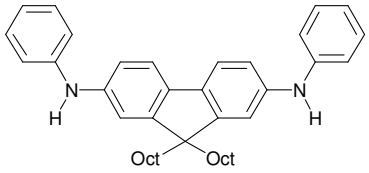
Synthesis and analysis of compounds P1, P2, P3 and P4

Compounds and polymers were synthesised as for the preparation of poly[1,8-bis(p-methoxydiphenylamino)-9-dioctylfluorenyl-alt-9-bis[2'-(2'-(2'-(2'-methoxy ethoxy)ethoxy) ethoxy)]ethyl fluorene from N,N´-bis-(4-methoxy-phenyl)-9,9-dioctyl-9H-fluorene-2,7-diamine and 2.7-bis-(p-iodophenyl)-9.9'- bis[2'-(2'-(2'-(2'-methoxy ethoxy)ethoxy)ethoxy)]ethyl-fluorene using published procedures.[1]

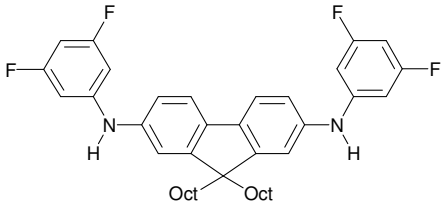
N,N´-Bisphenyl-9,9-dioctyl-9H-fluorene-2,7-diamine



Aniline (2.98 g, 32.09 mmol), dibromodioctylfluorene (8 g, 14.59 mmol), $Pd(OAc)_2$ (17 mg, 0.075 mmol, 2.5 mol%), dPPF (82 mg, 0.15 mmol, 5 mol%) and NaO*t*-Bu (3.8 g, 39 mmol) in toluene (100 ml) was heated to reflux under argon over night. The mixture was cooled to room temperature and water was added. The solution was then filtered through silica. The layers were separated and the aqueous layer extracted with toluene(3x). The combined organic layers were washed with brine and dried over magnesium sulphate. The solvent was removed under vacuum. The crude product was purified by flash chromatography (hexane/ethylacetate 6:1). R_f = 0.2 (hexane/ethylacetate 6:1) to give an off white solid which slowly oxidised to a dark green. Analyticaly pure material was isolated by recrystallisation from petroleum spitits at low temperature to give a colourless solid.Yield 98.8%.

^{1}H (C_6D_6 500 MHz) δ 7.451(d, 2H *J* = 7.1 Hz, Fl-H), 7.177(t, 4H *I* = 7.7 Hz, *m*-Ph), 7.049(d, 2H *J* = 2.0 Hz, Fl-H), 6.978(d, 4H *J* = 8.1 Hz, *o*-Ph), 6.910(dd, 2H *J* = 7.8 & 2.0 Hz, Fl-H), 6.836(t, 2H *J* = 7.3 Hz, *p*-Ph), 5.146(s, 2H, NH), 1.931-1.965(m, 4H, Fl-CH_2), 0.948-1.180(m, 24H, -(CH_2)-), 0.820(t, 3H *J* = 7.1 Hz, Me).
^{13}C{^{1}H} (C_6D_6 123 MHz) δ 152.164, 144.357, 141.871, 135.635, 129.623(Ar-H), 120.731(Ar-H), 120.021(Ar-H), 117.971(Ar-H), 117.508(Ar-H), 113.709(Ar-H), 55.313(*C*(CH_2)$_2$), 41.140(*C*H_2), 32.171(*C*H_2), 30.626(*C*H_2), 29.717(*C*H_2), 24.474(*C*H_2), 22.973(*C*H_2), 14.309 (Me).
MS ES(+ve): $C_{41}H_{53}N_2$ $[M+H]^+$, Calc. 573.4203, Found 573.4193.
EA Calc(%): C 85.96, H 9.15, N 4.89. Found(%) C 85.78, H 9.17, N 4.96.

