((3-aminophenoxy)carbonyl)phenyl 4-(alkoxy)benzoate (2a-h) (0.18 m.mol, 1.0 equiv.), absolute ethanol (10 ml) and catalytic amount of acetic acid was refluxed until the yellow solid precipitated out (2 h). The crude product obtained was collected by filtration and repeatedly washed with hot absolute ethanol. It was purified by repeated recrystallization with a mixture of absolute ethanol-dichloromethane (9:1) to get constant isotropic phase transition temperature. Yield: 85-91%.

I-6: A yellow solid; IR (KBr Pellet) \( \nu_{\text{max}} \) in cm\(^{-1} \) 2927, 2856, 1728, 1611, 1477 and 1085; \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta \) 13.36 (s, 1H, 1 x OH), 8.66 (s, 1H, CH=N), 8.29 (d, J = 8.7 Hz, 2H, Ar), 8.16 (d, J = 8.9 Hz, 2H, Ar), 7.86-7.82 (m, 1H, Ar), 7.49 (t, J =8.1 Hz, 1H, Ar), 7.45 (d, J = 8.5 Hz, 1H, Ar), 7.38 (d, J = 8.7 Hz, 2H, Ar), 7.23-7.16 (m, 3H, Ar), 6.99 (d, J = 8.9 Hz, 2H, Ar), 6.91 (d, J = 2.2 Hz, 1H, Ar), 6.86-6.80 (m, 2H, Ar), 4.13 (t, J = 6.5 Hz, 2H, 1 x OCH\(_2\)), 4.06 (t, J = 6.5 Hz, 2H, 1 x OCH\(_2\)), 1.90-1.79 (m, 4H, 2 x CH\(_2\)), 1.48-1.22 (m, 20H, 10 x CH\(_2\)) and 0.88 (t, J = 7.0 Hz, 6H, 2 x CH\(_3\)); MS (FAB\(^+\)): m/z for C\(_{50}\)H\(_{53}\)F\(_2\)NO\(_9\), Calculated: 849.3, Found: 851.3; Elemental analysis: Calculated (Found)%: C 70.66 (70.93) ; H 6.29 (6.20) ; N 1.65 (1.68).

I-7: A yellow solid; IR (KBr Pellet) \( \nu_{\text{max}} \) in cm\(^{-1} \) 2924, 2856, 1732, 1607, 1475 and 1084; \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta \) 13.36 (s, 1H, 1 x OH), 8.66 (s, 1H, CH=N), 8.29 (d, J = 8.8 Hz, 2H, Ar), 8.16 (d, J = 8.9 Hz, 2H, Ar), 7.86-7.81 (m, 1H, Ar), 7.49 (t, J =8.0 Hz, 1H, Ar), 7.45 (d, J = 8.5 Hz, 1H, Ar), 7.39 (d, J = 8.8 Hz, 2H, Ar), 7.22-7.16 (m, 3H, Ar), 6.99 (d, J = 8.9 Hz, 2H, Ar), 6.91 (d, J = 2.0 Hz, 1H, Ar), 6.86-6.80 (m, 2H, Ar), 4.13 (t, J = 6.5 Hz, 2H, 1 x OCH\(_2\)), 4.06 (t, J = 6.5 Hz, 2H, 1 x OCH\(_2\)), 1.88-1.79 (m, 4H, 2 x CH\(_2\)), 1.48-1.22 (m, 20H, 11 x CH\(_2\)) and 0.88 (t, J = 7.0 Hz, 6H, 2 x CH\(_3\)); MS (FAB\(^+\)): m/z for C\(_{51}\)H\(_{55}\)F\(_2\)NO\(_9\), Calculated: 863.4, Found: 865.4; Elemental analysis: Calculated (Found)%: C 70.90 (71.05) ; H 6.42 (6.05) ; N 1.62 (2.00).

