2-(4-Nitrophenyl)-thiophene 3

In an inert atmosphere of nitrogen, a mixture of commercial 1-bromo-4-nitrobenzene **2** (15.2 g, 75 mmol), $Pd(PPh_3)_4$ (0.76 g, 0.66 mmol, 1.3 mol%), 2M-aqueous sodium carbonate (30 ml) and toluene (75 ml) was heated under reflux for 30 minutes. The mixture was removed from the heat, a solution of commercial thiophene-2-boronic acid **1** (10.2 g, 80 mmol) in ethanol (30 ml) was added and reaction mixture was heated under continuous reflux for 5 days. Thereafter, the reaction was cooled, filtered through a glass wool plug and extracted in to diethyl ether (150 ml). The ether layer was washed with water (150 ml), dried ($MgSO_4$) and evaporated to dryness *in vacuo*. The resultant crude residue was purified by sublimation (70 ^oC, 10mm/Hg) followed by recrystallisation of the sublimate from ethanol to furnish the desired 2-(4-nitrophenyl)thiophene **3**, 6.15 g (41 %), m.p. (138-139 ^oC (Lit.[17] 137-138 ^oC) as pale yellow crystals: ν_{max} (KBr)/ cm^{-1}: 3103w ($C{=}C_{st}$), 2855w ($C\text{-}H_{st}$), 1592 & 1501s ($C{=}C_{st}$), 1507, 1338, 1106s ($N{=}O_{st}$), 1420s ($C\text{-}H_{def}$), 842 (p,p,di-sub); δ_H (400 MHz; $CDCl_3$) 7.7 (1 H, t, $ArH_{[Thio]}$, *J* = 4 Hz), 7.36 (1 H, d, $ArH_{[Thio]}$, *J* = 5 Hz), 7.39 (1 H, d, $ArH_{[Thio]}$, *J* = 4 Hz), 7.67 (2 H, d, ArH, *J* = 7 Hz), 8.15 (2 H, d, ArH, *J* = 7 Hz); δ_C (100 MHz: $CDCl_3$); 124.3 (ArC), 125.6 ($ArC_{[Thio]}$), 125.9 (ArC), 127.64 ($ArC_{[Thio]}$), 128.6 ($ArC_{[Thio]}$), 140.5 ($ArC_{Q[Thio]}$),141.5 (ArC_Q), 146.6 ($ArC_Q\text{-}NO_2$); tlc (CH_2Cl_2), single spot, R_f 075; $C_{10}H_7NO_2$: Expected: C, 58.52; H, 3.44; N, 6.82; Found: C, 58.5; H, 3.37; N, 6.67 %; MS: $[M+H]^+$ 206.

4-(2-Thienyl)aniline 4

Commercial palladium on charcoal (10 % Pd/C) (0.35 g) was carefully added to a solution of 2-(4-nitrophenyl)thiophene **3** (5 g, 24.4 mmol) dissolved in absolute ethanol (150 ml). The mixture was fitted to an atmospheric hydrogenator and stirred continuously at room temperature until the theoretical volume of hydrogen had been consumed. Thereafter, the reaction mixture was filtered through 'Celite', washed well with ethanol, and the filtrate was evaporated to dryness *in vacuo*. The resulting beige solid was recrystallised twice from ethanol to afford the desired 4-(2-thienyl)aniline **4**, 4 g (94 %), m.p. 75-76 ^oC, as white crystals: ν_{max} (KBr)/ cm^{-1}: 3441, 3358m ($N\text{-}H_{st}$), 3097w ($Ar\text{-}H_{st}$), 2864w ($C\text{-}H_{st}$), 1793, 1757w ($N\text{-}H_{def}$), 1616, 1501s ($C{=}C_{st}$), 1429s ($C\text{-}H_{def}$), 1291s ($N\text{-}H_{def}$), 816s (2 adjacent H); δ_H (400 MHz; $CDCl_3$); 6.68 (2 H, d, ArH, *J* = 7.5 Hz), 7.03 (1 H, m, $ArH_{[Thio]}$, *J* = 4 Hz), 7.16 (2 H, m, $ArH_{[Thio]}$), 7.43 (2 H, d, ArH, *J* = 7.5 Hz); δ_C (100 MHz: $CDCl_3$); 115.4 (ArC), 121.3 ($ArC_{[Thio]}$), 123.2 ($ArC_{[Thio]}$), 125.3 (ArC_Q), 127.3 (ArC), 127.9 ($ArC_{[Thio]}$), 145.1 ($ArC_{Q[Thio]}$), 146.1 ($ArC_Q\text{-}NH_2$); tlc (CH_2Cl_2), single spot, R_f; 0.5; $C_{10}H_9NS$ Expected: C, 68.53; H, 5.18; N, 7.99 %; Found: C, 68.11; H, 5.29; N, 7.64 %; MS: $[M+H]^+$ 176.

