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Flexible dimers as dopants for liquid crystal display mixtures with faster relaxation times

K Araya[a], D A Dunmur*[b], M C Grossel [b], G R Luckhurst [b], S E Marchant-Lane [b], and A Sugimura [c]

[a]*Hitachi Research Laboratory, Hitachi Limited, Omika, Hitachi City, Ibaraki 319-1292, Japan*

[b]*School of Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom*

[c]*Department of Information Systems Engineering, Osaka Sangyo University, 3-1-1 Nakagaito, Osaka, 574 Japan*

Supplementary Information
Experimental

The ^{1}H NMR and ^{13}C NMR spectra of compounds dissolved in deuteriated chloroform were recorded by the School of Chemistry NMR Service using a Bruker DPX 400 or Bruker 300 spectrometer. Melting points were measured on an electrothermal melting point apparatus. Electron-impact mass spectra (EIMS) were recorded by the School of Chemistry Mass Spectrometry Service. Thin Layer Chromatography (TLC) was carried out on aluminium-backed Merck Si 60/F_{254} sheets. All the chemicals used were reagent grade and were supplied the by Aldrich Chemical Company.

1,7-bis-(4-fluorophenyl-1-yloxy)heptane, FC7

4-Fluorophenol (13.4×10^{-3}mol, 1.50g) was dissolved in DMF (60ml) and potassium carbonate (7.4g) and sodium iodide (6.69×10^{-4}mol, 0.10g) were added. The mixture was then stirred at ~100°C under N_2 for 2 h. This was then followed by the dropwise addition of 1,7-dibromoheptane (1.72g, 1.14ml, 6.69×10^{-3}mol). The mixture was again stirred under nitrogen for seven days at room temperature. TLC at this stage showed the reaction to be complete (50% DCM in petroleum ether 40/60 eluent). Water (2 x 50ml) was added to the reaction mixture, which was then shaken vigorously, and a solid was recovered by filtration at the pump. The solid was recrystallised from the minimum quantity of hot ethanol (~5ml) to afford white crystals (1.53g, yield 71%, mp = 55.5°C).

^{1}H NMR($CDCl_3$) δ (ppm): 6.97 (m, 4H; $C^{3}H$, $C^{5}H$, $C^{16}H$, $C^{18}H$), 6.85 (m, 4H; $C^{2}H$, $C^{6}H$, $C^{15}H$, $C^{19}H$), 3.93 (t, J=6.5Hz, 4H; $C^{7}H_2$, $C^{13}H_2$), 1.77 (quintet, J=6.5Hz, 4H; $C^{8}H_2$, $C^{12}H_2$), 1.49 (m, 6H; $C^{9}H_2$, $C^{10}H_2$, $C^{11}H_2$).

^{13}C NMR ($CDCl_3$) δ (ppm): 158.7 (C^{4}, C^{17}, $^{1}J_{CF}$ = 238Hz), 155.7 (C^{1}, C^{14}, $^{4}J_{CF}$ = 2.9Hz), 116.2 (C^{3}, C^{5}, C^{16}, C^{18}, $^{2}J_{CF}$ = 23.3Hz), 115.8 (C^{2}, C^{6}, C^{15}, C^{19}, $^{3}J_{CF}$ = 8.7Hz), 68.9 (C^{7}, C^{13}), 29.6 (C^{8}, C^{12}), 29.5 (C^{10}), 26.2 (C^{9}, C^{11}).

EIMS (DCM) m/z: 320.3 ($[M]^+$, 20.8%), 112.0 ($[C_6H_5FO]^+$, 92.0%), 96.2 ($[C_6H_5F]^+$, 13.4%), 95.1 ($[C_6H_7O]^+$, 27.0%), 81.1 ($[C_5H_5O]^+$, 7.2%), 69.1 ($[C_5H_9]^+$, 7.6%), 55.0 ($[C_4H_7]^+$, 100%), 44.1 ($[C_3H_8]^+$, 13.1%), 41.1 ($[C_3H_5]^+$, 23.8%).

1,9-bis-(4-fluorophenyl-1-yloxy)nonane, FC9

The synthetic procedure was identical to that used for FC7 except that hot methanol was used for the recrystallisation. Quantities used were: 4-fluorophenol (1.08g, $9.6x10^{-3}$mol), DMF (40ml), K_2CO_3 (4.8g) and 1,9-dibromononane (1.15g, 0.82ml, $4.0x10^{-3}$mol,). White crystals were obtained (0.98g, yield 70%, mp = 64.5°C).

^{1}H NMR($CDCl_3$) δ (ppm): 6.97(m, 4H; C^3H, C^5H, $C^{18}H$, $C^{20}H$), 6.83 (m, 4H; C^2H, C^6H, $C^{17}H$, $C^{21}H$), 3.92 (t, J=6.6Hz, 4H; C^7H_2, $C^{15}H_2$), 1.77 (quintet, J=6.6Hz, 4H; C^8H_2, $C^{14}H_2$), 1.41 (m, 10H; C^9H_2, $C^{10}H_2$, $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$).