I-8: A yellow solid; IR (KBr Pellet) \( \nu_{\text{max}} \) in cm\(^{-1} \) 2922, 2854, 1733, 1603, 1475 and 1082; \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta \) 13.37 (s, 1H, 1 x OH), 8.66 (s, 1H, CH=N), 8.29 (d, J = 8.8 Hz, 2H, Ar), 8.16 (d, J = 8.9 Hz, 2H, Ar), 7.86-7.81 (m, 1H, Ar), 7.49 (t, J =8.0 Hz,
I-9: A yellow solid; IR (KBr Pellet) ν max in cm⁻¹ 2922, 2854, 1733, 1603, 1472 and 1082; ¹H NMR (400MHz, CDCl₃): δ 13.37 (s, 1H, 1 × OH), 8.66 (s, 1H, CH=N), 8.29 (d, J = 8.8 Hz, 2H, Ar), 8.16 (d, J = 8.9 Hz, 2H, Ar), 7.86-7.81 (m, 1H, Ar), 7.49 (t, J = 8.6 Hz, 1H, Ar), 7.45 (d, J = 8.5 Hz, 1H, Ar), 7.39 (d, J = 8.8 Hz, 2H, Ar), 7.22-7.16 (m, 3H, Ar), 6.99 (d, J = 9 Hz, 2H, Ar), 6.91 (d, J = 2.6 Hz, 1H, Ar), 6.86-6.80 (m, 2H, Ar), 4.13 (t, J = 6.5 Hz, 2H, 1 × OCH₂), 4.05 (t, J = 6.5 Hz, 2H, 1 × OCH₂), 1.90-1.79 (m, 4H, 2 × CH₂), 1.48-1.24 (m, 26H, 13 × CH₂) and 0.88 (t, J = 7.0 Hz, 6H, 2 × CH₃); MS (FAB⁺): m/z for C₅₂H₅₇F₂NO₉, Calculated: 877.4, Found: 879.4; Elemental analysis: Calculated (Found)%: C 71.13 (71.20); H 6.54 (6.35); N 1.60 (1.63).

I-10: A yellow solid; IR (KBr Pellet) ν max in cm⁻¹ 2920, 2852, 1731, 1604, 1473, and 1080; ¹H NMR (400MHz, CDCl₃): δ 13.37 (s, 1H, 1 × OH), 8.66 (s, 1H, CH=N), 8.29 (d, J = 8.8 Hz, 2H, Ar), 8.16 (d, J = 8.9 Hz, 2H, Ar), 7.86-7.81 (m, 1H, Ar), 7.49 (t, J = 8.6 Hz, 1H, Ar), 7.45 (d, J = 8.5 Hz, 1H, Ar), 7.39 (d, J = 8.8 Hz, 2H, Ar), 7.22-7.16 (m, 3H, Ar), 6.99 (d, J = 9 Hz, 2H, Ar), 6.91 (d, J = 2.1 Hz, 1H, Ar), 6.86-6.80 (m, 2H, Ar), 4.13 (t, J = 6.5 Hz, 2H, 1 × OCH₂), 4.05 (t, J = 6.5 Hz, 2H, 1 × OCH₂), 1.90-1.79 (m, 4H, 2 × CH₂), 1.48-1.24 (m, 26H, 13 × CH₂) and 0.88 (t, J = 6.7 Hz, 6H, 2 × CH₃); ¹³C NMR (100MHz, CDCl₃): 164.26, 164.25, 163.86, 162.60, 161.29, 155.55, 154.50, 153.27, 153.26, 153.25, 151.76, 150.53, 149.58, 140.40, 133.38, 132.38, 131.79, 130.19, 127.02, 126.64, 122.11, 120.97, 120.11, 119.08, 117.16, 114.44, 112.98, 111.04, 110.55, 108.55, 70.03, 68.40, 31.84, 29.47, 29.24, 29.06, 28.91, 25.94, 25.76, 22.62 and 14.03; MS (FAB⁺): m/z for C₅₄H₆₁F₂NO₉, Calculated: 905.4, Found: 907.2; Elemental analysis: Calculated (Found)%: C 71.58 (71.36); H 6.79 (6.87); N 1.55 (1.66).
I-12: A yellow solid; IR (KBr Pellet) ν<sub>max</sub> in cm<sup>-1</sup> 2920, 2852, 1731, 1605, 1473, 1275, 1165 and 1079; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 13.36 (s, 1H, 1 × OH), 8.66 (s, 1H, CH=N), 8.29 (d, J = 8.8 Hz, 2H, Ar), 8.16 (d, J = 8.8 Hz, 2H, Ar), 7.86-7.81 (m, 1H, Ar), 7.49 (t, J = 8.0 Hz, 1H, Ar), 7.45 (d, J = 8.5 Hz, 1H, Ar), 7.39 (d, J = 8.8 Hz, 2H, Ar), 7.22-7.16 (m, 3H, Ar), 6.99 (d, J = 8.9 Hz, 2H, Ar), 6.91 (d, J = 2.1 Hz, 1H, Ar), 6.86-6.80 (m, 2H, Ar), 4.13 (t, J = 6.5 Hz, 2H, 1 × OCH<sub>2</sub>), 4.05 (t, J = 6.5 Hz, 2H, 1 × OCH<sub>2</sub>), 1.90-1.79 (m, 4H, 2 × CH<sub>2</sub>), 1.48-1.24 (m, 32H, 16 × CH<sub>2</sub>) and 0.88 (t, J = 6.9 Hz, 6H, 2 × CH<sub>3</sub>); MS (FAB<sup>+</sup>): m/z for C<sub>56</sub>H<sub>65</sub>F<sub>2</sub>NO<sub>9</sub>, Calculated: 933.5, Found: 935.5; Elemental analysis: Calculated (Found)%: C 72.00 (71.71) ; H 7.01 (6.60) ; N 1.50 (1.52).