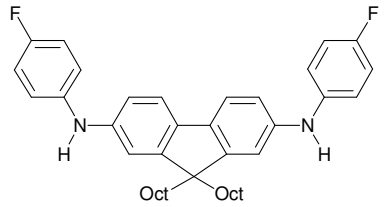
2.7-Bis-(3,5-difluoroanilino)-9.9'-bisoctyl-fluorene



The crude product was purified by flash chromatography (hexane/ethyl acetate 9:1). R_f = 0.23 (hexane/ethyl acetate 9:1). Pale yellow oil. Yield 3.31 g (75.0%).
^{1}H (C_6D_6 500 MHz) δ 7.496(d, 1H *J* = 8.0 Hz, Fl-H), 7.068(d, 1H *J* = 2.0 Hz, Fl-H), 6.861(dd, 1H *J* = 8.0 & 2.0 Hz, Fl-H), 6.405(pseudo dd, 2H $^3J_{HF}$ = 8.0 Hz and $^4J_{HH}$ = 2.0 Hz, *o*-$NC_6H_3F_2$), 6.289(tt, 1H $^3J_{HF}$ = 8.9 Hz $^4J_{HH}$ = 2.2 Hz, *p*-$NC_6H_3F_2$), 5.077(s,1H, NH), 2.005(m, 2H, α-CH_2), 1.12-1.32(m, 10H, CH_2's), 0.941-1.003(m, 2H, CH_2), 0.911(t, 3H J = 7.0 Hz, CH_3).

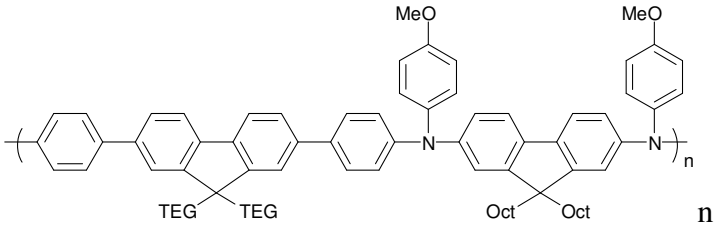
$^{13}C\{^1H\}$ (C_6D_6 123 MHz) δ 164.38(dd, $^1J_{CF}$ 243 Hz, $^3J_{CF}$ = 15.5 Hz, *m*-$NC_6H_3F_2$), 152.19, 147.23(t, $^3J_{CF}$ = 13.0 Hz, *i*-$NC_6H_3F_2$), 139.63, 136.68, 120.21, 115.76, 98.31(d, $^2J_{CF}$ = 28.8 Hz, *o*-$NC_6H_3F_2$), 94.68(t, $^2J_{CF}$ = 26.0 Hz, *p*-$NC_6H_3F_2$), 55.21, 40.70, 31.85, 30.30, 29.46, 29.41, 24.25, 22.69, 14.01(Me).
^{19}F (C_6D_6 376 MHz) δ –109.62(s)
MS ES(+ve): $C_{41}H_{49}N_2F_4$ $[M+H]^+$, Calc. 645.3826, Found 645.3828.
EA Calc(%): C 76.37, H 7.50, N 4.34. Found(%) C 76.27, H 5.50, N 4.31.

2.7-Bis-(4-fluoroanilino)-9.9'-bisoctyl-fluorene



Recrystallised from petroleum spirits at low temperature. Colourless crystals. Yield 3.79g (91%).
^1H (C_6D_6 400 MHz) δ 7.502(d, 2H *J* = 8.1 Hz, Fl-H), 6.97(d, 2H *J* = 2.0 Hz, Fl-H), 6.77-6.98(m, 10H, Ar-H), 4.981(s, 2H, N-H), 1.99-2.04(m, 4H, α-CH_2), 1.01-1.25(m, 24H, CH_2s), 0.870(t, 6H *J* = 7.0 Hz, Me)
$^{13}C\{^1H\}$ (C_6D_6 100 MHz) δ 158.10(d, $^1J_{CF}$ = 237.7 Hz, *p*-NC_6H_4F), 152.18, 142.56, 140.20(d, $^4J_{CF}$ = 2.2 Hz, *i*-NC_6H_4F), 135.34, 120.00, 119.78(d, $^3J_{CF}$ = 7.5 Hz, *o*-NC_6H_4F), 116.99, 116.11(d, $^2J_{CF}$ = 22.3 Hz, *m*-NC_6H_4F), 112.87, 55.29, 41.19, 32.13, 30.59, 29.68, 29.64, 22.92, 14.24(Me)
^{19}F (C_6D_6 376 MHz) δ –122.85(s)
MS ES(+ve): $C_{41}H_{51}N_2F_2$ $[M+H]^+$, Calc. 609.4020, Found 609.4000.
EA Calc(%): C 80.88, H 8.28, N 4.60. Found(%) C 80.79, H 8.26, N 4.54.