^{13}C NMR ($CDCl_3$) δ (ppm): 158.7 (C^4, C^{19}, $^1J_{CF}$ = 238Hz), 155.2 (C^1, C^{16}, $^4J_{CF}$ = 2.3Hz), 115.8 (C^3, C^5, C^{18}, C^{20}, $^2J_{CF}$ = 23.2Hz), 115.4 (C^2, C^6, C^{17}, C^{21}, $^3J_{CF}$ = 7.9Hz), 68.6 (C^7, C^{15}), 30.9 (C^8, C^{14}), 29.5 (C^{10}, C^{11}, C^{12}), 26.2 (C^9, C^{13}).

EIMS (DCM) m/z: 348.4 ($[M]^+$, 9.3%), 112.0 ($[C_6H_5FO]^+$, 100%), 96.2 ($[C_6H_5F]^+$, 6.4%), 95.2 ($[C_6H_7O]^+$, 22.0%), 81.2 ($[C_5H_5O]^+$, 7.6%), 69.3 ($[C_5H_9]^+$, 35.2%), 55.3 ($[C_4H_7]^+$, 37.2%), 44.2 ($[C_3H_8]^+$, 6.1%), 41.2 ($[C_3H_5]^+$, 25.9%).

HPLC: 99.7%.

1,10-bis-(4-fluorophenyl-1-yloxy)decane, FC10

The synthetic procedure used was identical to that for FC9. Quantities used were: 4-fluorophenol (1.08g, $9.6x10^{-3}$mol), DMF (40ml), K_2CO_3 (4.8g) and 1,10-dibromodecane (1.20g, $4.0x10^{-3}$mol). White crystals were obtained (1.37g, yield 95%: mp = 85°C)

^{1}H NMR($CDCl_3$) δ (ppm): 6.97 (m, 4H; C^3H, C^5H, $C^{19}H$, $C^{21}H$), 6.83 (m, 4H; C^2H, C^6H, $C^{18}H$, $C^{22}H$), 3.91 (t, J=6.6Hz, 4H; C^7H_2, $C^{16}H_2$), 1.77 (quintet, J=6.6Hz, 4H; C^8H_2, $C^{15}H_2$), 1.40 (m, 12H; C^9H_2, $C^{10}H_2$, $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$, $C^{14}H_2$).

^{13}C NMR ($CDCl_3$) δ (ppm): 158.8 (C^4, C^{20}, $^1J_{CF}$ = 237Hz), 155.2 (C^1, C^{17}, $^4J_{CF}$ = 2.3Hz), 115.9 (C^3, C^5, C^{19}, C^{21}, $^2J_{CF}$ = 22.6Hz), 115.6 (C^2, C^6, C^{18}, C^{22}, $^3J_{CF}$ = 7.9Hz), 68.7 (C^7, C^{16}), 31.1 (C^8, C^{15}), 29.5 (C^{10}, C^{11}, C^{12}, C^{13}), 26.2 (C^9, C^{14}).

EIMS (DCM) m/z: 362.5 ($[M]^+$, 8.4%), 112.2 ($[C_6H_5FO]^+$, 100%), 96.2 ($[C_6H_5F]^+$, 10.0%), 95.2 ($[C_6H_7O]^+$, 17.1%), 81.3 ($[C_5H_5O]^+$, 6.3%), 69.3 ($[C_5H_9]^+$, 17.6%), 55.3 ($[C_4H_7]^+$, 35.0%), 44.2 ($[C_3H_8]^+$, 16.4%), 41.2 ($[C_3H_5]^+$, 22.7%).

HPLC: 100%.

1,9-bis-(4-trifluoromethylphenyl-1-yloxy)nonane, CF3C9

The synthetic procedure was identical to that used for FC9. Quantities used were: 4-trifluoromethylphenol (1.56g, $9.6x10^{-3}$mol), DMF (40ml), K_2CO_3 (4.8g) and 1,9-dibromononane (1.15g, 0.82ml, $4.0x10^{-3}$mol). A white solid was obtained (1.46g, yield 81%, mp = 43.5°C).

^{1}H NMR($CDCl_3$) δ (ppm): 7.55(broad doublet, J=8.8Hz, 4H; C^3H, C^5H, $C^{18}H$, $C^{20}H$,), 6.95 (broad doublet, J=8.1Hz, 4H; C^2H, C^6H, $C^{17}H$, $C^{21}H$), 4.00 (t, J=6.6Hz, 4H; C^7H_2, $C^{15}H_2$), 1.80 (quintet, J=6.6Hz, 4H; C^8H_2, $C^{14}H_2$), 1.43 (m, 10H; C^9H_2, $C^{10}H_2$, $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$).