4-(4-Thiophen-2-yl-phenylazo)phenol 5

To a cooled (0 ^oC) solution of sodium nitrite (3.33 g, 0.05 mol) in water (50 ml) was added a cooled solution/suspension of 4-(2-thienyl)aniline **4** (8.8 g, 0.05 mol) in HCl / water (18 ml: 90 ml). The reaction mixture was maintained at 0 ^oC for 2 h to ensure successful diazotisation. Thereafter, a mixture of phenol (4.67 g, 0.05 mol), sodium hydroxide (6 g, 0.15 mol) and water (50 ml) was added, dropwise, with stirring to the above diazonium solution ensuring that the reaction temperature did not exceed 5 ^oC. After stirring for 2 h, the ensuing yellow/beige precipitate was filtered (Bűchner) and allowed to air-dry, whereupon the solid changed to a *forest green* colour. The crude product was mixed with CH_2Cl_2 and silica gel (40 g) and the slurry poured onto a pre-packed silica gel column. The crude residue was purified by flash column chromatography on silica gel eluting initially with dichloromethane followed by dichloromethane:ethanol (98:2). Solvent was removed *in vacuo* from the desired fractions and the crude residue recrystallised from hexane to furnish the desired 4-(4-thiophen-2-yl-phenylazo)phenol **5**, 5.6 g (40 %), m.p. 205 ^oC, as bronze crystals: ν_{max} (KBr)/ cm^{-1}: 3466-3066br s (OH_{st}), 3055w ($Ar\text{-}H_{st}$), 2902, 2864w ($C\text{-}H_{st}$), 1244-1101s ($C\text{-}O_{str}$), 845s (2 adjacent H); δ_H (400 MHz; $CDCl_3$); 2.99 (1 H, s, -OH), 6.88 (2 H, d, ArH), 7.04 (1 H, t, $ArH_{\{Thio]}$, *J* = 3.5 Hz), 7.27 (1 H, d, $ArH_{\{Thio]}$, *J* = 5 Hz), 7.34 (1 H, d, $ArH_{\{Thio]}$, *J* = 3.5 Hz), 7.66 (2 H, d, ArH), 7.8 (2 H, d, ArH), 7.83 (2 H, d, ArH); δ_C (100 MHz: $CDCl_3$); 115.7 (ArC), 123.4 (ArC), 123.8 ($ArC_{[Thio]}$), 124.9 (ArC), 125.6 ($ArC_{[Thio]}$), 126.2 (ArC), 128.2 ($ArC_{[Thio]}$), 136.0, 143.4 ($ArC_{Q[Thio]}$), 146.7 (ArC_Q), 151.7 (ArC_Q), 160.1 ($ArC_Q\text{-}OH$); tlc (CH_2Cl_2), single spot, R_f; 0.19; $C_{16}H_{12}N_2OS$: Expected: C, 68.55; H, 4.31; N, 9.99 %; Found: C, 66.43; H, 4.41; N, 9.75 %; MS: $[M+H]^+$ 281.2.

{4-[8-(2-Methyl-2-phenyl-[1,3] dioxan-5-yl)-octyloxyphenyl}-(4-thiophen-2-yl-phenyl)-diazene 7