I-20: A yellow solid; IR (KBr Pellet) ν<sub>max</sub> in cm<sup>-1</sup> 2918, 2849, 1732, 1604, 1473, 1272, 1161 and 1071; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 13.37 (s, 1H, 1 × OH), 8.66 (s, 1H, CH=N), 8.29 (d, J = 8.7 Hz, 2H, Ar), 8.16 (d, J = 8.8 Hz, 2H, Ar), 7.86-7.81 (m, 1H, Ar), 7.49 (t, J = 8.0 Hz, 1H, Ar), 7.45 (d, J = 8.5 Hz, 1H, Ar), 7.39 (d, J = 8.8 Hz, 2H, Ar), 7.22-7.16 (m, 3H, Ar), 6.99 (d, J = 8.9 Hz, 2H, Ar), 6.91 (d, J = 2.1 Hz, 1H, Ar), 6.86-6.80 (m, 2H, Ar), 4.13 (t, J = 6.5 Hz, 2H, 1 × OCH<sub>2</sub>), 4.05 (t, J = 6.5 Hz, 2H, 1 × OCH<sub>2</sub>), 1.90-1.79 (m, 4H, 2 × CH<sub>2</sub>), 1.48-1.24 (m, 32H, 16 × CH<sub>2</sub>) and 0.88 (t, J = 6.9 Hz, 6H, 2 × CH<sub>3</sub>); MS (FAB<sup>+</sup>): m/z for C<sub>64</sub>H<sub>81</sub>F<sub>2</sub>NO<sub>9</sub>, Calculated: 1045.6, Found: 1047.5; Elemental analysis: Calculated (Found)%: C 73.47 (73.42) ; H 7.80 (7.59) ; N 1.34 (1.41).

General procedure for 4-((3-(4-(4-(alkoxy)benzoyloxy)benzoyloxy)phenylimino)methyl)phenyl4-(decyloxy)-2,3-difluorobenzoate (II-6 to II-10)