^{13}C NMR ($CDCl_3$) δ (ppm): 161.7 (C^1, C^{16}), 127.0 (C^3, C^5, C^{18}, C^{20}), 126.9 (C^4, C^{19}), 122.8 (C^{22}, C^{23}), 114.5 (C^2, C^6, C^{17}, C^{21}), 68.3 (C^7, C^{15}), 29.6 (s; C^8, C^{14}), 29.4 (C^{10}, C^{11}, C^{12}), 26.1 (C^9, C^{13}).

EIMS (DCM) m/z: 448.0 ($[M]^+$, 13.0%), 175.2 ($[C_8H_6F_3O]^+$, 15.9%), 162.2 ($[C_7H_5F_3O]^+$, 52.2%), 95.2 ($[C_6H_7O]^+$, 25.5%), 81.2 ($[C_5H_5O]^+$, 19.4%), 69.3 ($[CF_3]^+$, $[C_5H_9]^+$, 100%), 55.3 ($[C_4H_7]^+$, 91.4%), 44.2 ($[C_3H_8]^+$, 30.4%), 41.2 ($[C_3H_5]^+$, 57.1%).
HPLC: 99.2%.

1,10-bis-(4-trifluoromethylphenyl-1-yloxy)decane, CF3C10

The procedure was identical to that used for FC9. Quantities used were: 4-trifluoromethylphenol (1.56g, $9.6x10^{-3}$mol), DMF (40ml), K_2CO_3 (4.8g) and 1,10-dibromodecane (1.20 g, $4.0x10^{-3}$mol). A white solid was obtained (1.20g, yield 65%, mp = 62.5°C).
^{1}H NMR($CDCl_3$) δ (ppm): 7.55(broad doublet, J=8.8Hz, 4H; C^3H, C^5H, $C^{18}H$, $C^{20}H$), 6.95 (broad doublet, J=8.1Hz, 4H; C^2H, C^6H, $C^{17}H$, $C^{21}H$), 4.00 (t, J=6.6Hz, 4H; C^7H_2, $C^{16}H_2$), 1.82 (quintet, J=6.62Hz, 4H; C^8H_2, $C^{15}H_2$), 1.40 (m, 12H; C^9H_2, $C^{10}H_2$, $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$, $C^{14}H_2$).
^{13}C NMR ($CDCl_3$) δ (ppm): 161.7 (C^1, C^{17}), 127.0 (C^3, C^5, C^{19}, C^{21}), 126.9 (C^4, C^{20}), 122.5 (C^{23}, C^{24}), 114.5 (C^2, C^6, C^{18}, C^{22}), 68.3 (C^7, C^{16}), 31.1 (C^8, C^{15}), 29.4 (C^{10}, C^{11}, C^{12}, C^{13}), 26.1 (C^9, C^{14}).
EIMS (DCM) m/z: 462.4 ($[M]^+$, 15.5%), 175.2 ($[C_8H_6F_3O]^+$, 17.0%), 162.2 ($[C_7H_5F_3O]^+$, 60.4%), 95.2 ($[C_6H_7O]^+$, 21.9%), 81.2 ($[C_5H_5O]^+$, 20.2%), 69.3 ($[CF_3]^+$, $[C_5H_9]^+$, 62.7%), 55.3 ($[C_4H_7]^+$, 100%), 41.2 ($[C_3H_5]^+$, 57.3%).
HPLC: 98.9%.

1,9-bis-(2,3-difluorophenyl-1-yloxy)nonane, 23FC9

The synthetic procedure was identical to that used for FC9 except that column chromatography on silica (0.5% DCM in petroleum ether 40-60) was required for purification. Quantities used were: 2,3-difluorophenol (0.50g, $3.84x10^{-3}$mol), DMF (25ml), K_2CO_3 (3.70g), 1,9-dibromononane (0.55g, 0.39ml, $1.92x10^{-3}$mol) and NaI (0.03g, $1.92x10^{-4}$mol). White crystals were obtained (0.31g, yield 42%, mp = 60.5°C).
^{1}H NMR($CDCl_3$) δ (ppm): 6.88 (m, 2H; C^5H, $C^{20}H$), 6.65 (m, 4H, C^6H, $C^{21}H$, C^4H, $C^{19}H$), 4.01 (t, J = 6.5Hz, 4H; C^7H_2, $C^{15}H_2$), 1.74 (quintet, J = 6.8Hz, 4H; C^8H_2, $C^{14}H_2$), 1.30 (m, 10H, C^9H_2, $C^{10}H_2$, $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$).
^{13}C NMR ($CDCl_3$) δ (ppm): 153.1 (C^3, C^{18}), 150.7 (C^1, C^{16}), 140.7 (C^2, C^{17}), 123.2 (C^5, C^{20}), 110.0 (C^6, C^{21}), 109.0 (C^4, C^{19}), 70.0 (C^7, C^{15}), 29.8 (C^8, C^{14}), 29.4 (C^{10}, C^{11}, C^{12}), 26.0 (C^9, C^{13}).
EIMS (DCM) m/z: 384.0 ($[M]^+$, 10.0%), 130.1 ($[C_6H_4F_2O]^+$, 67.7%), 113.1 ($[C_6H_3F_2]^+$, 16.5%), 95.2 ($[C_6H_7O]^+$, 22.0%), 81.2 ($[C_5H_5O]^+$, 15.1%), 69.3 ($[C_5H_9]^+$, 100%), 55.3 ($[C_4H_7]^+$, 92.8%), 41.2 ($[C_3H_5]^+$, 66.0%).

