**10.1071/CH09348_AC**



**Australian Journal of Chemistry 2009, 62(12), 1577–1582**

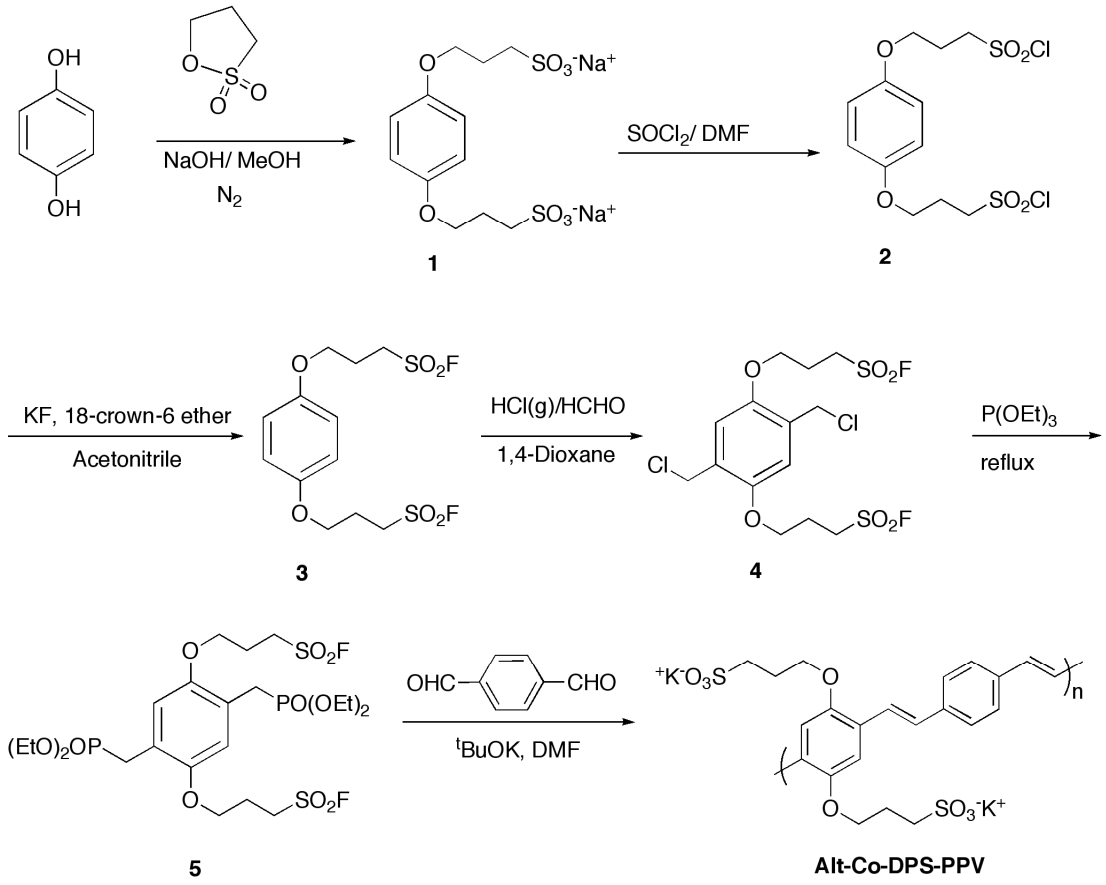
# Accessory Publication

## Synthesis and single chain fluorescence of a sulfonated conjugated polymer

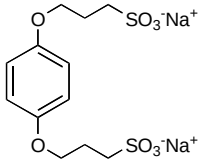
Daniel E. Gómez, Tina A. T. Tan, Jonathan M. White, Toby D. M. Bell and Kenneth P. Ghiggino*

*School of Chemistry and Bio21 Institute,*
*The University of Melbourne, Parkville, VIC, 3010. Australia*

## Synthesis of Alt-Co-DPS-PPV




**Sodium 3,3'-(1,4-phenylenebis(oxy)dipropane-1-sulfonate (1)**

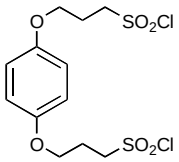


Hydroquinone (5.00 g, 45.30 mmol) was dissolved in a purged solution of MeOH (15 ml) was added dropwise, under nitrogen into 10 ml of nitrogen purged aqueous NaOH (3.69 g, 92.2 mmol) at room temperature. To this mixture, a nitrogen purged methanol solution (15 ml) of (11.14 g, 91.2 mmol) 1,3-propanesultone was added. The reaction mixture was stirred under nitrogen at room temperature for about 4 h. The solid product was filtered,

dissolved in minimal $H_2O$, precipitated in acetone and dried to give the title compound as a brown solid (11.15 g, 62%), **MP** >300 $^oC$.