A mixture of 4-(decyloxy)-2,3-difluorophenyl 4-formylbenzoate (1b) (0.2 m.mol, 1.0 equiv.), 4-((3-aminophenoxy)carbonyl)phenyl 4-(alkoxy)benzoate (2a-h) (0.2 m.mol, 1.0 equiv.), absolute ethanol (10 ml) and catalytic amount of acetic acid was refluxed until the white solid precipitated out (2 h). The crude product obtained was collected by filtration and repeatedly washed with hot absolute ethanol. It was purified by repeated recrystallization with a mixture of absolute ethanol-dichloromethane (9:1) to get constant isotropic phase transition temperature. Yield: 85-91%.
II-6: A white solid; IR (KBr Pellet) $\nu_{\text{max}}$ in cm$^{-1}$ 2923, 1731, 1612, 1515, 1476, 1273, 1168 and 1072; $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.49 (s, 1H, CH=N), 8.29 (d, $J = 8.7$ Hz, 2H, Ar), 8.15 (d, $J = 8.6$ Hz, 2H, Ar), 7.98 (d, $J = 8.6$ Hz, 2H, Ar), 7.87-7.83 (m, 1H, Ar), 7.45 (t, $J = 8.3$ Hz, 1H, Ar), 7.38 (t, $J = 6.2$ Hz, 4H, Ar), 7.12-7.10 (m, 3H, Ar), 6.97 (d, $J = 8.9$ Hz, 2H, Ar), 6.85-6.80 (m, 1H, Ar), 4.13 (t, $J = 6.5$ Hz, 2H, 1$\times$OCH$_2$), 4.05 (t, $J = 6.5$ Hz, 2H, 1$\times$OCH$_2$), 1.86-1.83 (m, 4H, 2$\times$CH$_2$), 1.48-1.28 (m, 20H, 10$\times$CH$_2$) and 0.93-0.87 (m, 6H, 2$\times$CH$_3$); MS (FAB$^+$): m/z for C$_{50}$H$_{53}$F$_2$NO$_8$, Calculated: 833.4, Found: 834.5; Elemental analysis: Calculated (Found)%: C 72.01 (72.38); H 6.41 (5.89); N 1.68 (1.62).

II-7: A white solid; IR (KBr Pellet) $\nu_{\text{max}}$ in cm$^{-1}$ 2919, 1729, 1603, 1475, 1293, 1130, and 1061; $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.50 (s, 1H, CH=N), 8.29 (d, $J = 8.6$ Hz, 2H, Ar), 8.16 (d, $J = 8.8$ Hz, 2H, Ar), 7.98 (d, $J = 8.64$ Hz, 2H, Ar), 7.88-7.83 (m, 1H, Ar), 7.46 (t, $J = 8.3$ Hz, 1H, Ar), 7.37 (t, $J = 8.0$ Hz, 4H, Ar), 7.16-7.10 (m, 3H, Ar), 6.97 (d, $J = 8.76$ Hz, 2H, Ar), 6.85-6.81 (m, 1H, Ar), 4.14 (t, $J = 6.6$ Hz, 2H, 1$\times$OCH$_2$), 4.05 (t, $J = 6.6$ Hz, 2H, 1$\times$OCH$_2$), 1.89-1.83 (m, 4H, 2$\times$CH$_2$), 1.48-1.28 (m, 22H, 11$\times$CH$_2$) and 0.92-0.87 (m, 6H, 2$\times$CH$_3$); MS (FAB$^+$): m/z for C$_{51}$H$_{55}$F$_2$NO$_8$, Calculated: 847.4, Found: 848.6; Elemental analysis: Calculated (Found)%: C 72.24 (72.38); H 6.54 (6.14); N 1.65 (1.68).