1,7-bis-(2,4-difluorophenyl-1-yloxy)heptane, 24FC7

The procedure was identical to that used for FC7 except that on addition of water an oil was formed which was extracted via an aqueous work-up followed by column chromatography on silica (DCM). Quantities used were: 2,4-difluorophenol (1.84ml, $19.2x10^{-3}$mol), DMF (50ml), K_2CO_3 (4.80g) and 1,7-dibromoheptane (1.64ml, $9.6x10^{-3}$mol,). A colourless liquid was obtained. (1.68g, yield 49% a mp = < 15°C).
^{1}H NMR($CDCl_3$) δ (ppm): 6.85 (m, 6H; C^3H, C^5H, C^6H, $C^{16}H$, $C^{18}H$ $C^{19}H$), 4.00 (t, J = 6.4Hz, 4H; C^7H_2, $C^{13}H_2$), 1.82 (quintet, J = 6.6Hz, 4H; C^8H_2, $C^{12}H_2$), 1.50 (m, 6H, C^9H_2, $C^{10}H_2$, $C^{11}H_2$).

^{13}C NMR ($CDCl_3$) δ (ppm): 158.0 (C^4, C^{17}), 154.4 (C^2, C^{15}), 143.8 (C^1, C^{14}), 115.7 (C^6, C^{19}), 110.3 (C^5, C^{18}), 104.9 (C^3, C^{16}), 70.3 (C^7, C^{13}), 29.3 (C^8, C^{12}), 29.2 (C^{10}), 26.0 (C^9, C^{11}).

EIMS (DCM) m/z: 356.0 ($[M]^+$, 10.0%), 130.1 ($[C_6H_4F_2O]^+$, 99.8%), 113.1 ($[C_6H_3F_2]^+$, 28.2%), 95.1 ($[C_6H_7O]^+$, 18.1%), 81.1 ($[C_5H_5O]^+$, 32.2%), 69.2 ($[C_5H_9]^+$, 41.0%), 55.1 ($[C_4H_7]^+$, 100%), 41.2 ($[C_3H_5]^+$, 61.2%).

1,8-bis-(2,4-difluorophenyl-1-yloxy)octane, 24FC8

The procedure was identical to that used for FC7. Quantities used were: 2,4-difluorophenol (1.10ml, $11.53x10^{-3}$mol), DMF (60ml), K_2CO_3 (6.40g), 1,8-dibromooctane (1.06ml, $5.77x10^{-3}$mol) and NaI (0.17g, $1.15x10^{-3}$mol,). White crystals were obtained (1.57g, yield 73%, mp = 52°C).

^{1}H NMR($CDCl_3$) δ (ppm): 6.85 (6H, m, C^3H, C^5H, C^6H, C^{17}H, C^{19}H, C^{20}H), 4.00 (t, J = 6.6Hz, 4H; C^7H_2, $C^{14}H_2$), 1.81 (quintet, J = 6.6Hz, 4H; C^8H_2, $C^{13}H_2$), 1.45 (m, 8H; C^9H_2, $C^{10}H_2$ $C^{11}H_2$, $C^{12}H_2$).

^{13}C NMR($CDCl_3$) δ (ppm): 158.0 (C^4, C^{18}), 154.8 (C^2, C^{16}), 151.0 (C^1, C^{15}), 115.6 (C^6, C^{20}), 110.3 (C^5, C^{19}), 104.9 (C^3, C^{17}), 70.3 (C^7, C^{14}), 29.3 (C^8, C^{13}), 25.9 (C^9, C^{10}, C^{11}, C^{12}).

EIMS (DCM) m/z: 370.4 ($[M]^+$, 7.0%), 143.0 ($[C_7H_5F_2O]^+$, 23.4%), 130.0 ($[C_6H_4F_2O]^+$, 80.0%), 113.1 ($[C_6H_3F_2]^+$, 8.9%), 81.2 ($[C_6H_9]^+$, 15.1%), 69.2 ($[C_5H_9]^+$, 100%), 55.0 ($[C_4H_7]^+$, 83.9%), 41.1 ($[C_3H_5]^+$, 70.8%).

1,9-bis-(2,4-difluorophenyl-1-yloxy)nonane, 24FC9

The procedure was identical to that used for 24FC7. Quantities used were: 2,4-difluorophenol (1.84ml, $19.2x10^{-3}$mol), DMF (50ml), K_2CO_3 (4.80g), 1,9-dibromononane (1.95ml, 9.6 $x10^{-3}$mol) and NaI (0.15g, 1.0 $x10^{-3}$mol). A colourless liquid was obtained (1.10g, yield 32%, mp= < 15°C).