**$^1$H NMR ($D_2O$)**: δ 7.01 4.15-4.12 (t, *J* = 7.6 Hz, 4H), 3.10-3.06 (t, *J* = 7.9 Hz, 4H) 2.20-2.16 (m, 4H). **$^{13}$C NMR ($D_2O$)**: δ 152.7, 116.5, 67.7, 48.0, 24.4. **IR (KBr)**: $Cm^{-1}$ 2960, 2920, 2880, 1510, 1480, 1400, 1220, 1200, 1110, 1060, 930, 830, 770, 610. **High res. ESI-MS [M+Na]$^+$**: 420.99756 Calculated = 420.99742.

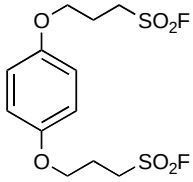
**3,3'-(1,4-phenylenebis(oxy)dipropane-1-sulfonyl chloride) (2)**




Thionylchloride (20 ml, 231 mmol) was added dropwise into **1 (**10 g, 25.1 mmol), suspended in dry DMF (40 ml) at $0^o$ C. The reaction mixture was stirred at room temperature for 45min and quenched by pouring into ice-cold water. A yellow, water-insoluble precipitate was filtered, washed with water and dried under vacuum at $60^oC$ overnight to give the title compound as a light brown solid (8.71 g, 89%), **MP** = 66-68 $^o$ C

**$^1$H NMR ($CDCl_3$)**: δ 6.83 (s, 4H), 4.11-4.08 (t, *J* = 7.6 Hz, 4H), 3.94 (t, *J* = 7.2 Hz, 4H), 2.53 (m, 4H). **$^{13}$C NMR ($CDCl_3$)**: δ152.7, 115.6, 65.1, 62.4, 24.8. **IR (KBr)**: $Cm^{-1}$ 3050, 2970, 2930, 2880, 1520, 1470, 1310, 1290, 1230, 1160, 1110, 1050, 930, 860, 820, 740, 730, 620. **High res. ESI-MS [M+Na]$^+$**: = 412.96590 Calculated = 412.96576.

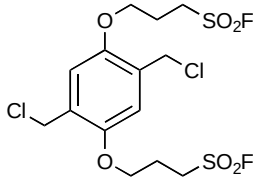
**3,3'-(1,4-phenylenebis(oxy)dipropane-1-sulfonyl fluoride) (3)**




Bissulfonyl chloride **2** (4.8 g, 12.2 mmol) was stirred in presence of 6 equivalents of KF (4.25 g, 73.3 mmol) and catalytic amounts of 18-crown-6-ether in acetonitrile (100 ml) for 12 h, under $N_2$. The reaction mixture was then poured in water and filtered to give a quantitative yield of the title compound (4.4 g, 99%) **MP** = 100-102$^oC$

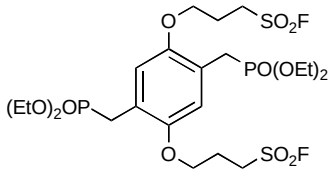
**$^{1}$H NMR (400 MHz, $CDCl_3$)**: δ 6.83 (s, 4H), 4.05 (m, 4H) 3.64 (m, 4H), 2.43 (m, 4H)
**$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 152.7, 115.5, 65.1, 48.0, 23.9
**High res. ESI-MS $[M+Na]^+$**: 381.02502 Calculated = 381.02486