II-8: A white solid; IR (KBr Pellet) $\nu_{\text{max}}$ in cm$^{-1}$ 2922, 1730, 1603, 1476, 1293, 1130, and 1060; $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.50 (s, 1H, CH=N), 8.29 (d, $J = 8.68$ Hz, 2H, Ar), 8.16 (d, $J = 8.9$ Hz, 2H, Ar), 7.96 (d, $J = 8.7$ Hz, 2H, Ar), 7.87-7.83 (m, 1H, Ar), 7.47 (t, $J = 8.3$ Hz, 1H, Ar), 7.37 (t, $J = 8.2$ Hz, 4H, Ar), 7.16-7.12 (m, 3H, Ar), 6.99 (d, $J = 8.92$ Hz, 2H, Ar), 6.85-6.81 (m, 1H, Ar), 4.14 (t, $J = 6.5$ Hz, 2H, 1$\times$OCH$_2$), 4.05 (t, $J = 6.6$ Hz, 2H, 1$\times$OCH$_2$), 1.85-1.83 (m, 4H, 2$\times$CH$_2$), 1.48-1.28 (m, 24H, 12$\times$CH$_2$) and 0.91-0.87 (m, 6H, 2$\times$CH$_3$); $^{13}$C NMR (100MHz, CDCl$_3$): 164.34, 164.26, 163.84, 161.56, 159.75, 155.45, 153.20, 153.12, 151.58, 133.88, 132.37, 131.76, 130.13, 129.87, 127.00, 126.86, 122.08, 121.01, 119.06, 118.78, 114.43, 114.11, 111.13, 111.05, 108.57, 70.04, 68.40, 31.83, 31.75, 29.46, 29.23, 29.16, 29.06, 28.92, 25.94, 25.75, 22.60 and 14.01; MS
(FAB\textsuperscript{+}) m/z for C\textsubscript{52}H\textsubscript{57}F\textsubscript{2}NO\textsubscript{8}, Calculated: 861.4, Found: 862.6; Elemental analysis: Calculated (Found)\%: C 72.45 (72.76); H 6.66 (6.44); N 1.62 (1.64).

II-9: A white solid; IR (KBr Pellet) \( \nu_{\text{max}} \) in cm\textsuperscript{-1} 2921, 1731, 1603, 1475, 1295, 1129, and 1061; \(^1\)H NMR (400MHz, CDCl\textsubscript{3}): \( \delta \) 8.50 (s, 1H, CH=N), 8.29 (d, \( J = 8.76 \) Hz, 2H, Ar), 8.16 (d, \( J = 8.9 \) Hz, 2H, Ar), 7.98 (d, \( J = 8.6 \) Hz, 2H, Ar), 7.88-7.83 (m, 1H, Ar), 7.46 (t, \( J = 8.3 \) Hz, 1H, Ar), 7.36 (t, \( J = 9 \) Hz, 4H, Ar), 7.16-7.10 (m, 3H, Ar), 6.98 (d, \( J = 8.96 \) Hz, 2H, Ar), 6.85-6.81 (m, 1H, Ar), 4.14 (t, \( J = 6.5 \) Hz, 2H, 1 \times OCH\textsubscript{2}), 4.05 (t, \( J = 6.5 \) Hz, 2H, 1 \times OCH\textsubscript{2}), 1.48-1.28 (m, 4H, 2 \times CH\textsubscript{2}), 1.90-1.79 (m, 26H, 13 \times CH\textsubscript{2}), and 0.90-0.87 (m, 6H, 2 \times CH\textsubscript{3}); MS (FAB\textsuperscript{+}): m/z for C\textsubscript{53}H\textsubscript{59}F\textsubscript{2}NO\textsubscript{8}, Calculated: 875.4, Found: 877; Elemental analysis: Calculated (Found)\%: C 72.66 (72.90); H 6.79 (6.59); N 1.60 (1.65).

II-10: A white solid; IR (KBr Pellet) \( \nu_{\text{max}} \) in cm\textsuperscript{-1} 2923, 1731, 1612, 1476, 1273, 1168 and 1072; \(^1\)H NMR (400MHz, CDCl\textsubscript{3}): \( \delta \) 8.50 (s, 1H, CH=N), 8.29 (d, \( J = 8.6 \) Hz, 2H, Ar), 8.15 (d, \( J = 8.8 \) Hz, 2H, Ar), 7.98 (d, \( J = 8.6 \) Hz, 2H, Ar), 7.88-7.83 (m, 1H, Ar), 7.48 (t, \( J = 8.4 \) Hz, 1H, Ar), 7.37 (t, \( J = 8.0 \) Hz, 4H, Ar), 7.17-7.10 (m, 3H, Ar), 6.98 (d, \( J = 8.8 \) Hz, 2H, Ar), 6.83-6.79 (m, 1H, Ar), 4.14 (t, \( J = 6.5 \) Hz, 2H, 1 \times OCH\textsubscript{2}), 4.05 (t, \( J = 6.5 \) Hz, 2H, 1 \times OCH\textsubscript{2}), 1.94-1.76 (m, 4H, 2 \times CH\textsubscript{2}), 1.47-1.28 (m, 28H, 14 \times CH\textsubscript{2}), and 0.90-0.87 (m, 6H, 2 \times CH\textsubscript{3}); MS (FAB\textsuperscript{+}): m/z for C\textsubscript{55}H\textsubscript{59}F\textsubscript{2}NO\textsubscript{8}, Calculated: 889.4, Found: 890.8; Elemental analysis: Calculated (Found)\%: C 72.87 (72.97); H 6.91 (6.8); N 1.57 (1.63).