^{1}H NMR($CDCl_3$) δ (ppm): 6.85 (m, 6H; C^3H, C^5H, C^6H, C^{18}H, C^{20}H C^{21}H), 4.00 (t, J = 6.6Hz, 4H; C^7H_2, $C^{15}H_2$), 1.81 (quintet, J = 6.6Hz, 4H; C^8H_2, $C^{14}H_2$), 1.42 (m, 10H, C^9H_2, $C^{10}H_2$, $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$).

^{13}C NMR ($CDCl_3$) δ (ppm): 158.0 (C^4, C^{19}), 154.7 (C^2, C^{17}), 151.0 (C^1, C^{16}), 115.7 (C^6, C^{21}), 110.3 (C^5, C^{20}), 104.9 (C^3, C^{18}), 70.4 (C^7, C^{15}), 29.6 (C^8, C^{14}), 29.4 (C^{10}, C^{11}, C^{12}), 26.0 (C^9, C^{13}).

EIMS (DCM) m/z: 384.2 ($[M]^+$, 48.1%), 143.1 ($[C_7H_5F_2O]^+$, 82.1%), 130.1 ($[C_6H_4F_2O]^+$, 100%), 113.1 ($[C_6H_3F_2]^+$, 32.3%), 95.2 ($[C_6H_7O]^+$, 41.6%), 81.2 ($[C_5H_5O]^+$, 34.2%), 69.1 ($[C_5H_9]^+$, 92.9%), 55.1 ($[C_4H_7]^+$, 92.2%), 41.2 ($[C_3H_5]^+$, 75.2%).

1,10-bis-(2,4-difluorophenyl-1-yloxy)decane, 24FC10

The procedure was identical to that used for FC7. Quantities used were: 2,4-difluorophenol (1.10ml, $11.53x10^{-3}$mol), DMF (60ml), K_2CO_3 (6.40g), 1,10-dibromodecane (1.73g, $5.77x10^{-3}$mol) and NaI (0.09g, $5.77x10^{-4}$mol). White crystals were obtained (1.79g, yield 78% mp= 60°C).

^{1}H NMR($CDCl_3$) δ (ppm): 6.85 (m, 6H; C^3H, C^5H, C^6H, C^{19}H, C^{21}H, C^{22}H), 4.00 (t, J = 6.6Hz, 4H; C^7H_2, $C^{16}H_2$), 1.80 (quintet, J = 6.6Hz, 4H; C^8H_2, $C^{15}H_2$), 1.40 (m, 12H; C^9H_2, $C^{10}H_2$ $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$, $C^{14}H_2$).

^{13}C NMR($CDCl_3$) δ (ppm):158.0 (C^4, C^{20}), 154.8 (C^2, C^{18}), 143.9 (C^1, C^{17}), 115.6 (C^6, C^{22}), 110.2 (C^5, C^{21}), 104.9 (C^3, C^{19}), 70.4 (C^7, C^{16}), 29.5 (C^8, C^{15}), 26.0 (C^9, C^{10}, C^{11}, C^{12}, C^{13}, C^{14}).

EIMS (DCM) m/z: 398.2 ($[M]^+$, 11.0%), 143.0 ($[C_7H_5F_2O]^+$, 16.3%), 130.0 ($[C_6H_4F_2O]^+$, 84.3%), 95.1 ($[C_6H_7O]^+$, 14.1%), 81.2 ($[C_6H_9]^+$, 16.8%), 69.2 ($[C_5H_9]^+$, 46.6%), 55.1 ($[C_4H_7]^+$, 100%), 41.1 ($[C_3H_5]^+$, 75.9%).

1,7-bis-(3,4-difluorophenyl-1-yloxy)heptane, 34FC7

The procedure was identical to that used for 24FC7. Quantities used were 3,4-difluorophenol (2.5g, $19.2x10^{-3}$mol), DMF (50ml), K_2CO_3 (4.80g), 1,7-dibromoheptane (1.64ml, $9.6x10^{-3}$mol,). A low melting solid was obtained (1.10g, yield 32%, mp = 28°C).

^{1}H NMR($CDCl_3$) δ (ppm): 7.06 (m, 2H; C^5H, $C^{18}H$), 6.72 (m, 2H; C^6H, $C^{19}H$), 6.59 (m, 2H; C^2H, $C^{15}H$), 3.92 (t, J = 6.4Hz, 4H; C^7H_2, $C^{13}H_2$), 1.80 (quintet, J = 6.6Hz, 4H; C^8H_2, $C^{12}H_2$), 1.50 (m, 6H; C^9H_2, $C^{10}H_2$ $C^{11}H_2$).

