Synthesis of Di-Xanthones and Poly(di-xanthone)s by Cyclization of 2-Aryloxybenzonitriles in Trifluoromethanesulfonic Acid

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Received Date

SUPPORTING INFORMATION

Methods and Instrumentation: Starting compounds were standard reagent grade and were used without further purification. Trifluoromethanesulfonic acid was distilled under dry nitrogen before use. All air-sensitive and/or moisture-sensitive reactions were conducted under a dry nitrogen atmosphere. Thin layer chromatography (TLC) was carried out on Polygram® SIL G/UV$_{254}$ SiO$_2$ plates. Column chromatography was conducted on silica gel, 230-400 mesh, 60Å. Proton and ^{13}C NMR spectra were recorded on a Bruker A300 spectrometer. Mass spectra (EI/CI/FAB) were run on a Kratos Concept spectrometer. Elemental analyses were provided by the analytical service of Manchester University. Melting points were determined by DSC under nitrogen using a Mettler *DSC20* system.

Synthesis of di-xanthones 7, 8 and 9: A mixture of 1,5-naphthalenediol (14.56 g, 90.91 mmol), potassium carbonate (15.08 g, 109.1 mmol), dimethylacetamide (DMAc, 200 mL) and toluene (100 mL) was heated to reflux with stirring under nitrogen and the water generated was removed by Dean-Stark distillation. When no further water was evolved, the toluene was distilled off and 2-fluorobenzonitrile (24.22 g, 200.0 mmol) was added while maintaining a nitrogen purge. The reaction was stirred at reflux for 20 h and then cooled and poured into water (2 L). After stirring for 2 h the precipitate was filtered off, washed base-free with water, dried under vacuum and recrystallised with carbon from 2-methoxyethanol to give 26.53 g of pale yellow crystalline dinitrile **1** (81% yield). This compound (1.00 g) was dissolved in trifluoromethanesulfonic acid (10 mL) and the deep red solution was allowed to stand at room temperature for 5 days. It was then added dropwise to water (100 mL) and the precipitated iminium triflate (**4**) was filtered off, washed with water until the washings were neutral, and dried under vacuum. This material (1.09 g) was suspended in 2.5M sodium hydroxide (100 mL) with stirring for 3 days, and the resulting di-imine was filtered off and dried (0.61 g). Hydrolysis of the di-imine (0.23 g) in 75% (w/w) sulfuric acid (50 mL) at reflux for 24 h was followed by dilution with water (150 mL), neutralisation with sodium hydroxide, filtration, washing to neutral pH with water, drying, and recrystallisation from DMAc to give di-xanthone **7** (0.18 g) in the form of pale yellow-green needles. The di-xanthones **8** and **9** were obtained by entirely analogous procedures.

Synthesis of di-xanthone 12 via imino-xanthone 11: A mixture of resorcinol (10.01 g, 90.91 mmol), potassium carbonate (15.08 g, 109.1 mmol), dimethylacetamide (DMAc, 250 mL) and toluene (100 mL) was heated to reflux with stirring under nitrogen and the water generated was removed by Dean-Stark distillation. When no further water was evolved, the toluene was distilled off and 2-fluorobenzonitrile (24.22 g, 200.0 mmol) was added while maintaining a nitrogen purge. The reaction was stirred at reflux for 9 h and then cooled and poured into water (2 L). After stirring for 2 h the precipitate was filtered off, washed base-free with water, dried under vacuum and recrystallised with carbon from ethanol to give 21.16 g of colourless crystalline dinitrile **10** (73% yield). This compound (1.00 g) was dissolved in trifluoromethanesulfonic acid (10 mL), and the deep red solution was allowed to stand at room temperature for 16 h and was then heated at 60 °C for a further 30 h. It was then added slowly to water (400 mL) and the resulting suspension was basified with sodium hydroxide. After stirring for a further 4 h the yellow solid was filtered off, washed base-free, and dried under vacuum to give 0.88 g of imino-xanthone **11** (88% yield). Crystals suitable for X-ray analysis were grown by slow-cooling of a solution in xylene. Hydrolysis of **11** (0.32 g) in 50% (w/w) sulfuric acid for 20 h afforded dixanthone **12** (0.22g, 69% yield).