**3,3'-(2,5-bis(chloromethyl)-1,4-phenylene)bis(oxy)dipropane-1 sulfonyl fluoride (4)**




Bissulfonyl fluoride **3** (2.02 g, 5.074 mmol) was dissolved in dioxane (30 ml) and mixed with 32% HCl (14 ml), followed by further addition of dioxane (20 ml) to obtain a clear solution The reaction mixture was purged with HCl gas for 15 min, prior to the addition of formaldehyde (22 ml) at room temperature. HCl gas was further purged through the reaction mixture for 3 h, after which, the reaction flask was sealed and left to stirred at room temperature for further 6 h. The white solid formed was filtered, washed with cold methanol (3 x 20 ml) and dried under vacuum to give the title compound as a white solid (1.9 g, 63%) **MP** =161-163$^{o}$C
**$^{1}$H NMR (400 MHz, $CDCl_3$)**: δ 6.83 (s, 2H), 4.82 (s, 4H) 4.05 (m, 4H), 3.64 (m, 4H), 2.43 (m, 4H). **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 152.7, 126.9, 115.5, 67.9, 65.1, 48.0, 23.9. **IR**: $cm^{-1}$ 2884, 1513, 1392, 1229, 1193, 1050, 930, 811, 749, 715. **High res. ESI-MS $[M+Na]^+$**: 476.97842 Calculated = 476.978321

**2,5-bis (3-(fluorosulfonyl)propoxy)- 1,4-phenylene) bis(methylene)-bis(diethyl phosphonate) (5)**

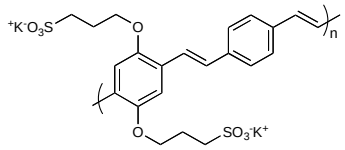



Bischloromethyl **4** (1.0 g, 2.1 mmol) was refluxed neat in triethylphosphite (25 ml) for 5 h. The excess triethylphosphite was then distilled off and further impurities removed via

Kugelrohr distillation under vacuum to give the title compound as a waxy white solid (1.0 g, 69%)

**$^1$H NMR(500 MHz, $CDCl_3$)**: δ 6.83 (s, 2H), 4 .12 (m, 4H), 4.00 (s, 8H), 3.98-3.76 (m, 4H) 3.18 (d, *J* = 2 Hz, 4H), 2.45 (m, 4H)**,** 1.24 (m, 12H)**. $^{13}$C NMR (125 MHz, $CDCl_3$)** δ 150.4, 120.2, 115.5, 105.0, 65.9, 62.6, 48.3, 48.1, 24.2, 16.4. **IR** $cm^{-1}$ 2983, 1508, 1402, 1197, 1025, 964, 908, 821, 729. **High res. ESI-MS $[M+Na]^+$**: 681.11407 Calculated = 681.11402

**Poly- (2,5-dipropylsulfonate-*p*-phenylene-vinylene)-*alt*-(*p*-phenylene-vinylene) (Alt-Co-DPS-PPV)**




Bisphosphonate **5** (1.0 g, 1.5 mmol) and terephthaldehyde (0.18 g, 1.5 mmol) were predissolved in dry DMF (20 ml) and degassed with $N_2$. 10 equivalents of $^t$BuOK in degassed dry DMF (30 ml) was added dropwise to the stirred solution of bisphosphonate **5** and terephthaldehyde. The reaction mixture turned dark red due to the generation of the ylide and gradually became yellow. The reaction mixture was allowed to stir overnight upon which, the mixture was poured over ice and washed with DCM (3 x 20 ml). The subsequent aqueous layer was then purified using dialysis, with a cut-off membrane of 12,400 g/mol for 7 days. Excess water was removed via freeze-drying to give polymer as a yellow powder (0.12 g, 23%)

**IR (KBr)** $cm^{-1}$ 2294, 2373, 2345, 1702, 1639, 1501, 1406, 1299, 1298, 1214, 1033, 965.

**$^1$H NMR**: broad (no structural information).

**UV-Vis $\lambda_{max}$** = 430 nm, **Molecular weight**: > 12,400 g/mol.

Gel-permeation chromatography of the polymer was carried out by Dr Elizabeth Hill, Department of Chemical Engineering, The University of Melbourne. The instrumentation consisted of a Shimadzu Model 10A LC system with two Waters Ultrahydrogel size exclusion columns (Ultrahydrogel 2000 and 250) linked in series, coupled to a Wyatt DAWN Light Scattering instrument and Optilab detector. Using 9:1 water:acetonitrile

solvent as an eluent resulted in an average molecular weight determination of 22,000 g/mol. No polydispersity index was obtained.