^{13}C NMR($CDCl_3$) δ (ppm): 155.4 (C^1, C^{14}), 152.0 (C^3, C^{16}, $^1J_{CF}$ = 233Hz, $^2J_{CF}$ = 13.9Hz), 146.4 (C^4, C^{17}, $^1J_{CF}$ = 285Hz, $^2J_{CF}$ = 12.9Hz), 117.2 (C^5, C^{18}, $^2J_{CF}$ = 18.0Hz), 109.7 (C^6, C^{19}, $^3J_{CF}$ = 12.5Hz, $^4J_{CF}$ = 6.0Hz), 104.1 (C^2, C^{15}, $^2J_{CF}$ = 20.3Hz), 68.7 (C^7, C^{13}), 29.0 (C^8, C^{12}, C^{10}), 25.9 (C^9, C^{11}).

EIMS (DCM) m/z: 356.0 ($[M]^+$, 6.0%), 130.0 ($[C_6H_4F_2O]^+$, 46.5%), 96.1 ($[C_6H_8O]^+$, 10.3%), 81.0 ($[C_6H_9]^+$, 9.8%), 55.0 ($[C_4H_7]^+$, 72.2%), 44.0 ($[C_3H_8]^+$, 100%), 41.1 ($[C_3H_5]^+$, 38.0%).

1,10-bis-(3,4-difluorophenyl-1-yloxy)decane, 34FC10

The procedure was identical to that used for 24FC7. Quantities used were: 3,4-difluorophenol (2.5g, $19.2x10^{-3}$mol,), DMF (50ml), K_2CO_3 (4.80g), 1,10-dibromodecane (2.16ml, $9.6x10^{-3}$mol,). White crystals were obtained (1.79g, yield 47%, mp = 41.5°C).

^{1}H NMR($CDCl_3$) δ (ppm): 7.05 (m, 2H; C^5H, $C^{21}H$), 6.69 (m, 2H; C^6H, $C^{22}H$), 6.58 (m, 2H; C^2H, $C^{18}H$), 3.90 (t, J = 6.6Hz, 4H; C^7H_2, $C^{16}H_2$), 1.77 (quintet, J = 6.6Hz, 4H; C^8H_2, $C^{15}H_2$), 1.40 (m, 12H; C^9H_2, $C^{10}H_2$ $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$ $C^{14}H_2$).

^{13}C NMR($CDCl_3$) δ (ppm): 155.7 (C^1, C^{17}, $^3J_{CF}$ = 9.4Hz), 152.3 (C^3, C^{19}, $^1J_{CF}$ = 233Hz, $^2J_{CF}$ = 13.7Hz), 146.6 (C^4, C^{20}, $^1J_{CF}$ = 239Hz, $^2J_{CF}$ = 12.9Hz), 117.4 (C^5, C^{21}, $^2J_{CF}$ = 18.3Hz), 109.9 (C^6, C^{22}, $^3J_{CF}$ = 8.6Hz, $^4J_{CF}$ = 4.9Hz), 104.1 (C^2, C^{18}, $^2J_{CF}$ = 20.1Hz), 68.9 (C^7, C^{16}), 29.5 (C^8, C^{15}), 25.9 (C^9, C^{10}, C^{11}, C^{12}, C^{13}, C^{14}).

EIMS (DCM) m/z: 398.2 ($[M]^+$, 21.0%), 130.0 ($[C_6H_4F_2O]^+$, 72.3%), 81.2 ($[C_6H_9]^+$, 13.8%), 55.0 ($[C_4H_7]^+$, 100%), 44.0 ($[C_3H_8]^+$, 19.2%), 41.1 ($[C_3H_5]^+$, 76.8%).

1,7-bis-(2,3,4-trifluorophenyl-1-yloxy)heptane, 234FC7

The procedure was identical to FC7 except that column chromatography on silica (50% DCM in petroleum ether 40-60) was used to remove the remaining DMF. ^{1}H NMR showed the presence of monomer (~10%). The product was then reacted with more 2,3,4-trifluorophenol (0.02g, $1.23x10^{-4}$mol,) and potassium carbonate. The 1,7-bis-(2,3,4-trifluorophenyloxy)heptane was isolated by column chromatography (50% DCM in petroleum ether 40-60) as an off-white solid. Quantities used were: 2,3,4-trifluorophenol (0.50g, $3.38x10^{-3}$mol), DMF (20ml), K_2CO_3 (1.68g) and 1,7-dibromoheptane (0.43g, 0.28ml, $1.69x10^{-3}$mol,). White crystals were obtained (0.11g, yield 17%, mp = 45.5°C).

^{1}H NMR($CDCl_3$) δ (ppm): 6.87 (m, 2H; C^5H, $C^{18}H$), 6.65 (m, 2H, C^6H, $C^{19}H$), 4.01 (t, J = 6.4Hz, 4H; C^7H_2, $C^{13}H_2$), 1.83 (quintet, J = 6.4Hz, 4H; C^8H_2, $C^{12}H_2$), 1.50 (m, 6H, C^9H_2, $C^{10}H_2$, $C^{11}H_2$).