A vigorously stirred mixture of 5-(8-bromo-octyl)-2-methyl-2-phenyl-[1,3]-dioxane **6** (1.98 g, 5.3 mmol), 4-(4-thiophen-2-yl-phenylazo)-phenol **5** (1.5 g, 5.3 mmol), dry 2-butanone (50 ml) and anhydrous potassium carbonate (1.47 g, 10.6 mmol) was heated under reflux for 72 h. Thereafter, the cooled reaction mixture was poured into water (100 ml) and extracted with dichloromethane, dried ($MgSO_4$) and the solvent removed *in vacuo*. The resultant orange solid was purified by boiling in ethanol (150 ml), the product does not dissolve and was collected by hot filtration. The residue was washed with a small volume of hot ethanol and allowed to dry to afford the desired {4-[8-(2-methyl-2-phenyl-[1,3] dioxan-5-yl)-octyloxyphenyl}-(4-thiophen-2-yl-phenyl)-diazene **7**, (70%), m.p. 170-72 ^oC, as an orange solid. ν_{max} (KBr)/ cm^{-1}: 3055w ($Ar\text{-}H_{st}$), 2902, 2874w (C-H$_{st}$), 1438, 1101s (C-O$_{str}$), 845; δ_H (400 MHz; CDCl$_3$);1.0-1.4 (7 H, comp. mult, alkyl), 1.49 (6H, comp. mult., CH$_2$), 1.8 (4H, quint., ArOCH$_2$$\underline{CH_2CH_2}$-), 2.0 (1H, comp. mult., -CH-), 3.3 (2H, t, CH$_2$), 3.7 (2H, dd, CH$_2$), 4.0 (2H, t, ArOCH$_2$), 6.95 (2 H, d, ArH, *J* = 7.5 Hz), 7.04 (1 H, t, ArH$_{\{Thio]}$, *J* = 4 Hz), 7.27 (1 H, d, ArH$_{\{Thio]}$, *J* = 5 Hz), 7.34-7.4 (6 H, m, ArH +ArH$_{[Thio]}$), 7.7 (2 H, d, ArH), 7.86 (4 H, m, ArH); δ_C (100 MHz: CDCl$_3$); 25.9, 26.1, 28.1, 29.1, 29.2, 29.3, 29.6, 32.4, 34.1, 66.6 ($\underline{C}$-O dioxane ring), 68.3 (ArO$\underline{C}$H$_2$-), 100.4 (quat C dioxane ring), 114.7 (ArC), 123.2 (ArC), 123.8 (ArC$_{[Thio]}$), 124.7 (ArC), 125.6 (ArC$_{[Thio]}$), 126.3 (ArC), 126.8, 127.6 (ArC$_{[Thio]}$), 128.2, 128.6, 136.2, 140.9 (ArC$_Q$), 143.6 (ArC$_{Q[Thio]}$), 146.9 (ArC$_Q$), 151.8 (ArC$_Q$), 161.7 (ArC$_Q$-O); MS: $[M+H]^+$ 569.

2-{7-[4-(4-Thiophen-2-yl-phenylazo)-phenoxy]-octyl}-propane-1,3-diol 8

A stirred mixture of {4-[8-(2-methyl-2-phenyl-[1,3] dioxan-5-yl)-octyloxyphenyl}-(4-thiophen-2-yl-phenyl)-diazene **7** (2.1 g, 3.7 mmol), ethanol (100 ml), conc. HCl / water (1 ml / 2 ml) was heated under reflux for 2 h. The orange solid dissolved as the reaction progressed. The reaction was cooled and resultant solid was filtered (Bűchner) and recrystallised with hot filtration from ethanol to furnish the desired 2-{7-[4-(4-thiophen-2-yl-phenylazo)-phenoxy]octyl}-propane-1,3-diol **8** (77%), as orange solid: m.p., Cryst 177.7 SmA 180.4 I (heating); I 178.2 SmA 167.7 Cryst (cooling): ν_{max} (KBr)/ cm^{-1}: 3422 br s (O-H str), 3055w (Ar-H$_{st}$), 2902, 2874w (C-H$_{st}$), 1438, 1101s (C-O$_{str}$), 845; δ_H (400 MHz; THF-d$_8$);1.1-1.6 (13 H, br comp. mult, alkyl), 1.8 – 1.9 (4 H, comp. mult.,), 3.4 (2 H, t, CH$_2$), 3.5-3.6 (5 H, m), 4.2 (2 H, t, ArOCH$_2$), 7.0 (2 H, d, ArH, *J* = 7.5 Hz), 7.1 (1 H, m, ArH$_{\{Thio]}$, *J* = 4 Hz), 7.4 (1 H, d, ArH$_{\{Thio]}$, *J* = 5 Hz), 7.5 (1 H, m, ArH$_{[Thio]}$), 7.8 (2 H, d, ArH), 7.9 (4 H, m, ArH); δ_C (100 MHz: THF-d$_8$); 25.2, 26.1, 27.6, 28.5, 28.9, 29.3, 29.6, 43.6 ($\underline{C}$H), 64.5 ($\underline{C}$H$_2$OH), 68.0 (ArO$\underline{C}$H$_2$-), 114.9 (ArC), 122.2 (ArC), 124.8 (ArC$_{[Thio]}$), 124.9 (ArC), 125.6 (ArC$_{[Thio]}$), 126.3 (ArC), 127.6 (ArC$_{[Thio]}$), 143.6 (ArC$_{Q[Thio]}$), 146.9 (ArC$_Q$), 151.9 (ArC$_Q$), 161.3 (ArC$_Q$-O); $C_{27}H_{34}N_2O_3S$: Expected: C, 69.50; H, 7.34; N, 6.00 %; Found: C, 69.28; H, 7.21; N, 5.99 %; MS: $[M+H]^+$ 467.