II-12: A white solid; IR (KBr Pellet) \( \nu_{\text{max}} \) in cm\textsuperscript{-1} 2923, 1731, 1612, 1476, 1273, 1168 and 1072; \(^1\)H NMR (400MHz, CDCl\textsubscript{3}): \( \delta \) 8.50 (s, 1H, CH=N), 8.29 (d, \( J = 8.8 \) Hz, 2H, Ar), 8.16 (d, \( J = 8.9 \) Hz, 2H, Ar), 7.98 (d, \( J = 8.7 \) Hz, 2H, Ar), 7.96-7.83 (m, 1H, Ar), 7.46 (t, \( J = 8.6 \) Hz, 1H, Ar), 7.36 (t, \( J = 9.0 \) Hz, 4H, Ar), 7.16-7.10 (m, 3H, Ar), 6.99 (d, \( J = 8.9 \) Hz, 2H, Ar), 6.85-6.80 (m, 1H, Ar), 4.14 (t, \( J = 6.5 \) Hz, 2H, 1 \times OCH\textsubscript{2}), 4.05 (t, \( J = 6.5 \) Hz, 2H, 1 \times OCH\textsubscript{2}), 1.94-1.76 (m, 4H, 2 \times CH\textsubscript{2}), 1.47-1.28 (m, 32H, 16 \times CH\textsubscript{2}), and 0.90-0.87 (m, 6H, 2 \times CH\textsubscript{3}); MS (FAB\textsuperscript{+}): m/z for C\textsubscript{56}H\textsubscript{65}F\textsubscript{2}NO\textsubscript{8}, Calculated: 917.5,
Found: 918.9; Elemental analysis: Calculated (Found)\%: C 73.26 (73.59); H 7.14 (6.74); N 1.53 (1.57).

II-20:
A white solid; IR (KBr Pellet) $\nu_{\text{max}}$ in cm$^{-1}$ 2923, 1731, 1612, 1476, 1273, 1168 and 1072; $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.50 (s, 1H, CH=N), 8.29 (d, $J = 8.7$ Hz, 2H, Ar), 8.16 (d, $J = 8.8$ Hz, 2H, Ar), 7.98 (d, $J = 8.6$ Hz, 2H, Ar), 7.87-7.86 (m, 1H, Ar), 7.46 (t, $J = 8.5$ Hz, 1H, Ar), 7.36 (t, $J = 9.0$ Hz, 4H, Ar), 7.16-7.10 (m, 3H, Ar), 6.98 (d, $J = 8.9$ Hz, 2H, Ar), 6.85-6.83 (m, 1H, Ar), 4.14 (t, $J = 6.6$ Hz, 2H, 1 $\times$ OCH$_2$), 4.05 (t, $J = 6.5$ Hz, 2H, 1 $\times$ OCH$_2$), 1.89-1.79 (m, 4H, 2 $\times$ CH$_2$), 1.48-1.25 (m, 48H, 24 $\times$ CH$_2$), and 0.88-0.87 (m, 6H, 2 $\times$ CH$_3$); MS (FAB$^+$): m/z for C$_{64}$H$_{81}$F$_2$NO$_8$, Calculated: 1029.5, Found: 1030.6; Elemental analysis: Calculated (Found)\%: C 74.61 (74.67); H 7.92 (7.74); N 1.36 (1.42).