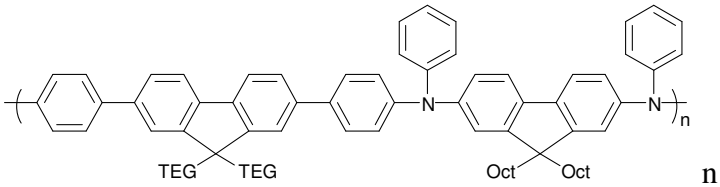
Poly[1,8-bis(p-methoxydiphenylamino)-9-dioctylfluorenyl-alt-9-bis[2'-(2'-(2'-(2'-methoxy ethoxy)ethoxy) ethoxy)]ethyl fluorene **P1**



n ≈ 21

Analytical data was as previously reported. Yield 0.77 g (27.5%).
EA Calc(%): C 77.79, H 8.046, N 2.109. Found(%) C 76.60, H 8.01, N 1.81.
Polymer analysis: Mn 10,470, Mw 28,310, Mz 138,200, Mp, 9716, Pd 2.70.

Poly[1,8-bis(diphenylamino)-9-dioctylfluorenyl-alt-9-bis[2'-(2'-(2'-(2'-methoxy ethoxy)ethoxy) ethoxy)]ethyl fluorene **P2**

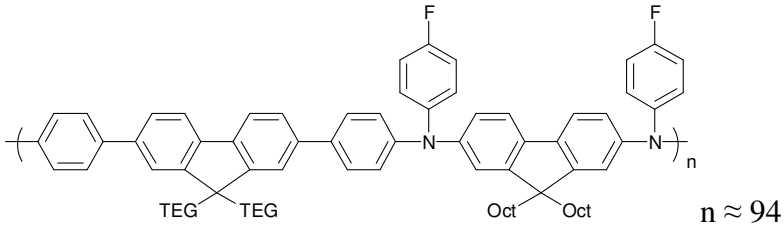


n ≈ 43

To a flask containing 2,7-bis(4-iodophenyl)-9,9-bis((((methoxy-ethoxy)-ethoxy)-ethoxy)-ethyl)-9H-fluorene (1.00 g, 1.05 mmole), N,N´-bisphenyl-9,9-dioctyl-9H-fluorene-2,7-diamine (0.61 g, 1.05 mmole), NaO^{t}Bu (0.30 g, 3.00 mmole), $Pd(OAc)_2$