Synthesis of the difluoro-dinitrile monomer 13: A solution of 4-bromo-2-fluorobenzonitrile (13.06 g, 65.44 mmol) in anhydrous DMF (150 mL) was added with stirring under nitrogen to bis(1,5-cyclooctadiene)nickel(0) (10.0 g) in anhydrous DMF (50 mL) at room temperature, and the mixture was stirred at 45 °C for 24 h. The reaction mixture was then stirred with 3% hydrochloric acid (200 mL) and dichloromethane (DCM, 200 mL) for 2 h, and the solid was filtered off, washed with 3% HCl (200 mL), DCM (50 mL), water until neutral, and finally with diethyl ether. After drying under vacuum at room temperature, the difluoro-dinitrile **13** (5.97 g) was obtained as a colourless powder. Recrystallisation from toluene afforded 5.14 g of very pure **13** (5.14 g, 65% yield, purity 99.8% by DSC).

Polycondensation of monomer 13 with 4,4'-hexafluoroisopropylidene-diphenol: A mixture of monomer (0.800 g, 3.33 mmol), 4,4'-hexafluoroisopropylidene-diphenol (1.110 g, 3.302 mmol), sodium carbonate (0.360 g, 3.397 mmol) and diphenylsulfone (solvent, 7.4 g) was heated and stirred under a very slow nitrogen purge, the temperature being raised progressively to 250 °C over 5 h. The temperature was then raised to 275 °C and held for a further 2 h before pouring the viscous solution onto aluminium foil. The resulting solid was ground to a powder, extracted three times with refluxing methanol (150 mL) then three times with boiling water, and then once more with methanol before drying under vacuum to give colourless polymer **14** (1.56 g), soluble in acetone, dichloromethane, and N-methyl pyrrolidone.

Cyclization of polymer 14 to poly-xanthoneimine 15 and hydrolysis to poly-xanthone 16: Polymer **14** (0.80 g) was dissolved in dichloromethane (20 mL) and trifluoromethanesulfonic acid (40 mL) was added slowly with vigorous stirring under nitrogen. After stirring for 4 days the solution was added dropwise to water (600 mL), giving a pale yellow fibrous precipitate. Dichloromethane was removed under vacuum, and the solid was filtered off, washed acid free and dried under vacuum to give 0.79 g of a poly-iminium triflate. This polymer (0.68 g) was stirred with 10% (w/v) sodium hydroxide in 10% aqueous ethanol to give, after filtration and washing, 0.61 g of poly-xanthoneimine **15**. Hydrolysis of 15 (0.40 g) in 50% (w/w) sulfuric acid at reflux for 30 h afforded polyxanthone **16** (0.37 g) as a pale beige fibrous powder.

Characterization Data

1: M.p. 219 °C. IR 2230 cm^{-1}, m, (ν C≡N). ^{1}H NMR ($CDCl_3$) δ 6.80 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 7.16 (td, J = 7.4 and 0.8 Hz, 2H), 7.42-7.48 (m, 4H), 7.71 (dd, J = 7.7 and 1.6 Hz, 2H), 7.96 (d, J = 8.3 Hz, 2H) ppm. MS (CI, NH_3) m/z = 380 $[M+NH_4]^+$. Anal. Calcd for $C_{24}H_{14}N_2O_2$: C, 79.55; H, 3.89; N 7.73. Found: C, 79.31; H, 3.93; N 7.75%.

2: M.p. 152 °C. IR 2229 cm^{-1}, m, (ν C≡N). ^{1}H NMR (DMSO-d_6) δ 7.05 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.1 Hz, 4H), 7.31 (td, J = 7.2 and 0.8 Hz, 2H), 7.69 (m, 4H), 7.76 (d, J = 8.1 Hz, 4H), 7.92 (dd, J = 7.7 and 1.6 Hz, 2H) ppm. MS (EI) m/z = 388 $[M]^+$. Anal. Calcd for $C_{26}H_{16}N_2O_2$: C, 80.40; H, 4.15; N 7.21. Found: C, 80.45; H, 4.13; N 7.11%.