EIMS (DCM) m/z: 392.2 ($[M]^+$, 4.5%), 113.1 ($[C_6H_3F_2]^+$, 9.4%), 81.2 ($[C_6H_9]^+$, 12.3%), 69.1 ($[C_5H_9]^+$, 22.1%), 55.0 ($[C_4H_7]^+$, 100%), 41.1 ($[C_3H_5]^+$, 38.8%).

1,9-bis-(2,3,4-trifluorophenyl-1-yloxy)nonane, 234FC9

The procedure was identical to that used for FC7 except that column chromatography (15% DCM in petroleum ether 40-60) was used for purification. Quantities used were: 2,3,4-trifluorophenol (0.50g, $3.38x10^{-3}$mol), DMF (25ml), K_2CO_3 (1.66g) and 1,9-dibromononane (0.47g, 0.33ml, $1.65x10^{-3}$mol). White crystals were obtained (0.17g, yield 25%, mp= 36.5°C).

^{1}H NMR($CDCl_3$) δ (ppm): 6.87 (m, 2H; C^5H, $C^{20}H$), 6.65 (m, 2H, C^6H, $C^{21}H$), 4.01 (t, J = 6.6Hz, 4H; C^7H_2, $C^{15}H_2$), 1.82 (quintet, J = 6.6Hz, 4H; C^8H_2, $C^{14}H_2$), 1.43 (m, 10H, C^9H_2, $C^{10}H_2$, $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$).

^{13}C NMR ($CDCl_3$) δ (ppm): 165.5 (C^1, C^{16}), 145.9 (C^4, C^{19}, ^{1}J = 265Hz), 145.7 (C^5, C^{18}, ^{1}J = 261Hz), 140.7 (C^6, C^{17}), 111.4 (C^5, C^{20}, ^{2}J = 18.4Hz, ^{3}J = 4.8Hz), 109.5 (C^6, C^{21}), 71.6 (C^7, C^{15}), 30.5 (C^8, C^{14}), 30.3 (C^{10}, C^{11}, C^{12}), 27.0 (C^9, C^{13}).

EIMS (DCM) m/z: 420.4 ($[M]^+$, 5%), 161.0 ($[C_7H_4F_3O]^+$, 16.6%), 131.1 ($[C_6H_2F_3]^+$, 12.3%), 81.2 ($[C_6H_9]^+$, 18.5%), 69.2 ($[C_5H_9]^+$, 100%), 55.1 ($[C_4H_7]^+$, 90.8%), 41.1 ($[C_3H_5]^+$, 76.6%).

1,7-bis-(3,4,5-trifluorophenyl-1-yloxy)heptane, 345FC7

The procedure was identical to that used for FC7 except that column chromatography (15% DCM in petroleum ether 40-60) was twice used for purification. Quantities used were: 3,4,5-trifluorophenol (1.00g, $6.75x10^{-3}$mol), DMF (30ml), K_2CO_3 (3.70g), 1,7-dibromoheptane (0.58ml, $3.38x10^{-3}$mol) and NaI (0.05g, $3.38x10^{-4}$mol). A white solid was obtained (0.59g, yield 44%, mp = 59.0°C).

^{1}H NMR($CDCl_3$) δ (ppm): 6.50 (m, 4H; C^2H, C^6H, $C^{15}H$, $C^{19}H$), 3.90 (t, J = 6.4Hz, 4H; C^7H_2, $C^{13}H_2$), 1.68 (quintet, J = 6.4Hz, 4H; C^8H_2, $C^{12}H_2$), 1.45 (m, 6H, C^9H_2, $C^{10}H_2$, $C^{11}H_2$).

^{13}C NMR ($CDCl_3$) δ (ppm): 153.0 (C^1, C^{14}, ^{3}J = 8.7Hz, ^{4}J = 2.9Hz), 151.3 (C^3, C^5, C^{16}, C^{18}, ^{1}J = 248Hz, ^{2}J = 16.5Hz, ^{3}J = 5.8Hz), 134.2 (C^4, C^{17}, ^{1}J = 243Hz), 97.7 (C^2, C^6, C^{15}, C^{19}, ^{2}J = 17.4Hz, ^{3}J = 6.8Hz), 67.4 (C^7, C^{13}), 28.0 (C^8, C^{10}, C^{12}), 24.5 (C^9, C^{11}).

EIMS (DCM) m/z: 392.1 ($[M]^+$, 21.0%), 161.0 ($[C_7H_4F_3O]^+$, 25.0%), 131.0 ($[C_6H_2F_3]^+$, 14.5%), 81.2 ($[C_6H_9]^+$, 12.4%), 69.2 ($[C_5H_9]^+$, 17.4%), 55.1 ($[C_4H_7]^+$, 100%), 41.1 ($[C_3H_5]^+$, 35.1%).