(8.3 mg, 0.0037 mmole) and P(^{t}Bu)$_3$ (15.0 mg, 0.0074 mmole) under nitrogen was added 25 mls of dry degassed toluene. The reaction mix was heated to 80 °C overnight. After reaction was completed the reaction mix was cooled to RT, and poured into 250 mls of MeOH. The precipitated solid was collected by filtration, dissolved in a minimum of DCM and filtered through a short plug of silica. The solvent was removed and the residue dissolved in a minimum of DCM and precipitated by slow addition to 250 mls of MeOH. The solids were washed with MeOH and dried under vacuum. Pale yellow solid. Yield 0.86 g (64.5%).
^{1}H (C_6D_6 500 MHz) δ 7811(s, 1H, Ar-H), 7.701(d, 1H *J* = 7.9 Hz, Ar-H), 7.60-7.66(m, 3H, Ar-H & *o*-Ph), 7.527(d, 1H *J* = 8.2 Hz, Ar-H), 7.486(s, 1H, Ar-H), 7.418(t, 4H *J* = 7.9 Hz, Ar-H), 7.308(dd, 1H *J* = 8.1 &1.5 Hz, Ar-H), 7.252(t, 2H *J* = 7.9 Hz, *m*-Ph), 6.981(t, 1H *J* = 7.3 Hz, *p*-Ph), 3.42-3.48(m, 4H, OCH_2), 3.40-3.41(m, 2H, OCH_2), 3.362(t, 2H *J* = 5.0 Hz, OCH_2), 3.285(t, 2H *J* = 5 Hz, OCH_2), 3.152(s, 3H, OMe), 3.060(brm, 4H, OCH_2), 2.593(brs, 2H, CH_2), 1.784(brs, 2H, CH_2), 1.15-1.35(m, 10H, CH_2), 1.032(brs, 2H, CH_2), 0.961(t, 3H *J* = 7.1 Hz, Me).
^{13}C{^{1}H} (C_6D_6 100 MHz) δ 152.72, 152.26, 151.05, 148.59, 147.83, 147.02, 140.45, 139.60, 136.94, 135.97, 129.68(Ar-H), 128.52(Ar-H), 126.49(Ar-H), 124.56(Ar-H), 124.49, 124.13(Ar-H), 123.19(Ar-H), 121.80(Ar-H), 120.59(Ar-H), 120.49(Ar-H), 119.77(Ar-H), 117.84(Ar-H), 72.33, 70.96, 70.93, 70.83, 70.79, 70.37, 65.57, 58.67(OMe), 55.48(*C*(CH_2)$_2$), 52.11(*C*(CH_2)$_2$), 40.44, 40.37, 32.24, 30.47, 29.82, 29.77, 24.59, 23.08, 14.40(Me).
EA Calc(%): C 79.58, H 8.109, N 2.209. Found(%) C 78.50, H 8.00, N 2.10.
GPC (methyl methacrylate standards): Mn 17,750, Mw 54,880, Mz 133,700, Mp 32,500, Pd 3.092.

Poly[1,8-bis(p-fluorodiphenylamino)-9-dioctylfluorenyl-alt-9-bis[2'-(2'-(2'-(2'-methoxy ethoxy)ethoxy) ethoxy)]ethyl fluorene **P3**



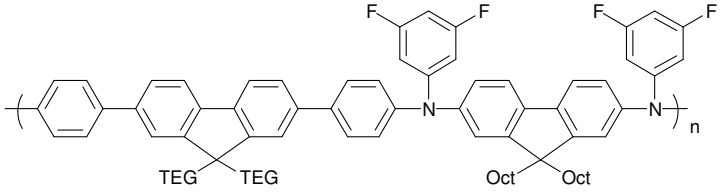
n ≈ 94

As above. Yield 0.46 g (66%)

^{1}H (C_6D_6 500 MHz) δ 7.832(s, 2H, Ar-H), 7.644-7.725(m, 8H, Ar-H), 7.549(d, 2H *J* = 8.2 Hz, Ar-H), 7.427(d, 2H *J* = 1.5 Hz, Ar-H), 7.358(d, 4H *J* = 13.5 Hz, Ar-H), 7.249(dd, 2H *J* = 8.0 & 1.4 Hz, Ar-H), 7.15-7.20(m overlapping solvent, 4H, Ar-H), 6.911(t, 4H *J* = 8.5 Hz, Ar-H), 3.34-3.47(m, 16H, TEG-CH_2), 3.276(t, 4H *J* = 5.0 Hz, -OCH_2-), 3.151(s, 6H, OMe), 3.04-3.15(m, 8H, -OCH_2-), 2.589(brs, 4H, -OCH_2-), 1.818(brs, 4H, Oct-α-CH_2), 1.23-1.38(m, 12H, Oct-CH_2), 1.185(brs, 8H, Oct-CH_2), 1.035(brs, 4H, Oct-CH_2), 0.962(t, *J* = 7.1 Hz, Me).
^{13}C{^{1}H} (C_6D_6 100 MHz) δ 159.42(d, $^1J_{CF}$ = 242.0 Hz, *p*-NC_6H_4F), 152.78, 151.12, 147.81, 147.03, 144.50(d, $^4J_{CF}$ = 2.4 Hz, *i*-NC_6H_4F), 140.39, 139.63, 136.74, 135.93, 128.55, 127.47, 126.66(d, $^3J_{CF}$ = 7.7 Hz, *o*-NC_6H_4F), 126.48, 123.92, 123.54, 121.85, 120.53, 119.18, 116.47(d, $^2J_{CF}$ = 22.2 Hz, *m*-NC_6H_4F), 72.31, 70.94, 70.91, 70.82, 70.77, 70.36, 67.58, 58.65(OMe), 55.50, 52.12, 40.41, 32.23, 30.45, 29.81, 29.75, 24.60, 23.06, 14.32(Me)
^{19}F (C_6D_6 376 MHz) δ –119.2(s)
EA Calc(%): C 77.39, H 7.731, N 2.148. Found(%) C 77.20, H 7.68, N 2.07.