3: M.p. 144 °C. IR 2232 cm^{-1}, m, (ν C≡N). ^{1}H NMR (DMSO-d_6) δ 7.19 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 9.0 Hz, 4H), 7.36 (td, J = 7.2 and 0.8 Hz, 2H), 7.45, (d, J = 8.7 Hz, 4H), 7.73 (m, 4H), 7.94 (dd, J = 7.7 and 1.7 Hz, 2H) ppm. MS (CI, NH_3) m/z = 556 $[M+NH_4]^+$. Anal. Calcd for $C_{28}H_{16}F_6N_2O_2$: C, 64.69; H, 3.00; N 5.20. Found: C, 64.91; H, 2.82; N 5.18%.

7: M.p. 451 °C. IR 1664 cm^{-1}, s, (ν C=O). ^{13}C NMR (CD_2Cl_2/CH_3SO_3H, 2:1) δ 116.65, 116.77, 120.13, 122.25, 123.44, 126.76, 128.78, 129.19, 142.85, 156.25, 158.46, 178.44 ppm. MS (EI, high resoln.) m/z = 364.0729 $[M]^+$. Calcd for $C_{24}H_{12}O_4$: 364.0735. Details of the single crystal X-ray structure-determination for this compound are given in the supplementary crystallographic data.

8: M.p. 299 °C. IR 1662 cm^{-1}, s, (ν C=O). ^{1}H NMR (CD_2Cl_2/CH_3SO_3H, 2:1) δ 7.97 (t, J = 7.5 Hz, 2H), 8.18 (d, J = 8.4 Hz, 2H), 8.35 (d, J = 8.4 Hz, 2H), 8.45, (m, 2H), 8.81 (m, 4H), 9.18 (d, J = 2.0 Hz, 2H) ppm. ^{13}C NMR (CD_2Cl_2/CH_3SO_3H, 2:1) δ 115.45, 115.63, 119.62, 120.98, 124.83, 126.67, 128.09, 136.95, 140.77, 142,66, 158.47, 158.66, 178.56 ppm. MS (EI) m/z = 390 $[M]^+$. Anal. Calcd for $C_{26}H_{14}O_4$: C, 79.99; H, 3.62. Found: C, 79.86; H, 3.45%.

9: M.p. 239 °C. IR 1669 cm^{-1}, s, (ν C=O). ^{1}H NMR (DMSO-d_6) δ 7.50 (t, J = 7.5 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.82, (m, 4H), 7.90 (m, 2H), 8.16 (d, J = 7.8 Hz, 2H), 8.28 (s, 2H) ppm. ^{13}C NMR (CD_2Cl_2/CH_3SO_3H, 2:1) δ 115.57, 115.73, 119.86, 121.34, 127.00, 128.56, 128.87, 131.44, 141.75, 143.45, 158.59, 158.98, 178.95 ppm. MS (EI) m/z = 540 $[M]^+$. Anal. Calcd for $C_{29}H_{14}F_6O_4$: C, 64.45; H, 2.61. Found: C, 63.84; H, 2.37%.

10: M.p. 102 °C. IR 2231 cm^{-1}, m, (ν C≡N). ^{1}H NMR ($CDCl_3$) δ 6.83 (t, J = 2.3 Hz, 1H), 6.94 (dd, J = 8.3, 2.2 Hz, 2H), 6.99, (d, J = 8.5 Hz, 2H), 7.20 (td, J = 7.6, 0.9 Hz, 2H), 7.43 (t, J = 8.3 Hz, 1H), 7.55 (m, 2H), 7.68 (dd, J = 7.7, 1.7 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ 104.13, 111.26, 115.72, 115.93, 117.75, 123.54, 131.22, 133.93, 134.42, 156.60, 158.79 ppm. MS (EI) m/z = 312 $[M]^+$.