1,9-bis-(3,4,5-trifluorophenyl-1-yloxy)nonane, 345FC9

The procedure was identical to that used for 345FC7. Quantities used were: 3,4,5-trifluorophenol (1.00g, $6.75x10^{-3}$mol,), DMF (50ml), K_2CO_3 (3.70g), 1,9-dibromononane (0.69ml, $3.38x10^{-3}$mol) and NaI (0.05g, $3.38x10^{-4}$mol). A white solid was obtained (0.34g, yield 24%, mp = 49.5°C).

^{1}H NMR($CDCl_3$) δ (ppm): 6.40 (m, 4H; C^2H, C^6H, $C^{17}H$, $C^{21}H$), 3.80 (t, J = 6.4Hz, 4H; C^7H_2, $C^{15}H_2$), 1.68 (quintet, J = 6.4Hz, 4H; C^8H_2, $C^{14}H_2$), 1.33 (m, 10H, C^9H_2, $C^{10}H_2$, $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$).

^{13}C NMR ($CDCl_3$) δ (ppm): 153.1 (C^1, C^{16}, ^{3}J = 8.7Hz, ^{4}J = 2.9Hz), 151.3 (C^3, C^5, C^{18}, C^{20}, ^{1}J = 248Hz, ^{2}J = 16.5Hz, ^{3}J = 5.8Hz), 134.4 (C^4, C^{19}, ^{1}J = 243Hz), 97.7 (C^2, C^6, C^{17}, C^{21}, ^{2}J = 17.4Hz, ^{3}J = 6.8Hz), 67.5 (C^7, C^{15}), 28.0 (C^8, C^{14}), 27.8 (C^{10}, C^{11},C^{12}), 24.5 (C^9, C^{13}).

EIMS (DCM) m/z: 420.1 ($[M]^+$, 13.7%), 161.0 ($[C_7H_4F_3O]^+$, 22.8%), 131.0 ($[C_6H_2F_3]^+$, 12.0%), 81.2 ($[C_6H_9]^+$, 16.5%), 69.2 ($[C_5H_9]^+$, 100%), 55.1 ($[C_4H_7]^+$, 98.5%), 41.1 ($[C_3H_5]^+$, 86.4%).

1,7-bis-(2,3,4,5,6-pentafluorophenyl-1-yloxy)heptane, PFC7

The procedure was identical to that used for FC7 except that column chromatography on silica (10% diethyl ether in petroleum ether 40-60) was used for purification. Quantities used were: 2,3,4,5,6-pentafluorophenol (2.00g, 10.87×10^{-3}mol), DMF (60ml), K_2CO_3 (6.0g), 1,7-dibromoheptane (1.40g, 0.93ml, 5.44×10^{-3}mol) and NaI (0.08g, 5.44×10^{-4}mol). A colourless liquid was obtained (0.82g, yield 33%, mp < 15°C).

^{1}H NMR($CDCl_3$) δ (ppm): 4.08 (t, J = 6.4Hz, 4H; C^7H_2, $C^{13}H_2$), 1.72 (quintet, J = 6.6Hz, 4H; C^8H_2, $C^{12}H_2$), 1.40 (m, 6H, C^9H_2, $C^{10}H_2$, $C^{11}H_2$).

^{13}C NMR ($CDCl_3$) δ (ppm): 75.7 (C^7, C^{13}), 29.7 (C^8, C^{12}), 28.8 (C^{10}), 25.4 (C^9, C^{11}).

EIMS (DCM) m/z: 464.0 ($[M]^+$, 1.0%), 184.1 ($[C_6HF_5O]^+$, 6.2%), 97.1 ($[C_6H_9O]^+$, 26.6%), 69.1 ($[C_5H_9]^+$, 9.8%), 55.1 ($[C_4H_7]^+$, 100%), 44.1 ($[C_3H_8]^+$, 8.4%), 41.1 ($[C_3H_5]^+$, 23.6%).

1,9-bis-(2,3,4,5,6-pentafluorophenyl-1-yloxy)nonane, PFC9

The procedure was identical to FC7 except that column chromatography on silica (1% DCM in petroleum ether 40-60) was used for purification. Quantities used were 2,3,4,5,6-pentafluorophenol (1.50g, 8.15×10^{-3}mol), DMF (60ml), K_2CO_3 (4.50g), 1,9-dibromononane (1.16g, 0.83ml, 4.08×10^{-3}mol) and NaI (0.06g, 4.08×10^{-4}mol). A colourless liquid was obtained (0.46g, yield 25%, mp < 15°C).

^{1}H NMR($CDCl_3$) δ (ppm)**:** 4.15 (t, J = 6.4Hz, 4H; C^7H_2, $C^{15}H_2$), 1.78 (quintet, J = 6.4Hz, 4H; C^8H_2, $C^{14}H_2$), 1.40 (m, 10H, C^9H_2, $C^{10}H_2$, $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$).

^{13}C NMR ($CDCl_3$) δ (ppm): 76.2 (C^7, C^{15}), 30.2 (C^8, C^{14}), 29.7 (C^{11}), 29.5 (C^{10}, C^{12}), 25.9 (C^9, C^{13}).