GPC (methyl methacrylate standards) Mn 33,930, Mw 123,100, Mz 278,000, Mp 81,310, Pd 3.628

Poly[1,8-bis(3,5-difluorodiphenylamino)-9-dioctylfluorenyl-alt-9-bis[2'-(2'-(2'-(2'-methoxy ethoxy)ethoxy) ethoxy)]ethyl fluorene **P4**



n ≈ 38

As above.

^{1}H (C_6D_6 500 MHz) δ 7.815(s,2H, Ar-H), 7.731(d, 2H *J* = 8.0 Hz, Ar-H), 7.58-7.69(m, 6H, Ar-H), 7.512(d, 2H *J* = 8.0 Hz, Ar-H), 7.428(s, 2H, Ar-H), 7.311(d, 4H *J* = 8.5 Hz, Ar-H), 7.16-7.19(m overlapping solvent, 2H, Ar-H), 6.852(dd, 4H *J* = 9.5 & 2.1 Hz, Ar-H), 6.347(tt, 2H *J* = 9.7 & 2.1 Hz, Ar-H), 3.34-.47(m, 16H, -OCH_2-), 3.284(t, 4H J = 4.9 Hz, -OCH_2-), 3.151(s, 6H, OMe), 3.080(t, 8H *J* = 4.9 Hz, -OCH_2-), 2.619(brt, 4H, -OCH_2-), 1.835(brm, 4H, Oct-α-CH_2), 1.20-1.37(m, 20H, Oct-CH_2), 0.89-1.07(m, 10H, CH_2 and Me)

^{13}C{^{1}H} (C_6D_6 100 MHz) δ 164.33(dd, $^1J_{CF}$ 244.6 Hz, $^3J_{CF}$ = 15.1 Hz, *m*-$NC_6H_3F_2$), 153.13, 151.17, 150.87(t, $^3J_{CF}$ 12.4 Hz, *i*-$NC_6H_3F_2$), 146.12, 145.83, 140.03, 139.85, 137.97, 137.72, 128.79, 127.46, 126.67, 125.77, 125.39, 121.98, 121.16, 120.89, 120.59, 104.51(d, $^2J_{CF}$ 28.1 Hz, *o*-$NC_6H_3F_2$), 97.06(t, $^2J_{CF}$ 25.6 Hz, *p*-$NC_6H_3F_2$),, 72.30, 70.93, 70.91, 70.82, 70.77, 70.41, 67.55, 58.64(OMe), 55.66, 52.18, 40.36, 32.19, 30.44, 29.78, 29.70, 24.65, 23.04, 14.36(Me)

^{19}F (C_6D_6 376 MHz) δ -109.25(s) main peak, minor singlets at –109.25 and –109.61.

EA Calc(%): C 75.30, H 7.37, N 2.09. Found(%) C 75.30, H 7.43, N 2.07.

GPC (methyl methacrylate standards) Mn 21470, Mw 51,000, Mz 119,000, Mp 32,500, Pd 2.375

1 S. A. Haque, T. Park, C. Xu, S. Koops, N. Schulte, R. J. Potter, A. B. Holmes and J. R. Durrant, *Adv. Funct. Mater.*, 2004, **14**, 435.