11: M.p. 239 °C. ^{1}H NMR (CD_2Cl_2/CH_3SO_3H, 2:1) δ 7.90 (t, J = 7.0 Hz, 2H), 8.04 (d, J = 8.1 Hz, 1H), 8.18, (d, J = 9.6 Hz, 1H), 8.27 (m, 3H), 8.48 (d, J = 8.3 Hz, 1H), 8.64 (dd, J = 8.3, 1.3 Hz, 1H), 8.96 (d, J = 9.6 Hz, 1H) ppm. ^{13}C NMR (CD_2Cl_2/CH_3SO_3H, 2:1) δ 107.99, 108.53, 112.02, 118.09, 118.30, 118.95, 119.78, 124.71, 126.53, 128.22, 128.33, 134.31, 139.84, 141.18, 153.82, 155.23, 156.53, 159.62, 163.14, 177.95 ppm. MS (EI) m/z = 313 $[M]^+$. Details of the single crystal X-ray structure-determination for this compound are given in the supplementary crystallographic data.

12: M.p. 263 °C. IR 1663 cm^{-1}, s, (ν C=O). ^{1}H NMR (CD_2Cl_2/CH_3SO_3H, 2:1) δ 8.01 (t, J = 7.8 Hz, 1H), 8.07 (t, J = 7.7 Hz, 1H), 8.18, (d, J = 8.6 Hz, 1H), 8.28 (d, J = 9.5 Hz 1H), 8.45 (m, 3H), 8.76 (m, 2H), 9.23 (d, J = 9.5 Hz 1H) ppm. ^{13}C NMR (CD_2Cl_2/CH_3SO_3H, 2:1) δ 108.35, 113.96, 116.90, 118.47, 120.38, 120.48, 120.98, 127.40, 127.58, 130.05, 130.32, 137.32, 143.58, 158.07, 158.61, 159.32, 165.69, 177.97, 179.11 ppm. MS (EI) m/z = 314 $[M]^+$.

13: M.p. 244 °C. ^{1}H NMR (DMSO-d_6) δ 7.82 (d of d, *J* = 14.7 and 2.7 Hz, 2H), 8.00 (m, 4H) ppm. ^{13}C NMR (DMSO-d_6) δ 100.35 (d, $J_{C\text{-}F}$ = 15.6 Hz), 113.33, 115.03 (d, $J_{C\text{-}F}$ = 21.2 Hz), 123.99, 134.22, 144.01 (d, $J_{C\text{-}F}$ = 5.8 Hz), 162.53 (d, $J_{C\text{-}F}$ = 254 Hz) ppm. MS (EI) *m/z* = 240 $[M]^+$. Anal. Calcd for $C_{14}H_6F_2N_2$: C, 70.00; H, 2.52; N, 11.66. Found: C, 69.74; H, 2.88; N, 11.54%.

Polymer 14: Amorphous, T_g = 197 °C (onset). Inherent viscosity (1% w/v in NMP at 25 °C) 0.42 dL g^{-1}. IR (film from chloroform) 2230 cm^{-1}, m, (ν C≡N). ^{1}H NMR (DMSO-d_6) δ 7.16 (d, *J* = 8.5 Hz, 4H), 7.34 (d, *J* = 8.1 Hz, 4H), 7.59 (s, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H) ppm. ^{13}C NMR (DMSO-d_6) δ 63.22 (sept., $J_{C\text{-}F}$ = 29 Hz) 104.77, 115.23, 117.77, 119.03, 123.88 (quart., $J_{C\text{-}F}$ = 288 Hz), 124.20, 127.60, 131.69, 134.94, 144,43, 156.58, 157.07 ppm.

Polymer 16: Amorphous, T_g = 372 °C (onset). Inherent viscosity (1% w/v in 96% H_2SO_4 at 25 °C) 0.69 dL g^{-1}. IR (film from dichloroacetic acid) 1674 cm^{-1}, m, (ν C=O). ^{1}H NMR (CD_2Cl_2/CH_3SO_3H, 2:1) δ 8.27 (d, *J* = 9 Hz, 2H), 8.39 (m, 4H), 8.62 (s, 2H), 8.81 (s, 2H), 8.92 (s, *J* = 7.5 Hz, 2H) ppm. ^{13}C NMR (CD_2Cl_2/CH_3SO_3H, 2:1) δ 66.34 (sept., $J_{C\text{-}F}$ = 30 Hz) 118.09, 118.44, 120.75, 123.13, 125.40 (quart., $J_{C\text{-}F}$ = 284 Hz), 129.15, 130.19, 130.73, 133.22, 143.71, 151.98, 160.56, 160.72, 180.82 ppm.